

Metal Catalysts for the Electrochemical Reduction of CO₂

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par

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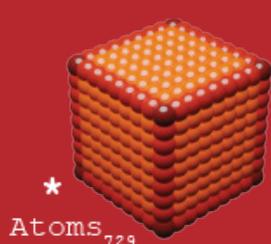
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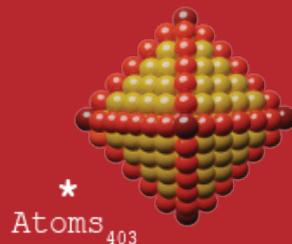




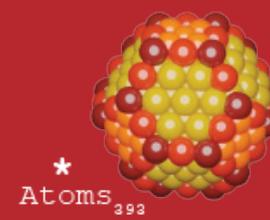
Metal Catalysts for the Electrochemical Reduction of CO₂



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я люблю тебя дорогая. Лучшей команды не существует.



Abstract

The world by and large has adopted the The Paris Agreement, which commits any signing party to cut greenhouse emissions drastically and prevent global heating above 2 °C beyond pre-industrial levels. For this ambitious goal to be met, ratifying states need to undergo a rapid energy transition away from fossil fuels to renewables for which large scale energy storage is needed.

Fuels such as acetaldehyde and ethanol offer a cost-effective measure to store low-energy-density renewable energy in the form of chemical bonds. One promising technology that achieves both CO₂ emissions reduction and energy storage is the electrochemical CO₂ reduction reaction (CO₂RR). In here, CO₂ is converted using electricity into value added chemicals. Although promising, several hurdles will need to be taken for this technology to become competitive: 1) catalysts with high product selectivity will need to be designed, 2) reactor design will need to be optimized for specific products, 3) reactors will need to run >10,000 of hours at high conversion.

In this thesis, great attention was spent to the design, synthesis, characterization and CO₂RR performance of electrocatalysts on the lab scale. Special focus was placed on Cu-based catalysts for their unique capabilities to make carbon-carbon bonds, required to produce energy-dense fuels. Design strategies to fashion selective metal catalysts were discussed in depth based on experimental data spanning three decades. Based on this discussion, two size regimes were selected that could yield promising potential catalysts, and lacked previous investigations.

The first regime is that of the bulk, where in particular the role of the catalyst surface, i.e., the facet exposed and the electronic structure, affects the selectivity in CO₂RR. These effects were investigated by synthesizing Cu-M with M = Ag and Ag-Pd nanoparticles >10 nm of specific shapes having, therefore, specific facets, i.e., (100) and (111), exposed at the surface and a specific electronic structure as based on their relative composition.

To achieve this, a new wet-chemistry synthesis was developed that allowed to produce facet-controlled surface alloys independent of component miscibility. Further, a new characterization method based on inductively coupled plasma mass spectrometry was established to determine the composition distribution of said alloys with ensemble representative statistics. Based on the deconvolution of composition, i.e., electronic structure and facet, a clear trend in the selectivity for liquid fuels in CO₂RR could be discerned.

The second regime is that of clusters in which electrocatalyst performance is governed to a large degree by the total number of atoms in the cluster and composition and to a lesser degree by the cluster-support interaction. To probe the effect of cluster size, composition and support in CO₂RR, Cu(-Ag) clusters <1 nm were synthesized using spark ablation and immobilized on heteroatom doped carbonaceous supports. A remarkable high selectivity towards acetaldehyde (>90%) was observed for the Cu clusters independent of support.

Finally, we draw conclusions and offer perspectives on the further improvement of the technological readiness level of promising electrocatalysts beyond the lab scale. And propose avenues based on reactor design that are considered most promising in bringing CO₂RR technologies to fruition.

Keywords

CO₂ reduction, electrochemistry, model catalysts, wet-chemistry, inductively-coupled plasma mass spectrometry, spark ablation

Résumé

Le monde entier a adopté l'accord de Paris, qui engage toutes les parties signataires à réduire considérablement les émissions de gaz à effet de serre et à empêcher le réchauffement de la planète de dépasser de 2 °C les niveaux de l'ère préindustrielle. Pour atteindre cet objectif, les États doivent opérer une transition énergétique rapide, pour lesquelles un stockage de l'énergie à grande échelle est nécessaire.

Les carburants tels que l'acétaldéhyde et l'éthanol constituent une mesure rentable pour stocker l'énergie renouvelable sous forme de liaisons chimiques. La réaction électrochimique de réduction du CO₂ (CO₂RR) est une technologie prometteuse qui permet à la fois de réduire les émissions de CO₂ et de stocker de l'énergie. Dans ce cas, le CO₂ est converti en produits chimiques à valeur ajoutée grâce à l'électricité. Bien que prometteuse, plusieurs obstacles devront être surmontés pour que cette technologie devienne compétitive.

Dans cette thèse, une grande attention a été portée à la conception, synthèse, et performance CO₂RR des électrocatalyseurs à l'échelle du laboratoire. Une attention particulière a été accordée aux catalyseurs à base de Cu pour leurs capacités uniques à établir des liaisons carbone-carbone, nécessaires à la production de carburants. Les stratégies de conception de catalyseurs métalliques sélectifs ont été discutées. Sur la base de cette discussion, deux régimes de taille ont été sélectionnés qui pourraient produire des catalyseurs potentiels prometteurs et qui n'ont pas fait l'objet d'études antérieures.

Le premier régime est celui du bulk, où en particulier le rôle de la surface du catalyseur, c'est-à-dire la facette exposée et la structure électronique, affecte la sélectivité en CO₂RR. Ces effets ont été étudiés en synthétisant des nanoparticules Cu-M avec M = Ag et Ag-Pd >10 nm de formes spécifiques ayant, par conséquent, des facettes spécifiques exposées à la surface et une structure électronique spécifique en fonction de leur composition relative.

Pour y parvenir, une nouvelle synthèse par chimie humide a été mise au point, qui a permis de produire des alliages de surface à facettes contrôlées, indépendamment de la miscibilité des composants. En outre, une nouvelle méthode de caractérisation basée sur la spectrométrie de masse à plasma inductif a été établie pour déterminer la distribution de la composition. Sur la base de la déconvolution de la composition et de la facette, une tendance claire de la sélectivité pour les carburants dans le CO₂RR a pu être discernée.

Le deuxième régime est celui des clusters dans lequel la performance est régie dans une large mesure par le nombre total d'atomes dans le cluster et la composition et dans une moindre mesure par l'interaction entre le cluster et le support. Pour étudier l'effet de la taille, de la composition et du support, des clusters de Cu(-Ag) <1 nm ont été synthétisés par ablation par étincelle et immobilisés sur des supports carbonés dopés à l'hétéroatome. Une sélectivité élevée remarquable envers l'acétaldéhyde (>90%) a été observée pour les clusters de Cu indépendamment du support.

Enfin, nous tirons des conclusions et offrons des perspectives sur l'amélioration du niveau de maturité technologique des électrocatalyseurs prometteurs au-delà de l'échelle du laboratoire. Et nous proposons des pistes basées sur la conception des réacteurs qui sont considérées comme les plus prometteuses pour faire fructifier les technologies CO₂RR.

Mots clés

Réduction du CO₂, électrochimie, catalyseurs modèles, chimie humide, spectrométrie de masse à plasma inductif, ablation par étincelle





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Chapter 1

Research Background

1.1. Energy Transition

The rapid pace of human civilization's development in the last century is literally and figuratively fueled by fossil fuels. Energy demand is by an overwhelming majority supplied by the consumption of fossil fuels such as coal, oil and natural gas. For instance, in the Netherlands in 2022, a shocking 87% of the total energy demand was covered by fossil fuels. Further, many products and commodities of modern-day life find their origin in refinery as well. Naturally, fossil fuels are a finite commodity and as such, obtaining them is becoming increasingly difficult. Further, their widespread consumption has led to the massive release of carbon in to the atmosphere in the form of CO_2 . And heaps of evidence implicate this greenhouse gas (GHG) in the acceleration of climate change with rising global temperatures, higher frequency of extreme weather events, rising sea levels and the melting of our polar ice caps and glaciers, as a result. Therefore, in order to sustain our development in the long term, and to reduce carbon emissions in the short term, we need a rapid transformation of our economic model towards circularity.

- We need to transition away from fossil fuel-based energy consumption to renewable energy instead
- We need to find substitutes for the fossil fuel originated products and commodities of modern-day life.

On this roadmap towards sustainable growth, the first milestone is to reach net neutrality. Thankfully, most countries have pledged to do so as early as 2050 adhering to the goals set in The Paris Agreement. However, the road towards a complete energy transition is far from obvious. The electrochemical CO_2 reduction reaction (CO_2RR), in which electricity is used to convert CO_2 in value added chemicals, using renewable energy is a promising solution to help mitigate climate change, integrate renewables into our traditional carbon-based economy, and achieve net neutrality.

In the coming sections, we will discuss the issue of the global energy demand, associated CO_2 emissions, induced climate change and highlight the challenges ahead to achieve a complete energy transition. Then, we will discuss the potential of CO_2RR as a proposed tool to catalyze this transition.

1.2. World energy demand, GHG emissions, climate change

Since the dawn of time, man has used technology to improve upon his condition. Such improvements led to increases in life expectancy, lower child mortality and higher birthrate and therefore, the opportunity for the population to grow. However, for the vast majority of man's existence, his industrious nature was energy limited. Notably, until the last 1800s, the world population was stagnant. Not until a continuous conversion of thermal energy into mechanical motion was achieved, which greatly facilitated the taming of the elements (i.e. steam engine),¹ did the population start to develop (**Figure 1A**).² Notably, the world's energy demand and the appearance of fossil fuels (coal) in the energy mix and its subsequent dominion over the world's energy supply is in step

with this development (**Figure 1B**).³ Then, from the last 1950s, the world population shows clear signs of exponential growth doubling from 2.5 to 5 billion in less than 40 years. The Green revolution, facilitated by the Haber-Bosch process, enabled in feeding this ever-growing population.⁴ Spanning the same period, and brought forth by the heaps of new humans added daily and their desire to improve upon their way of life, the global energy demand soared by 350% to ~100,000 TWh by 1984. Until now, energy demand has grown even further to staggering 170,000 TWh. And with the global population projected to reach 9.7 billion by 2050, it is expected to show sustained growth for the foreseeable future.

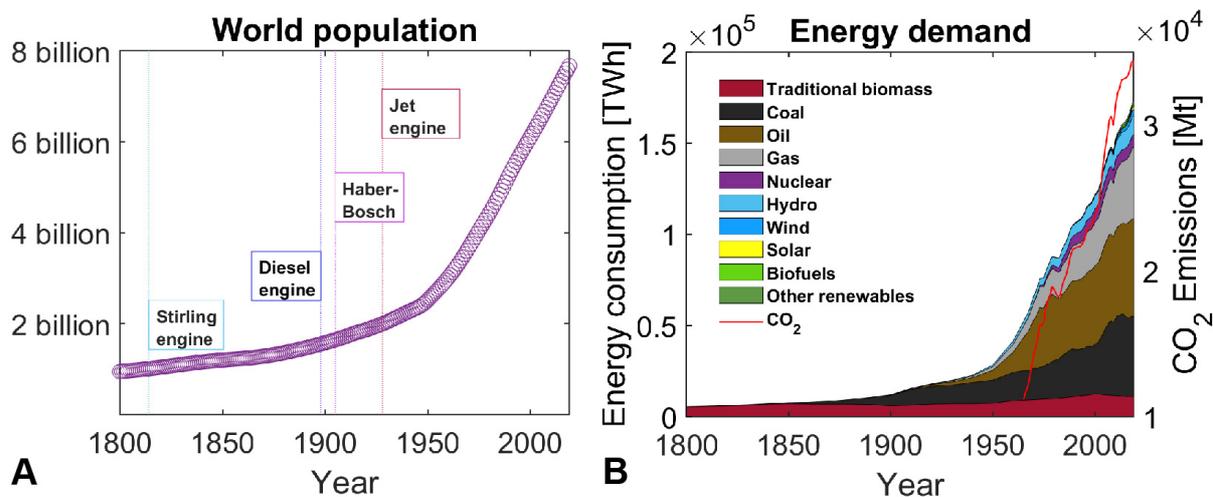


Figure 1. (A) Development of the world population since 1800. Indicated by the colored lines are the filing dates of the patent for relevant technologies that have helped advance civilization. Data extracted from Ref. ² (B) The energy demand in TWh since 1800 on the left ordinate. Contribution of coal, oil and gas dominate the energy mix starting the 1900s. Global CO₂ emissions in megaton since 1957 as estimated by BP.

Unsurprisingly, massive emissions of CO₂ accompanied this rapid increase in fossil fuel consumption (**Figure 1B**, right ordinate). Interestingly, in the same period, the atmospheric CO₂ levels started to rise as well (**Figure 2A**).^{5,6} And with a staggering pace. In less than 60 years the average concentration had increased by 130% from ~316 ppm in 1958 to ~418 ppm by 2017 (the fastest rate in last 66 million years).⁷ Since CO₂ is a GHG, it is suggested as a major contributing factor in inducing climate change. Indeed, the average global temperature has spiked ever since the consumption of fossil fuels started to rise, hovering around the +1.2°±0.1 in 2020 (above 1850 levels, **Figure 2B**).⁸

With the most severe adverse effects of

climate change predicted to occur for global warming of >1.5°,^{9,10} countries that ratified The Paris Agreement have committed to keeping the temperature rise below this value.

Thankfully, efforts in curbing CO₂ emissions already seem to be taking effect, with the year-to-year change in emission from 2016 to 2020: +1.1%, -1.8%, +0.1%, and -5.9%, respectively (effects of COVID-19 not considered). However, this still distances away from commitments to reach net zero. Therefore, to achieve this ambitious goal, a rapid switch from fossil fuel-based energy consumption to renewables is required. In the next section we will see what is putting the brakes on this transition and how this can be mitigated.

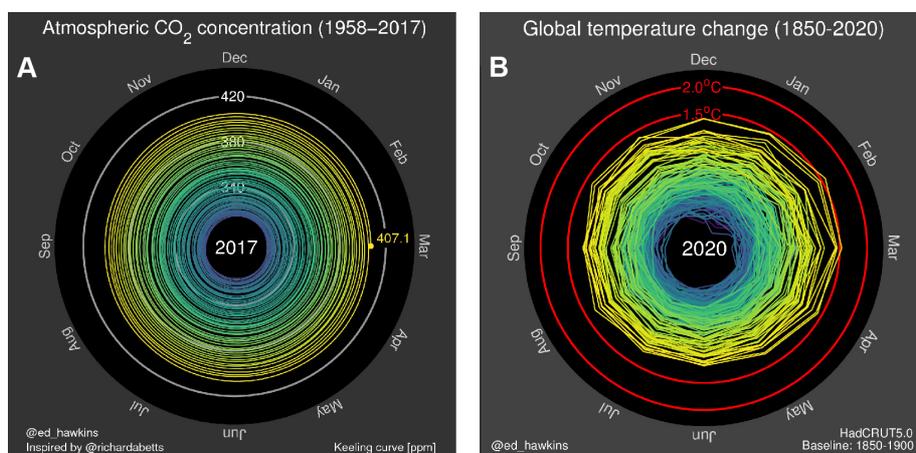


Figure 2. A) Climate spiral showing the increase in atmospheric CO₂ concentration in ppm starting 1958 as measured at the Mauna Loa Observatory established by C.D. Keeling.^{5,6} B) The average global temperature change compared to 1850 levels.⁸ Each complete convolution construes one year. Reprinted with permission from Ref.⁵.

1.3. Renewable energy: storage capacity

Countries, including developed and developing ones, are now heavily investing in renewable energy generation, such as hydro-power, solar energy and wind energy etc. In the last 10 years, the installed capacity of solar and wind generated electricity has increased ~17- and ~4-fold, respectively, for instance.¹¹ However, the availability is often intermittent. In example, for solar power, peak consumption takes place during the night whereas peak production, depending on the geolocation, happens around midday. Further, seasonal variation, which is again location bound, significantly thwarts mass-deployment (**Figure 3**).

In order for the energy transition to reach completion, large-scale energy storage must thus be achieved. Battery technology is often suggested as a likely candidate for this purpose.

However, the associated low energy density, relatively short lifetime and high costs puts doubts on scalability (**Table 1**).¹² Never mind the enormous amounts of raw materials it would require. Consider the global energy demand in 2019 (1.8×10^5 TWh, **Figure 1**). With an energy density of 0.16 kWh kg^{-1} for the Li ion battery (the most energy dense on the market), and a typical battery containing ~7% Li,¹³ back of the envelope calculation puts the required amount of Li at ~80 Gt if storage capacity is to meet consumption. With the total Li reserves estimated at ~14 Mt, the supply of raw material misses the mark by four orders of magnitude. The case for Co is even worse (7.1 Mt reserve). Even if only a fraction of the global energy consumption is to be stored (1%), not nearly enough raw material can be mined to reach capacity.

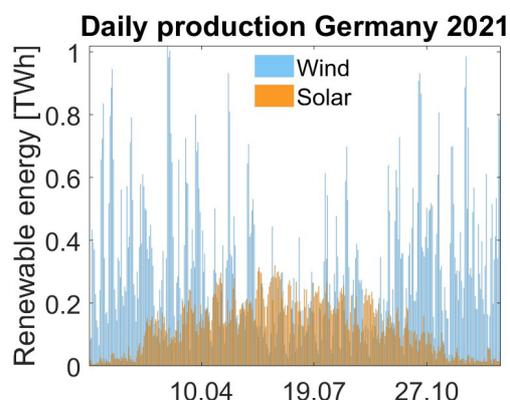


Figure 3. Daily production of solar and wind energy in Germany in 2021. Both large daily fluctuations as well as seasonal can be distinguished.⁵

Synthetic fuels offer a much cheaper and more facile approach instead. For one, their calorific value is much better as energy is stored in covalent bonds instead of through a chemical potential difference (**Table 1**). Further, they can be produced catalytically and require, therefore, little to no raw material for their production. Also, since the infrastructure is for the most part already in place (from fossil fuels), transitioning should be more cost-efficient. Further, electricity generation is expected to become fully *green* by 2050,^{14,15} putting tremendous pressure on pricing. Pathways towards electricity prices as low as 0.03 USD kWh⁻¹ have already been proposed.^{16,17} That, and the possibility of a carbon tax put into place,¹⁸ greatly benefits the business case of synthetic fuels.

Two roadmaps can be foreseen towards the utilization of CO₂ in the form of synthetic fuels. The first, and the most advanced, is the catalytic hydrogenation of CO₂ towards value-added products such as CO, CH₄, and CH₃OH (**Figure 4**).^{19,20,21} This, of course, requires first the splitting of H₂ from H₂O.

Certainly, polymer electrolyte membrane (PEM) electrolyzers have reached maturity with efficiencies of 50% and >30 years of operation.²² In case of the Sabatier reaction for the production of CH₄, overall power-to-gas efficiencies of ~35% can be achieved in this way.²³ However, the low natural gas price (not considering relevant geopolitical tensions) and volumetric energy density puts constraints on this reaction.

Synthesis of the more energy dense light-olefins such as octane, which can be produced from CH₃OH instead using zeolite-catalysts or via the Fischer-Tropsch process, is more promising.²⁴ Such processes can achieve up to 57% energy efficiency of the energy stored in H₂ (power-to-fuel efficiency of 28.5%).²² Recently, the first industrial scale CO₂ hydrogenation plant has been commissioned, With the aim to produce methanol.

Fuel	Calorific value	
	[kWh kg ⁻¹]	[MJ L ⁻¹]
Octane	13.0	34.7
Kerosene	12.8	37.9
Ethanol	8.2	23.4
Methane	14.85	0.04
Li ion	0.16	0.68

Table 1. Energy density of a selection of synthetic fuels. Data extracted from Ref.¹²

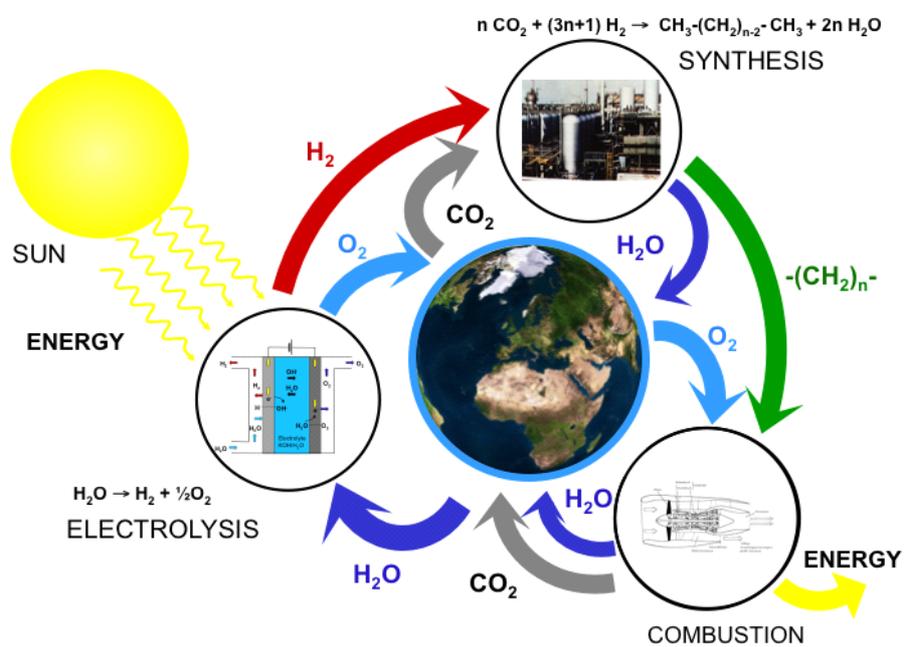


Figure 4. Schematic of the catalytic hydrogenation of CO₂.²⁵

The second, is the direct electrochemical conversion of CO₂ into products such as CO, HCOOH, CH₄, CH₃OH, CH₃CHO, C₂H₄, C₂H₅OH, C₃H₇OH, etc.^{26,27,28,29,30} Naturally, CO₂RR has the advantage of producing fuels directly, without the need of first H₂ production (which in many cases would require storage at additional capital cost) followed by a thermal or biocatalytic process. Especially, the two-birds-one stone CO₂ to C₂₊ products such as C₂H₅OH and C₃H₇OH is highly attractive. Not only are H⁺ and CO₂ reduced simultaneously, C-C coupling is achieved as well greatly improving the energy stored per pass. This would dramatically reduce cost of operation (if CO₂ electrolyzer can be made as cost-efficiently as PEM electrolyzers). For the CO₂RR to compete with CO₂ hydrogenation, comparable energy efficiencies need to be achieved. For the case of C₂H₅OH, with 0.69 the calorific value of octane, this would mean >41% power-to-fuel efficiency.

Considering that the next generation of H₂ electrolyzers (alkaline electrolyzers) run at an efficiency of 88% this number jumps to ~73%.³¹ Recent techno economic analysis put the breakeven point for CO₂RR to C₂₊ products at ~50% for an electricity price of 0.01 USD kWh⁻¹.¹¹ Unfortunately, CO₂RR to C₂₊ suffers from poor selectivity (<50%) putting energy efficiencies in the 15% range.³² For this reaction to become competitive more selective electrocatalysts need to be designed. In the following chapter, we will introduce design concepts based on a vast survey of the literature of CO₂RR to optimize catalyst design and improve the selectivity towards C₂₊ products and in particular liquid fuels.

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Chapter 2: Introduction

Metal catalysts in different size regimes for CO₂ electroreduction

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Keywords

CO₂ electrochemical reduction, metal catalysts, review, size, reaction mechanism

Abstract

With the electrochemical CO₂ reduction reaction (CO₂RR), CO₂ can be used as a feedstock to produce value-added chemicals and fuels whilst storing renewable energy. For its enormous potential, an extensive research effort has been launched to find the most active electrocatalyst. The reduction of catalyst size has been tested and proven as a key approach to increase the activity of CO₂RR whilst reducing capital cost. However, the catalytic selectivity is not linearly related to the catalyst size due to the influence of many other structural factors. Thus, in-depth knowledge of structure-performance relationships of metals catalysts with different sizes aid in designing efficient electrocatalysts for CO₂RR. This review surveys three decades worth of research on CO₂RR and categorizes various metal catalysts into four size regimes, namely bulk materials in the form of single-crystals, nanoparticles, clusters, and single-atom catalysts. The effect of different structural factors, including crystal facet, coordination environment, and metal-support interactions etc. are discussed for metal catalysts in each size regime. Finally, general conclusions are provided with perspectives on future directions for better understanding and further development of active and selective catalysts for CO₂RR.

2.1. Introduction

Since the rapid industrialization of the 19th century, the world energy demand has shown exponential growth, which in large has been met by the consumption of fossil fuels.¹ The associated emission of various greenhouse gases such as CO₂ have led to the steady increase of the global average temperature inducing climate change.^{2,3} In the last 200 years, global atmospheric concentrations of CO₂ have risen from 280 ppm to over 400 ppm, and the global temperature has increased by more than 1 °C. In their latest report, the International Panel for Climate Change (IPCC) issued its starkest warning yet.⁴ If emissions are not cut drastically within the decade, rising sea levels and extreme weather events, amongst others, will no longer be an anomaly. Facing the energy and environmental crisis, countries, including developed and developing ones, are now shifting their energy mix from fossil fuels towards renewable energies, such as hydro-power, solar energy and wind energy etc. In the last 10 years, the installed capacity of solar and wind generated

electricity has increased ~17- and ~4-fold, respectively, and price is projected to drop as low as 0.03 USD·kWh⁻¹ in the near future.⁵ However, compared to fossil fuels, the energy density of renewables is much lower and the availability is often intermittent. In the past decade, the electrochemical CO₂ reduction reaction (CO₂RR) has emerged as a promising solution in tackling the above-mentioned issues. By bringing CO₂RR to scale, in which CO₂ is converted into fuels and chemicals using renewable electricity, net zero emissions are within reach and low density renewable energy can be stored at high capacity in chemical bonds.⁶ With its major products including drop-in fuels and base-chemicals such as C₂H₅OH, C₂H₄ and CH₄ (**Figure 5.**), its industrial potential is enormous.⁷

Although promising, several significant challenges remain before this technology can become economically competitive. First, despite that CO₂RR is thermodynamically feasible (**Table S1**), large kinetic barriers exist in the activation of CO₂ and the following reaction intermediates, resulting in high overpotentials (the potential needed on top of the equilibrium potential for the reaction to take place) and low energy efficiency.^{9,10,11} In addition, in aqueous solutions, the hydrogen evolution reaction (HER) is in competition with CO₂RR, which decreases the faradaic efficiencies for

CO₂RR products (see **Note S1** for a list of equilibrium potentials of CO₂RR products and other relevant reactions). Further, up to 16 products have been produced from CO₂RR, resulting in low selectivity towards certain products, especially multi-carbon products.^{12,13} Therefore, the design of advanced electrocatalysts is needed to activate the CO₂ molecule and accelerate the desired reaction pathways for an increased conversion rate and product selectivity.

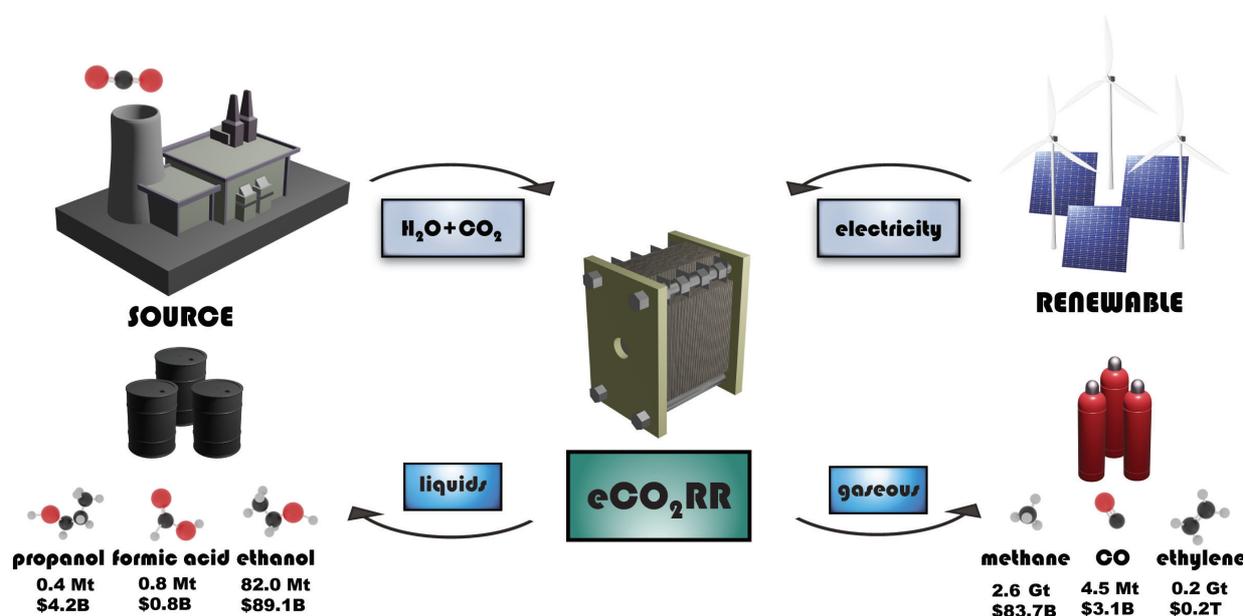


Figure 5. Electrochemical CO₂ reduction reaction. The schematic shows the conversion of CO₂ and water using renewable electricity to produce various gaseous and liquid products of the CO₂RR with the current market size and value. Mt = megaton; Gt = gigaton; B = billion, M = million. Note that formate (HCOO⁻) is the direct reduction product of CO₂RR when neutral or basic electrolyte is used, and thus further conversion is needed to yield formic acid.⁸

Over the past three decades, various types of materials, such as metals, oxides, and carbon-based materials have been used for CO₂RR.^{10,14,15,16,17} Of which, a comprehensive body of work has been dedicated to metal catalysts for CO₂RR.^{18,19,20,21,22,23,24,13,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45}

Among them, one of the most important contributions came from Hori and co-workers. Based on systematic studies using bulk single-crystal and polycrystalline electrodes, metal catalysts were classified into four groups based on their selectivity: HCOO⁻ selective metals (e.g., Pb, Hg, Tl, In, Sn, Cd, and Bi), CO selective metals (e.g., Au, Ag, Zn, Pd, and Ga), H₂ selective metals (e.g., Ni, Fe, Pt, and Ti), and Cu, which is selective for a number of hydrocarbons and oxygenates.^{6,18,19,20,21,22,23,24,46} Guided by this early classification, researchers have searched for catalysts with better activity and selectivity ever since. An elegant attempt has been to reduce catalyst size to retain or improve selectivity but increase the gravimetric active site density (mass activity) thereby improving upon atom economy (active sites per catalyst mass). With the

development of synthesis methods, i.e., in colloidal chemistry, dip-pen nanolithography and pyrolysis,^{47,48,49,50,51,52} ever more precise catalyst have been produced. For example, nanoparticles of Au, Ag, Pd, and Cu etc. have been synthesized with sizes ranging from several hundreds of nanometers down to a single nanometer, showing significant performance improvements in CO₂RR.^{31,35,36,37,44,40,53} Recently, catalysts with sizes beyond the nanometer regime, such as clusters (< 1 nm) and single-atom catalysts on conductive supports (SACs, with maximum atom utilization), have also been designed and applied for CO₂RR with superior catalytic activity.^{54,55} These recent studies show, however, that not only the activity, but also the product selectivity may vary with decreasing catalyst dimensions. For example, while bulk Ni is not selective for CO₂RR due to its high HER activity, Ni SACs are proven to be highly selective for the conversion CO₂ to CO.^{56,57} This is not entirely unexpected however, as the electronic properties of the metal particles change significantly at sub-nanometer range, and in the case of Ni, its single atom

form can have oxidation states of Ni^+ and Ni^{2+} (Figure 6).^{58,59} Indeed, the distinct catalytic performance of nanoparticles in different size ranges for several important thermal reactions have been systematically

studied and thoroughly discussed.^{60,61} However, a comprehensive review of how metal catalysts in different sizes catalyze CO_2RR is still missing.

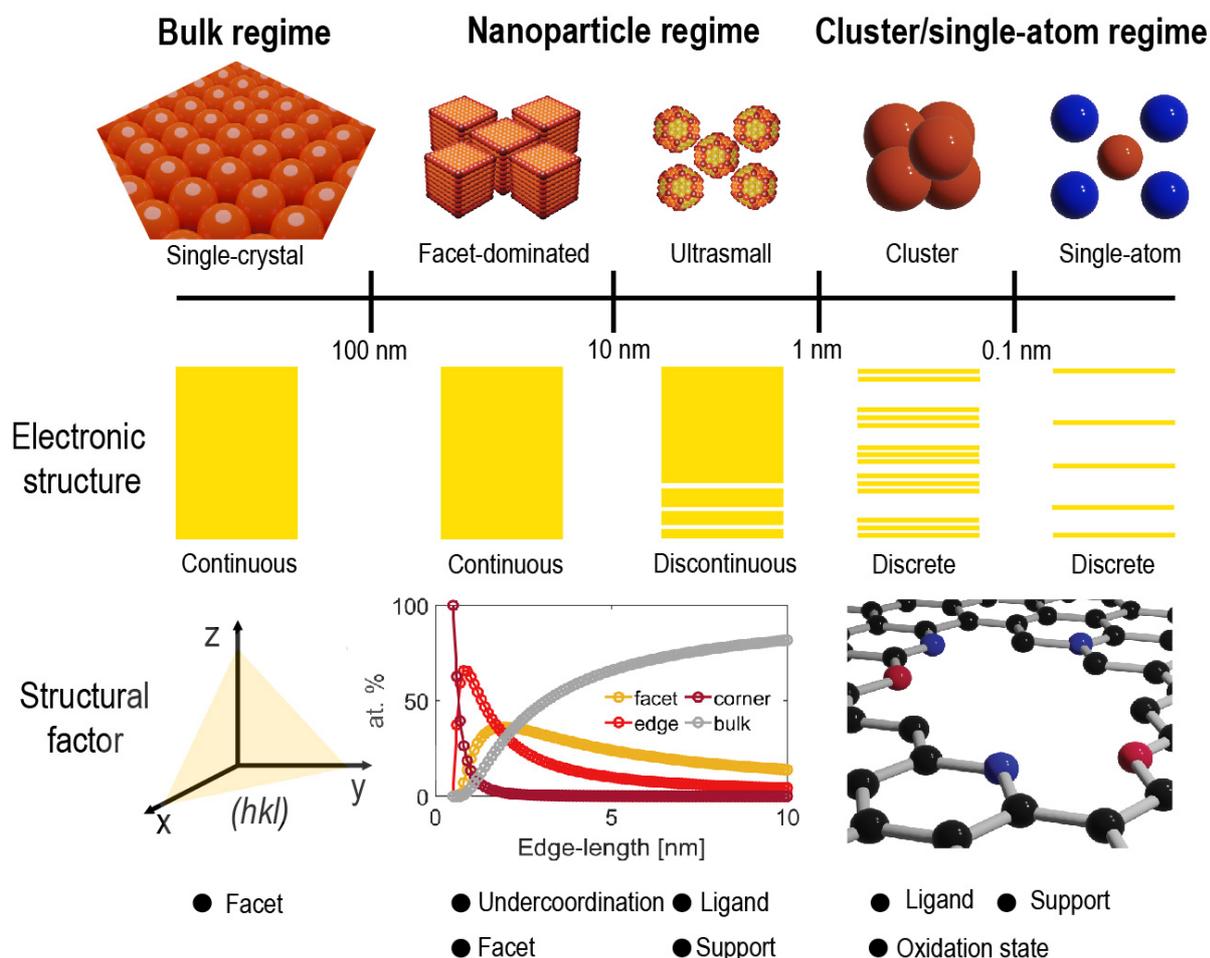


Figure 6. Classification of metal catalysts for CO_2RR based on the particle size. With the decrease of the catalyst size, the electronic structure changes, and different structural factors can be used to describe the reactivity.

Revealing a complete catalytic mechanism for CO₂RR is extremely challenging due to the various material properties and diverse mechanistic steps involved.¹⁰ Thus, most studies have simplified this task and instead tried to find key descriptors to predict the activity of the catalysts or to explain the observed results. Nørskov and co-workers performed pioneering work herein based on density functional theory (DFT) calculations, where the adsorption energies of *COOH, *CO, and *OH were identified as key descriptors.^{62,63,64,65} Although the adsorption energy of different intermediates on a model surface can be determined via vacuum techniques (e.g., temperature programmed desorption and XPS), it is still challenging to identify the reaction intermediates and quantify their adsorption energies on a real catalytic surface during the electrochemical process. Thus, experimentalists have tried to tie the catalytic performance to the structural properties of catalysts instead, including crystal facet, coordination environment, and metal-support interactions etc.^{44,66,45} For example, the CO₂RR selectivity can be dramatically affected by the facet

orientation of bulk Cu: whereas the Cu(111) facet is more selective for CH₄, Cu(100) favors C₂H₄ production.^{18,23,46,44} As another example, CO₂RR activity has been found to be closely related to the grain boundary density of Au and Cu.^{67,68,69} Yet, it is worth noting that with the decrease of particle size, the structural properties of the catalyst vary (**Figure 6**), which in turn changes the CO₂RR performance. Also, we note the importance of accurate electrochemical active surface area (ECSA) determination to exclude surface area effects with decreasing particle size to thoroughly and unequivocally study the intrinsic activity of metal catalysts.¹⁰

To better understand the catalytic behavior of metal catalysts in CO₂RR, we propose a new classification system based on the size of the catalyst as the key structural factors change with catalyst dimension (**Figure 6**): (i) the bulk regime, exemplified by single-crystals (i.e., sizes >100 nm), (ii) the nanoparticle regime, subdivided into large nanoparticles (i.e. 10 nm < sizes ≤100 nm) and ultrasmall particles (i.e., 1 nm < sizes ≤10 nm), (iii) the cluster regime (sizes

≤1nm.), and (iv) the single-atom regime. To cover all structural properties of metal catalysts in all size regimes is neither possible nor advisable. Instead, we have selected for experimentally accessible factors that dominate the reaction kinetics of CO₂RR, including the element, crystal-facet, the coordination number, the ligand effect, the metal-support interaction, and the coordination environment (**Figure 6**). Where appropriate, we have extended on our discussion of structural factors to include computational activity descriptors. **Figure 7** provides an overview of the studies reported in the literature, in which the majority product of CO₂RR (and HER)

is related to the element(s) of the metal catalysts and the size-class. In the following chapters, we will use ample representative examples to show how structural properties influence the catalytic performance and moreover, change with decreasing catalyst dimensions. Finally, we will present a general conclusion and an outlook on the challenges and opportunities in catalyst selection and screening in CO₂RR. We hope this review will provide the reader with insights on improving the selectivity of CO₂RR over HER, the selectivity towards specific CO₂RR products, the overall catalytic activity and atom economy.

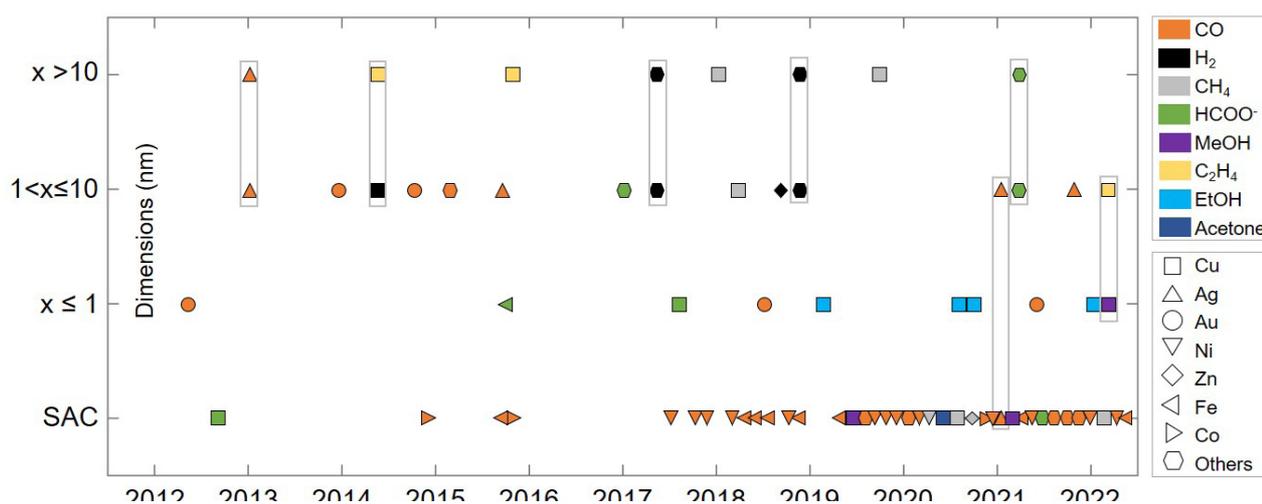


Figure 7. The most common products of CO₂RR for typical metal catalysts in different size regimes: single-crystal and facet dominated nanoparticle (>10 nm), ultra-small particle ($1 < x \leq 10$ nm), cluster (≤ 1 nm), and SAC. The metal utilized to obtain the results is indicated by shape, and the product is indicated by color. The ‘others’ series includes Cu alloys and other metals. Each point represents a published study, where studies covering different size regimes are included in the gray box. For a list of the publications, see **Note S2** of the Supporting Information. Note that publications in **Figure 7** have been selected for their investigation of metal catalysts of different sizes using the same synthesis technique. Further, to highlight the differing performance of metal catalysts versus their SAC counterparts, we have included a selection of those as well.

2.2. Bulk regime: single-crystal electrodes

In bulk systems, polycrystalline metal foils are often used as reference samples and are therefore, the most widely used electrodes for CO₂RR. However, it is difficult to gain mechanistic insights with such crudely defined catalysts. Various types of facets, steps, and defects collectively contribute to the activity, which cannot be deconvoluted. Single-crystals, on the other hand, are of preferential orientation, and can thus be used to study the relationship between CO₂RR performance and crystal facet.^{6,18,19,20,21,22,23,24,46} Single-crystals can be prepared by different methods. For example, they can be manufactured through controlled cooling from a liquid phase, which are then cut and polished with respect to a specific crystallographic orientation. Alternatively, single-crystal thin films can be prepared via epitaxial growth on other single-crystal surfaces (e.g., Si wafers) with the same crystallographic

orientations.²⁸ Characterization of their bulk crystal orientation can be achieved via X-ray diffraction (XRD), while the atomic surface structure can be examined by the reversible adsorption of probing ions (e.g., Cl⁻ and OH⁻) using cyclic voltammetry.²⁸ A number of single-crystal electrodes have been prepared and used for CO₂RR. Among them, face centered cubic metals (FCC, such as Cu, Pd, Au, and Ag) are most frequently studied. This includes low-index *hkl* surfaces, such as (100), (111), and (110) planes, as well as higher-ordered *hkl* planes, which have various degrees of undercoordination. Based on these studies, important insights about the CO₂RR mechanism have been gained. In the following, the effect of crystal structure will be discussed in detail starting with non-Cu based transition metals, followed by Cu-based low and high-index *hkl* surfaces.

2.2.1. Non-Cu-based single crystals

In the last 90s, Hori and co-workers carried out a series of studies on CO₂RR using metal single-crystals including Pt group metals (Pt, Ir, Rh, and Pd) and Ag to reveal the relation between the atomic arrangement and the catalytic activity. For example, a remarkable activity dependence was observed for Pd single-crystals, i.e., (110)>(111)>(100), with the (110) stepped-surface reaching a 3-fold enhanced rate over the (111) surface at the same potential (-1.0 V vs RHE).²⁰ Similarly, the (110) plane of Ag also showed the highest activity, showing a 5-fold higher partial current density for CO versus the (111) surface and with the (100) plane the least active (-1.44 V vs. SHE).²² Much later, the high activity of stepped surface facets was further verified by extended experimental studies congruently with DFT.²⁷ The high activity of Ag(110), for example, is attributed to its binding of the key intermediate *COOH and an enhanced electric field stabilization on undercoordinated surface atoms of step sites. The same conclusions were also reached on another CO selective catalyst, Au and Zn. The stepped Au surfaces (e.g.,

Au(211) and Au(110)) better stabilize the *COOH intermediate than the Au(100) and Au(111) facets and are thus more active. The enhanced activity has been shown to be at least a factor of 20 for undercoordinated Au i.e. Au(110) and steps of Au(211) versus Au(100) by Chorkendorff and co-workers.⁷⁰ Similarly, the *COOH intermediate binding strength inversely scales with the coordination number of Zn surfaces explaining faster CO evolution on undercoordinated Zn.⁷¹ Note that strong evidence exists that for the production of CO on Au and Ag, the rate limiting step is the formation of *CO₂⁻ and that the proton-electron transfer to form *COOH is actually decoupled.⁷² However, modelling a decoupled proton-electron transfer step is challenging and since the following formation of *COOH from *CO₂⁻ is anyhow a non-electrochemical step and fast, *COOH is often used as a descriptor to predict relative rates instead.⁷³

The above studies on non-Cu-based single-crystals indicate that although the catalytic activity of CO₂RR is facet-dependent, the selectivity towards CO₂RR products is less sensitive to the crystal orientation. This is due to the fact that these metals typically reduce CO₂ to CO (or HCOO⁻ as a minor product), which involve only a 2e⁻ transfer and a limited number of intermediates (e.g., *COOH and *OCHO), and that changes in the surface atomic arrangement and thus adsorption energies are not large enough to switch between pathways but do influence the specific rates.⁷⁴ Instead, Cu surfaces can bind a multitude of intermediates (e.g., *COOH, *OCHO, *CO, *CHO, and *COH etc.) with comparable strength, making it especially sensitive to the facet orientation, as we will see in the following sections.

2.2.2. Low index Cu single crystals

As mentioned in the introduction, Cu is the sole metal to produce any meaningful currents towards multi-carbon products. This was first quantitatively presented by Hori and co-workers in their seminal works on CO₂RR on polycrystalline Cu.^{6,18,62} To reveal the unique properties of Cu, fundamental studies using low index Cu single-crystals followed.^{23,13,75} Hori and co-workers found that the selectivity of CO₂RR is highly sensitive to the crystal facet of Cu. Specifically, Cu(100) produced C₂H₄ most selectively (FE of 31.7 % at -1.44 V vs. NHE and 1.6 mA cm⁻²), Cu(111) produced CH₄ predominantly (21.8% at -1.41 V vs. NHE and 1.1 mA cm⁻²),⁶⁵ and Cu(110) showed a mixed product distribution with CH₄ and C₂H₄ FEs of 23.3% and 18.9% (-1.35 V vs. NHE and 0.9 mA cm⁻²), respectively. Note that these experiments were performed at a constant current with relatively long reaction times, thus detailed information on the origin of the facet-dependent selectivity is missing.

Much later, Koper and co-workers gave insightful explanations through experimental and theoretical methods based on a series of studies on CORR (CO is the key intermediate to C₂₊ products).^{76,77}

Using non-quantitative time-resolved online electrochemical mass spectrometry (OLEMS), they observed two distinctive pathways for the formation of C₂H₄ (**Figure 8**). One, which is catalyzed on both Cu(100) and Cu(111), where the rates differ not too strongly and occurs at high-overpotential (**Figure 8a,b**). The other, occurs at much lower overpotential and is only observed on the Cu(100) surface (**Figure 8a**). They proposed that the rate-determining step in the latter involves a chemisorbed CO dimer (i.e., *C₂O₂). Instead, in the former, an intermediate is shared with the reaction pathway for CH₄ (most likely via CHO*). These assumptions were later supported by their DFT calculations and *in situ* Fourier transform infrared spectroscopy (FTIR) results.^{78,77} And the unique ability of Cu(100) for reducing CO to C₂H₄ at low overpotential was attributed to two factors. First, square-like sites on Cu(100) allow for suitable conformation of *C₂O₂, and second, sites formed by four atoms donate more charges to facilitate the C-C coupling than sites of hexagonal-symmetry formed by three atoms.⁷⁹

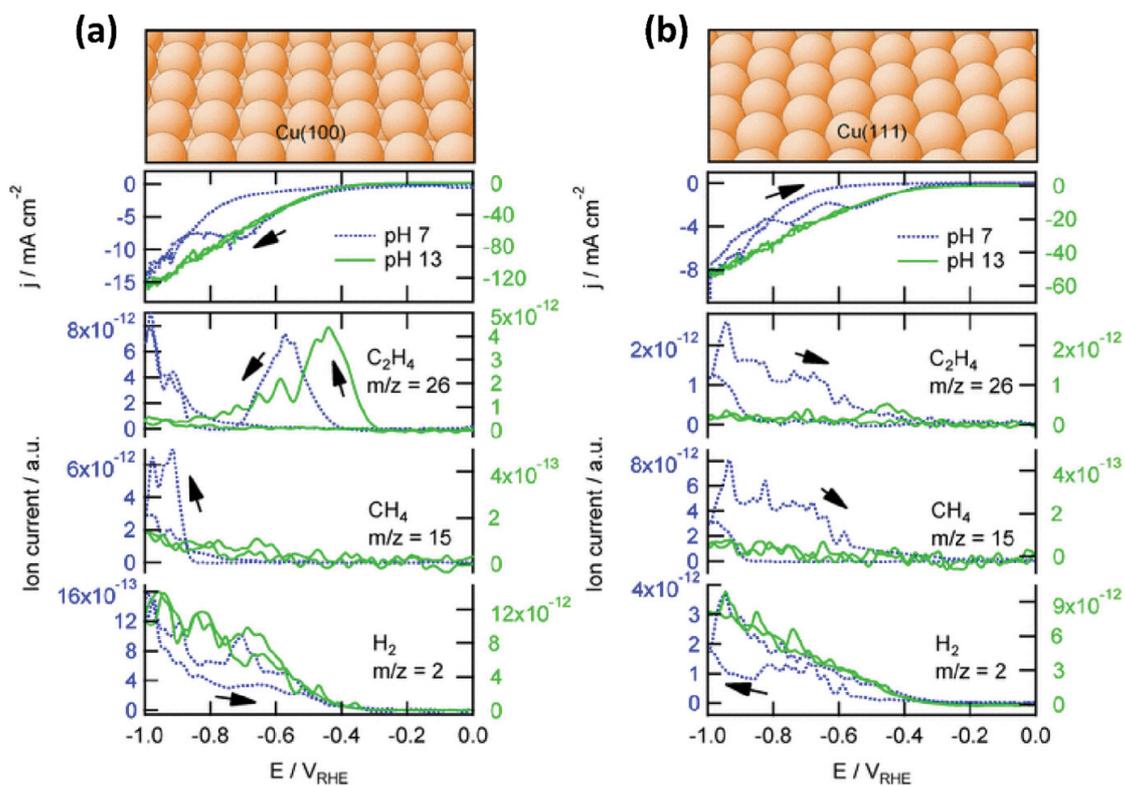


Figure 8. OLEMS data of CORR of **(a)** Cu(100) and **(b)** Cu(111) single-crystals in neutral (blue, KH_2PO_4 pH=7) and basic conditions (green, NaOH pH = 13) reproduced from ref. ⁷⁶. Copyright 2012, American Chemical Society. Both the total current as well as the ion specific current are provided. Note the roughly 200 mV earlier onset potential of C_2H_4 on Cu(100) vs Cu(111) as well as the 200 mV shift towards the equilibrium potential when switching electrolyte on Cu(100).

2.2.3. High index Cu single crystals

Apart from low-index Cu single-crystals, Hori and co-workers further prepared high-index Cu single-crystals for CO₂RR to investigate the influence of undercoordinated sites on the product distribution.¹³ These crystals consisted of n atomic rows of (100) terraces and one atomic height of (111) or (110) steps, namely Cu(S)-[$n(100) \times (111)$] and Cu(S)-[$n(100) \times (110)$], respectively. They found that introduction of (111) steps to a Cu(100) basal plane can dramatically enhance the C₂H₄ selectivity and suppress the production of CH₄ (**Figure 9**). The Cu(711) surface ($n = 4$) showed the highest selectivity for C₂H₄ (FE 58.5% at -1.37 V vs. SHE and 2.9 mA cm⁻²) and the highest ratio of C₂H₄/CH₄ (~8.5).^{23,24,13} Interestingly, the introduction of (110) steps into (100) terraces, also promoted C₂H₄ formation and suppressed CH₄. Additionally, it was shown that by increasing the step-density of Cu(S)-[$n(111) \times (111)$] surfaces an increased selectivity to oxygenates followed (H₃CCOO⁻, H₃CCHO and C₂H₅OH, **Figure 9**).¹³ The Cu(110) surface, with the Cu(S)-[$2(111) \times (111)$] orientation, showed the best H₃CCOO⁻ FE well over 20% (-1.6 V vs. SHE and 1.0 mA cm⁻²). The Cu(S)-[$n(100) \times (110)$]

electrodes showed the inverse trend with respect to H₃CCOO⁻ formation (**Figure 9**). These results indicate that stepped facets on the Cu surface can improve the selectivity to multi-carbon products compared to the planar single crystals. Later on, stepped surfaces such as Cu (211) facet have also been computationally determined to be more active in comparison to flat surfaces (similar to that of Ag and Au).^{64,27}

Based on the reported results, a relatively clear performance trend can be distinguished in CO₂RR on Cu single-crystals (**Figure 9**). Cu(111) surface is selective for CH₄ and portrays a limited rate towards C-C coupling, especially at low overpotential. The Cu(100) surface, in turn, shows especially strong C-C coupling reactivity, with the main product being C₂H₄. Introduction of (111) or (110) step sites further enhances the C-C coupling rate. Cu(110) shows mixed selectivity towards hydrocarbons, but does

show a clear trend in the production of oxygenates: the higher the number of (111) steps on (111) terraces, the higher the oxygenate production rates. Interestingly, in a recent publication by Cuenya and co-workers, pristine Cu(111) and Cu(100) surfaces produced via UHV techniques showed no meaningful activity for CO₂RR.²⁹ The majority of the current (80%) went towards HER instead. Hydrocarbons only became the majority product after the introduction of defects. Also, significant restructuring under the applied potential was observed. Even though defects in Cu single crystals have both experimentally and computationally been shown to improve CO₂RR to hydrocarbons,^{80,81,82,83} the inactivity of the clean Cu(100) and Cu(111) as well as the significant restructuring of the catalyst under operation is a non-trivial result. It begs the question, if single crystals in general, under applied potential and *in operando*, reconstruct. Therefore, the use of single-crystals for CO₂RR mechanistic studies should be further investigated and validated in combination with operando techniques to monitor the catalytic surface in real time.

To conclude, the crystal orientation of metals greatly affects the binding energy to the reactants, i.e., CO₂ and H₂O, and various intermediates, e.g., *CO, *H, and *COOH etc., thus affecting both catalytic activity and the selectivity in CO₂RR. Despite those different metals (e.g., Pt, Ag, Au and Cu etc.) show distinct product distributions in CO₂RR, stepped-surfaces of these metals are generally more active than planar surfaces. Although inducing changes to adsorbate binding energies, crystal facets of most metals (e.g., Pt, Ag and Au) do not change their inherent selectivity for specific products. Cu is the sole exemption i.e., Cu(111) is CH₄ selective, Cu(100) is C₂H₄ selective and Cu(110) shows a mixed selectivity but enhanced production of oxygenates such as C₂H₅OH and H₃CCOO⁻. Finally, single-crystals, due to their large surface energy, may reconstruct under operation possibly making them proto-catalysts.

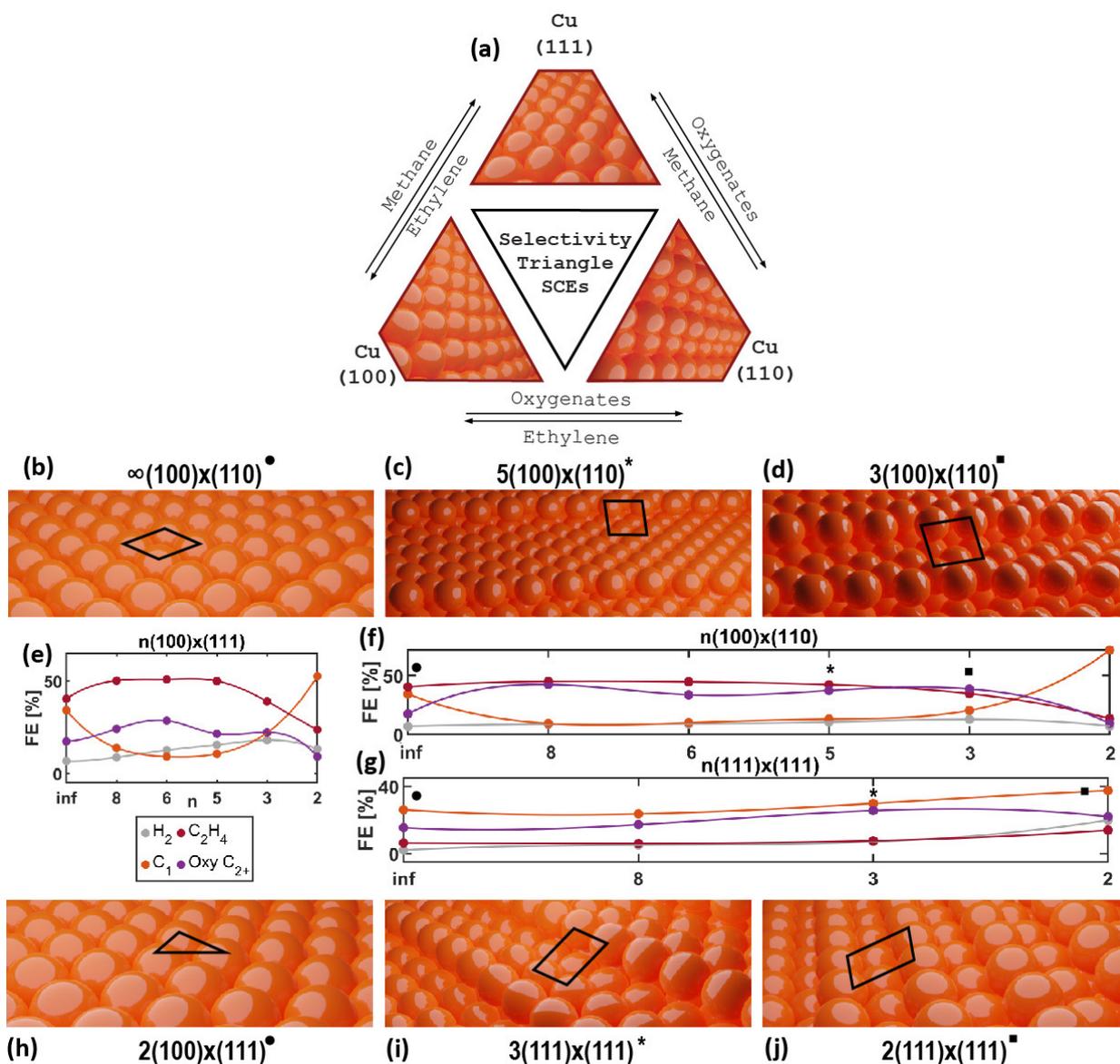


Figure 9. (a) The selectivity triangle of Cu single-crystal electrode in the CO₂RR summarizing data reported by Hori and co-workers and Koper and co-workers.^{13,23,24,76,84} (b-d) Cu(100), Cu 5(100)x(110) and Cu 3(100)x(110). (e-f) Selectivity for H₂, C₁ products, C₂H₄ and C₂₊, oxygenates on a Cu(100) surface with increasing (111) and (110) step-density. (g) Selectivity on a Cu(111) surface with increasing (111) step-density. (h-j) Cu(111), Cu 3(111)x(111) and Cu(110). Circle, star and square in (b-d) correspond to (f) and in (h-j) to (g). Black inset denotes the proposed active site for the majority product.⁸⁵ Note that the electrochemical performances were reported at the most selective potential ($\Delta U \sim 200$ mV). All reactions were carried out in 0.1 M KHCO₃ at 5 mA cm⁻².

2.3. Nanoparticle catalysts

2.3.1. Nanoparticles: facet dominated regime

With a well-defined surface structure, single-crystals are excellent systems to understand the CO₂RR mechanism. However, due to their low surface area, and thus poor atom economy, their potential is limited in real-world applications. To improve this, nanocrystals that expose specific facets but with a higher degree of surface atom density have been synthesized and used for CO₂RR. For example, as an FCC metal, Cu nanocrystals can be prepared with a cubic shape exposing (100) facet and a tetrahedral shape exposing (111) facets. However, with the decrease of catalyst size from extended surface to nanoparticles, other factors besides the crystal facet begin to play a role (or even a dominant role) in the catalytic reaction. For instance, the increased number of low coordinated atoms (**Figure 10**), the interactions between

NPs and support materials, and the organic ligands used in synthesis, etc. In this section, we will summarize some representative examples that use NPs larger than 10 nm, of which the facet still dominates the surface and, thus the reactivity. We lay emphasize on examples that include particles in a size range produced with the same method to deconvolute contributing factors. Through this section, we can better understand the synergistic effect of crystal facet, edge and corner on the catalytic performance, as well as other key factors that influence the reactivity.

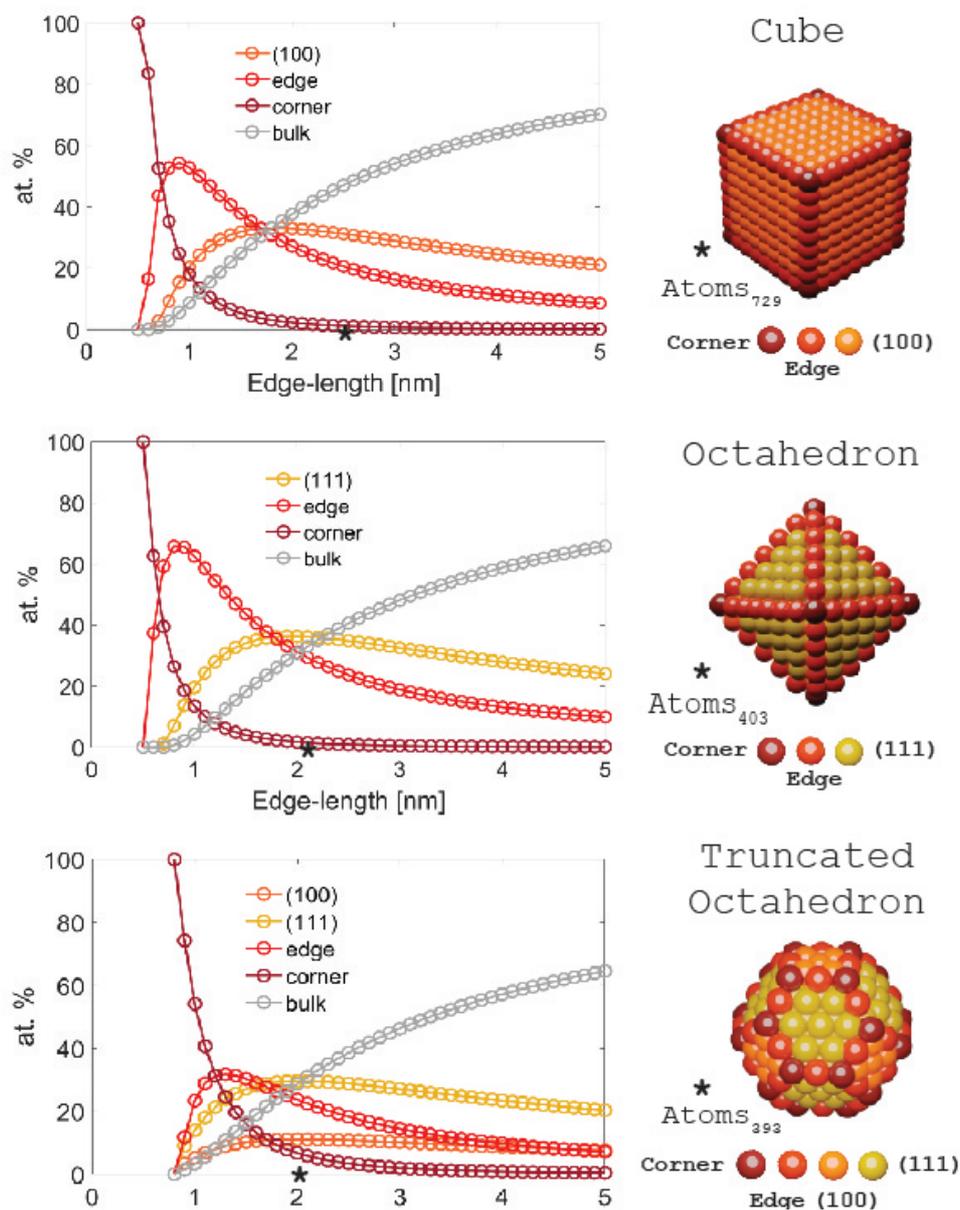


Figure 10. Evolution of the relative contribution of the surface atoms (denoted as corner (in rust-brown), edge (in red), and facet ((111) in yellow and (100) in orange)) versus the bulk atoms (in grey) as a function of the particle edge-length, spanning three different geometries: cubic, octahedral and truncated octahedral. The asterisk in each figure indicates the edge-length of the particle depicted by the corresponding ball-model. For particles >5nm, independent of the geometry, the major contribution to the surface atoms is from the facets. The in-house developed geometrical model is based on the definition of various subsurfaces, see **Note S3** of the Supporting Information.⁸⁶

Motivated by the work on single-crystals, a few research groups have synthesized Cu NPs that expose certain facets for CO₂RR. Buonsanti and co-workers prepared Cu octahedra particles that expose predominately (111) facets (75, 150 and 310 nm) for CO₂RR (**Figure 11a-c**).⁸⁷ In agreement with the results obtained from single crystals (**Figure 10**), these particles are CH₄ selective. In addition, both the CO₂RR partial current density and the CH₄ selectivity increased with the decrease of particle size (**Figure 11h**). Alternatively, the same group used a different colloidal synthesis to yield (100) faceted Cu cubes of various sizes (24, 44 and 62 nm edge-length) (**Figure 11d-f**). However, they found that the 44 nm particles, not the smallest one, showed the highest C₂H₄ selectivity, with an FE of 42% at -1.1V vs. RHE and 2.3 mA cm⁻² (**Figure 11g**). Here, the authors argue that an optimal ratio of edge-sites over (100) facet-sites for the 44 nm Cu cube particle is key for the high C₂H₄ selectivity. Later, in collaboration with theoreticians, the same group explained these results through DFT simulations: the C-C coupling step does not take place through the CO-CO dimerization mechanism typical of the Cu(100) facet, but exploits through the COH-CO coupling at the interfaces of the terraces and the

edges.⁸⁸ The notion that edges improve C₂H₄ selectivity is in agreement with that observed by Hori and co-workers on high-index Cu single-crystals, as cube edges are chemically equivalent to Cu(110) steps (i.e., coordination number of 7). Notably, this mechanism does not explain why 44 nm particles exhibited the best C₂H₄ selectivity, as smaller particles (24 nm) have higher numbers of interfacial sites at the same catalyst loading. It is speculated that the *in operando* restructuring of the Cu NPs may instead have contributed to the poor performance of the smallest particle.^{89,90} Indeed, with operando electrochemical atomic force microscopy (ECAFM), Cuenya and co-workers have observed morphology changes of Cu nanocubes during CO₂RR.⁴⁵ Similarly, Buonsanti and co-workers performed ex situ TEM analysis of three different sized Cu nanocubes (16 nm, 41 nm, and 65 nm) and found that the cubic structure became ill-defined during CO₂RR and the CO₂RR activity decreased.⁹¹ Both studies concluded that smaller Cu nanocubes suffer from faster morphology changes, and more importantly, degradation immediately starts at the edges where C-C coupling is argued to take place. Therefore, these results indicate that it is still worthwhile to conduct more controlled

studies to understand the synergistic effects of different facets. Further, it is important to note the challenges involved in normalization of the ECSA. Roughness factors can have tremendous influence on the current densities and techniques to determine it vary widely.¹⁰ Therefore, the effect of the enhanced surface area by particle size reduction are far from excluded in this size-regime.

Another important factor that can affect the CO₂RR performance of NP catalyst is the support material. In contrast to the self-standing single-crystals, a suitable support material (i.e., glassy carbon or carbon paper) is required to ensure good dispersion, conductivity, and mechanical stability of the NPs. In such case, the interactions between NPs and supports can change the electronic and geometric structures of the NP, and therefore the catalytic properties. In example, wetting behavior of transition metals varies on different supports and, thereby influence particle shape.⁹² However, studies focusing on the impact of support in CO₂RR are scarce. Cuenya and co-workers reported that CO₂RR selectivity of Cu cubes is indeed both size- and support-dependent.⁴⁵ In here, Cu cubes of 220, 320 and 580 nm were electrodeposited on

carbon paper and tested at -1.1 V vs. RHE. The smallest cubes were most selective for CH₄, reaching a maximum FE of 50% (~5 mA cm⁻²). When the Cu cubes were electrodeposited on Cu foil, C₂H₄ was the major product (~50% FE). Furthermore, the authors observed fast dynamic changes on particles with small size and with carbon support. The dynamic changes, including the roughening and the disappearance of the (100) facets, loss of Cu, and reduction of Cu(I) species, are suggested to be the origin of the decreased selectivity for C₂ products versus CH₄. Finally, what only is starting to be considered to affect the CO₂RR performance is adsorbed organic molecules and ligands on the surface of NPs. To synthesize NPs, particularly the ones with orientated facets, organic ligands are often required. Broekmann and co-workers showed that polyvinylpyrrolidone (PVP) present at the surface of 100 nm Ag cubes (used as a shape-directing agent) thwarted the performance. The FE for CO became poor (<50% at >-0.75 V vs RHE and ~45 mA cm⁻²) when PVP was present at the surface. Instead, when they applied briefly a cathodic potential of -1.1 V vs. RHE desorbing the PVP, FE well over 70% could be maintained up to -0.65 V vs. RHE (~85 mA cm⁻²). On the other hand, organic

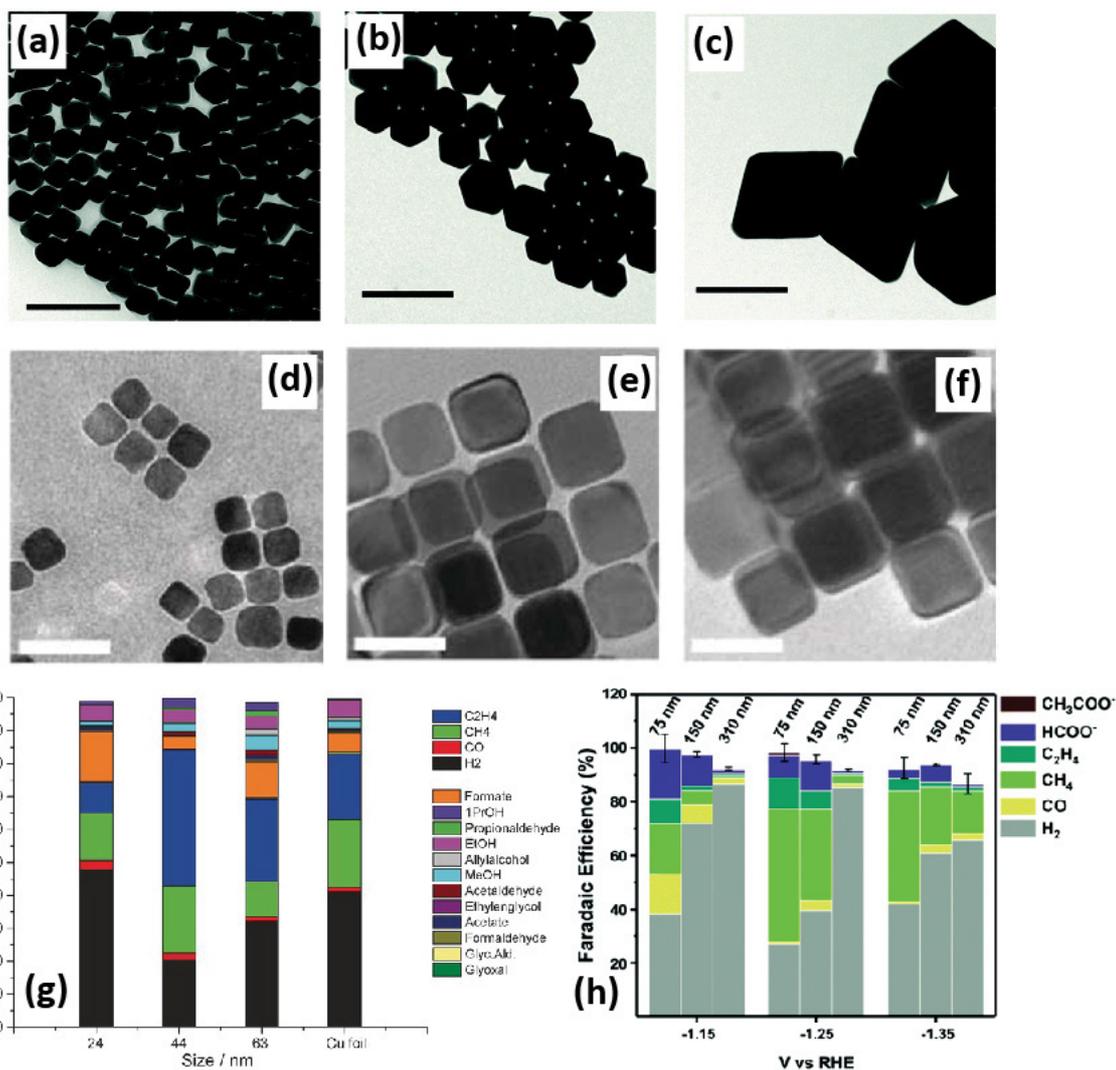


Figure 11. (a-c) TEM images of geometrical Cu octahedra of size 75, 150 and 310 nm, respectively. (d-f) TEM micrographs of Cu single-crystal nanocubes of size 24, 44 and 63 nm. (g) Deconvoluted size and shape effect on the product distribution, determined at -1.1 V vs. RHE in 0.1 M KHCO₃, polycrystalline Cu is added as a reference. Whereas the activity increases with size, the selectivity to the major product, C₂H₄, reaches an optimum near 44 nm. (h) Effect of the applied potential deconvoluted from the size and shape-effect in the facet dominated regime of Cu showing that both the selectivity and activity towards CH₄ increases with decreasing size. Reproduced from ref. ^{44,87}. Copyright 2016 Wiley-VCH and 2019 RSC Publishing, respectively.

molecules can also be introduced onto the surface of NPs to improve the performance. For instance, Kim and co-workers showed that the presence of cysteamine on their 5 nm Ag NPs immobilized on carbon black lowered the overpotential by 300 mV in the CO₂RR to CO.³⁹ DFT calculation pointed towards a stronger affinity of the anchoring agent capped Ag NPs for the *COOH intermediate fastening the rate. In fact, recent studies have begun to use organic molecules or polymers to modulate the electronic structure and/or the local environment of the catalyst to tune the catalytic performance.^{93,94,95} These examples further indicate that the chemical nature of the surfactant of colloiddally synthesized NPs needs to be considered in CO₂RR, something that is not often addressed.

Overall, for NPs with size of 10-1000 nm, most of the atoms are still in the bulk region (**Figure 10**). Therefore, like single-crystals, these NPs are mainly used for fundamental studies for understanding the structure-performance relationships and their selectivity is largely governed

by the crystal facets exposed. In contrast to single-crystals, however, studies propose that the edges and corners of the NPs in this size range already played an important role in the catalytic reaction, despite, according to our model (**Figure 10**), that the ratios of edge/facet and corner/facet are still very low. Since other factors, such as catalyst-support and catalyst-ligand interactions, also start to play a role, we would like to highlight the need for more fundamental studies on nanoparticles in this size regime to decouple the effects of crystal facet from other effects. In addition, similar to single-crystals, the surface energy of these nanoparticles is high, thus restructuring of the surface under CO₂RR condition can easily take place and should be further studied.

2.3.2. Nanoparticles: undercoordinated sites dominated regime

For NPs with any given geometry, the density of undercoordinated surface atoms grows with decreasing particle size as can be seen from **Figure 10**. Therefore, as we continue to go down in particle size, the contribution of the edges and corners starts to dominate the reaction kinetics. Rates may be enhanced several orders of magnitude on increasingly undercoordinated sites, meaning that minor contributions to the surface can actively impact the reaction. However, as HER and the different reaction pathways of CO₂RR take place over a similar potential range, simply increasing the number of undercoordinated sites will not necessarily enhance the production of specified products from CO₂. Thus, it is essential to understand the geometrical effect on CO₂RR for NPs with size of 2-10 nm, where the ratio of undercoordinated sites to coordinated sites becomes significant.

Actually, most NP-catalysts used for CO₂RR are in this size-class, because they can easily be prepared with various methods, and still remain stable whilst improving the activity. As factors like facets, metal-support interactions and organic ligands have been discussed in **Section 2.3.1**, herein, we will focus especially on the size dependent catalytic behavior of both non-Cu based catalysts and Cu-based catalysts.

2.3.2.1. Non-Cu based nanoparticle catalysts

For Ag-based CO₂RR catalysts, size-dependent catalytic behavior has been observed in several studies, however, the origin of the size effect remains controversial. Kenis and co-workers found that Ag NPs of 5 nm size showed a 10-fold higher CO partial current density than both the bulk sample and the 1 nm sample (**Figure 12a-e**).³¹ They suggested that an optimized adsorption strength of reaction intermediates on 5 nm sized Ag NP is the key, however, why the binding energy varies was not explained. While the above results were obtained in organic electrolyte, Hwang and co-workers studied the size effect of Ag NPs in aqueous electrolyte (**Figure 12f-g**).³⁹ Despite that they also found 5 nm Ag NPs to be the most active ones (**Figure 12f**), DFT simulation showed that the binding energy difference of *COOH is marginal for NPs larger than 3 nm. Thus, the cysteamine used for the synthesis of Ag NP was considered as the dominating factor. With an optimal coverage of the 5 nm sized Ag

NPs with the cysteamine anchoring agent, a suitable amount of Ag-S bonds are formed which enhanced the stabilization of *COOH (**Figure 12g**). Very recently, Kaufmann and co-workers synthesized a series of Ag NPs with average diameters of 2 to 6 nm through physical vapor deposition to avoid the influence of organic ligands, and the best CO activity and selectivity were observed on NPs of ~4 nm.⁹⁶ Combining DFT simulation and microkinetic modeling, the authors found that CO₂RR and HER activity was dominated by Ag(100) and Ag edge sites, respectively. The high prevalence of Ag edge sites on NPs smaller than 4 nm leads to a higher HER activity. Unfortunately, the highly oriented pyrolytic graphite was used as a support for Ag NPs and the weak Ag-C bond may lead to rapid aggregation of Ag NPs, which was not considered in this work.

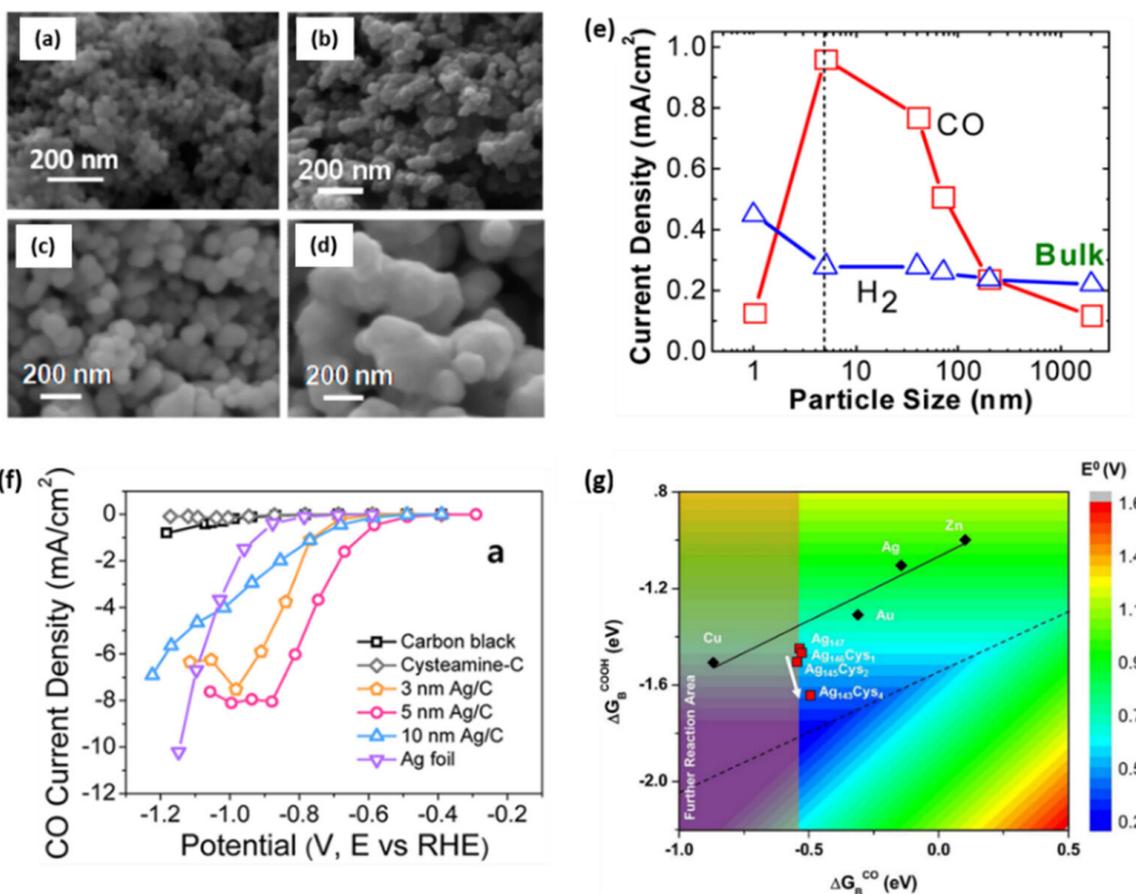


Figure 12. (a–d) SEM images of 1, 5, 70, and 200 nm silver NPs, respectively. (e) Volcano trend in the activity of ultrasmall to bulk Ag NPs in the CO₂RR towards CO in CO₂ saturated 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) electrolyte.³¹ Reproduced from ³¹. Copyright 2013 ACS Journals. Current densities for CO and H₂ formation reported are the differences in the current density with CO₂ and Argon at –0.75 V vs SHE and –1.14 V vs SHE, respectively. (f) CO partial current density for Ag NP samples and control samples. (g) Effect of anchoring agents on COOH and CO binding energies examined using Ag_(147–n)Cys_n (n = 0,1,2,4) models. Reproduced from ref. ³⁹. Copyright 2015 American Chemical Society.

The size effect of Au NPs was studied by Sun and co-workers using 4, 6, 8 and 10 nm particles (**Figure 13a**).³⁵ Notably, the NPs were immobilized on carbon black and the organic ligands were removed through annealing before the reaction (**Figure 13b**). The authors found that the CO partial mass current increased with decreasing particle size (**Figure 13d**), but the selectivity followed a volcano trend, peaking at the 8 nm particle (**Figure 13c**). After calculating the CO₂-to-CO and the HER pathways on Au (211), Au (111) and Au₁₃ cluster, the authors concluded that the highest CO production rate for the 8 nm particles is due to the presence of an optimum ratio of the edge sites. It must be noted that the crystalline size determined by XRD was much smaller than the one reported based on TEM, suggesting the existence of different types of uncoordinated sites on the surface of Au NPs, making the Au (211) surface possibly too simple to simulate the real surface. Cuenya and co-workers also investigated the size effect of Au NPs in CO₂RR (**Figure 13g-i**), however, they found that the majority of the current went towards

H₂, especially at large overpotential (**Figure 13j**).³⁷ The authors argued, based on DFT, that while the formation of *COOH is increasingly favored with decreasing particle size, H⁺ is as well and to a higher degree. This explains both the enhanced activity on smaller Au NPs as well as the change in selectivity, similar to that from Sun and co-workers.³⁷ Note that the particles were produced with the inverse-micelle encapsulation method, and that the influence of the polymer was not considered. Another fact worth mentioning is that the standard deviation of particle diameter is in the order of ±1 nm, the reactivity reported is actually the average of an ensemble. It would therefore, be very interesting to see these measurements repeated with better size-selection.

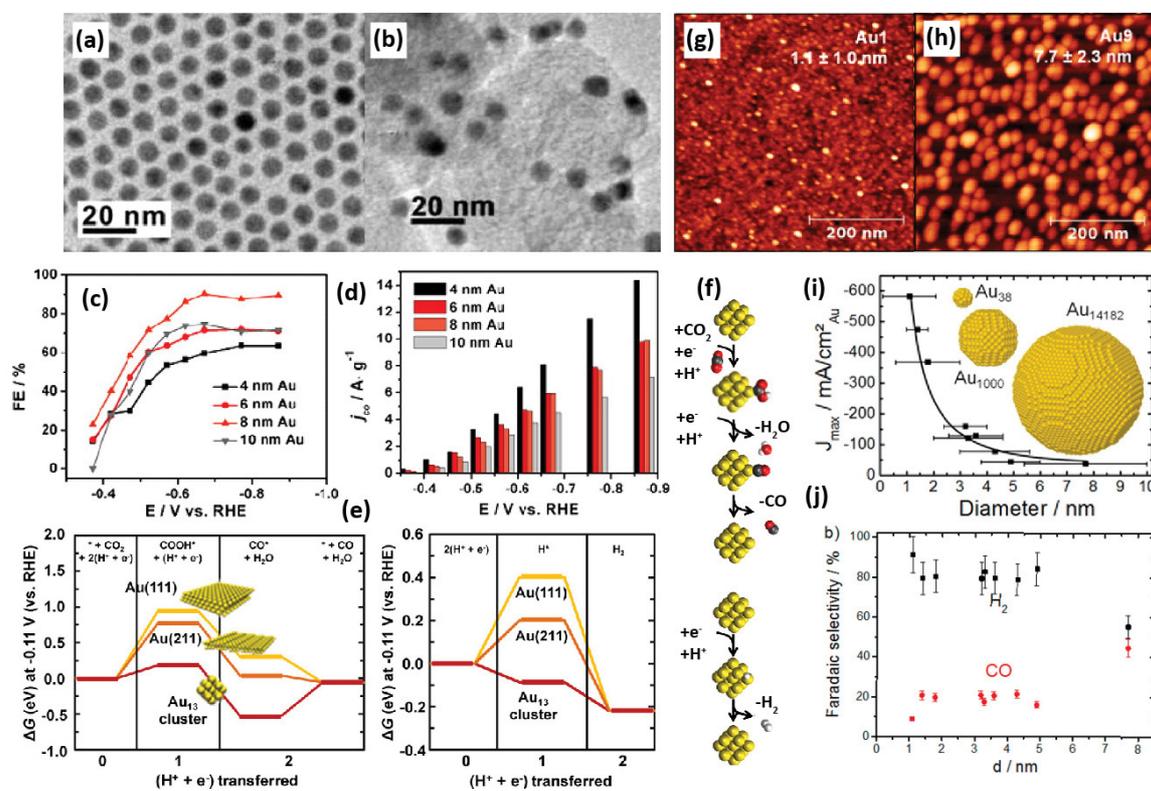


Figure 13. (a-b) TEM images of the 6 nm sized Au NPs as well as the composite material used as cathode of NP-decorated activated carbon, respectively. (c) Size-dependent CO selectivity of Au NPs as a function of applied potential (V vs. RHE) in 0.1 M KHCO_3 . (d) CO specific mass current as a function of size and potential. (e) DFT calculation using the computational hydrogen electrode showing the free-energy diagram at a potential of -0.11 V vs RHE on Au(211), Au(111) and Au_3 clusters for the conversion of CO_2 into CO as well as the parasitic HER. (f) Schematic representing the conversion of CO_2 to CO on Au clusters. Reproduced from ref. ³⁵. Copyright 2013 American Chemical Society. (g-h) AFM images of the Au NPs of 1.1 ± 1.0 nm and 7.7 ± 2.3 nm produced via the encapsulated-micelle approach. (i) Size-dependent current density of Au NPs at -1.2 V vs. RHE in 0.1 M KHCO_3 . (j) Faradaic efficiency as a function of size at -1.2 V vs. RHE. Reproduced from ref. ³⁷. Copyright 2014 American Chemical Society.

As has been mentioned before, Zn is another CO selective metal. Interestingly, oxidized Zn NPs (1.7 to 6.8 nm) showed a similar trend to that of Au and Ag:⁴² while the overall activities increased with the decrease of particle size, the CO selectivity did not. Here, Zn NPs in the size regime of 3 to 5 nm benefited the most from undercoordinated atoms, maintaining a high CO selectivity (>70% FE) at a relatively high current density (3.5–5.6 mA cm⁻²). Notably, the authors also suggested that Zn(OH)₂ species could be directly involved in the mechanism as a partial reduction of oxidized-Zn was observed using *operando* XAS.

Besides CO-selective metals, other size-selected particles in CO₂RR have also been reported. In a study by Li and co-workers, In₂O₃ nanocrystals were investigated covering both isotropic and cubic crystals.⁹⁷ In, being a typical HCOO⁻ selective catalyst, showed improved selectivity when switching from the bulk to the nanoscale. However, similar to results obtained for CO selective NPs, smaller did not necessarily mean better. The highest FE (>90% and 6.3 mA cm⁻²) for HCOO⁻ was observed for the 15-nm In₂O₃ cubes from -0.71 to -0.9 V vs.

RHE. Instead, the 5-nm spheres peaked at 83% at -0.71 V vs. RHE and rapidly became H₂ selective at larger overpotentials (FE HER >70%). DFT calculations of In(101), In₁₆₅ and In₈₅ clusters, showed *H adsorption gradually approached thermoneutrality as the particle size decreased. Thereby, the acceleration in HER for the 5-nm NP could be explained.

While all the above examples showed the effects of structural factors on a single product from CO₂ (e.g., CO or HCOO⁻), the selectivity of Pd NPs is tunable towards CO and HCOO⁻.³⁸ By the reduction of PdCl₂ with citrate as capping agent, 2–10 nm Pd NPs were obtained and tested (**Figure 14a–f**).³⁸ Similar to other metal NPs, the overall activity increases with decreasing size of Pd NPs, but the difference is that the selectivity is also improved (**Figure 14h**). An excellent CO FEs over 90% could be obtained between -0.7 and -1.0 V vs. RHE for particles <5 nm (**Figure 14g**). Based on a DFT model, the authors use *CO poisoning to explain the deceleration of the rate for the 2.4 nm Pd NP. Further, it was shown that *H binding did not benefit equally from the reduction of size versus the *COOH intermediate. This made CO₂RR the preferred pathway.

Interestingly, Broekmann and co-workers showed that HCOO^- was the main product for Pd NPs of the same size range (3.8, 6.5 and 10.7 nm) but synthesized with a PVP capping strategy (**Figure 14i-k**).⁴⁰ The highest selectivity of 98.3% was obtained at a strikingly low overpotential (-0.1 V vs. RHE and $\sim 1.5 \text{ mA cm}^{-2}$) for the 6.5 nm sized NPs. Noteworthy is the equilibrium potential of HCOO^- at -0.12 V vs. RHE (**Table S1**), which seems at odds with

the values reported by Broekmann and co-workers reported. The authors claimed that the active phase was PdH, not metallic Pd, providing a likely explanation for this discrepancy.

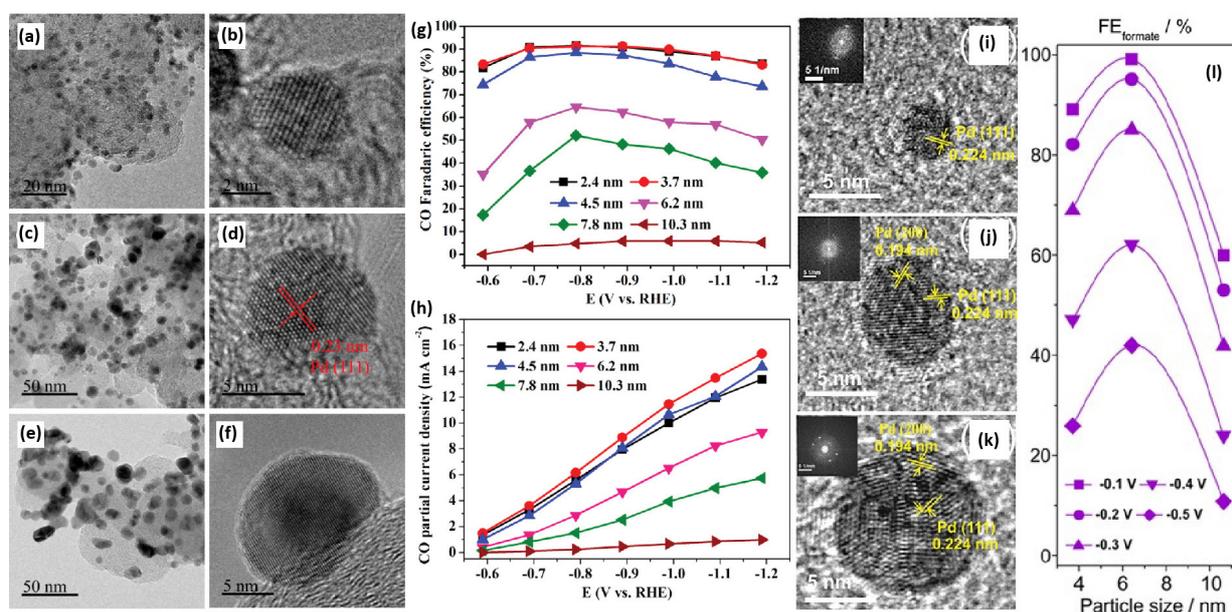


Figure 14. (a-f) TEM and HRTEM micrographs of the 2.4, 6.2 and 10.3 nm Pd NPs. (g) Effect of size in the ultrasmall particle regime of Pd on the selectivity towards CO as a function of potential in 0.1 M KHCO_3 . (h) CO partial current density as a function of size and potential in the ultra-small particle regime of Pd. Reproduced from ref. ³⁸. Copyright 2015 American Chemical Society. (i-k) HRTEM micrographs of the 3.8, 6.5 and 10.7 nm Pd NPs. (h) HCOO^- FE as a function of particle size at -0.1 V vs RHE in 0.5 M NaHCO_3 . Reproduced from ref. ⁴⁰. Copyright 2017 Wiley-VCH.

2.3.2.2. Cu-based nanoparticle catalysts

As discussed above, tuning the facet and particle size of non-Cu based catalysts generally changes the activity of CO₂RR, and, therefore the ratio of CO₂ reduction products to H₂. However, for Cu-based catalysts, due the large variance in products generated, the product distribution is very sensitive to the facet and particle size. For example, Cuenya and co-workers investigated size selected Cu NPs deposited on glassy carbon (2 to 15 nm) and observed a clear activity trend as a function of particle size (**Figure 15**).³⁶ The formation of hydrocarbons decreased drastically with decreasing particle size, with the FE for C₂H₄ and CH₄ reaching a plateau at <15 nm (**Figure 15h**). At particle sizes <5 nm, at least an order higher currents for H₂ and CO in comparison to the bulk were produced (**Figure 15g**). The authors explained this trend for the fact that the number of undercoordinated sites goes up exponentially in this size regime suggesting much stronger binding to intermediates.

Different catalytic behaviors for Cu NPs in this size regime have been observed. Kibsgaard

and co-workers showed that 5 nm sized Cu NPs prepared using magnetron sputtering exhibited excellent C₂H₄ selectivity (FE >40% at -0.8 V vs RHE and 4 mA cm⁻²) in CORR.⁹⁸ Further, Cu-phthalocyanine derived 2±1 nm sized Cu NPs showed high FEs towards CH₄ in CO₂RR (66% at -1.06 V vs. RHE and ~15 mA cm⁻²).⁹⁹ It is possible that the inverse-micelle encapsulation method used by Cuenya and co-workers introduces carbonaceous material to the particle surface that interferes with the reaction. Especially when considering the behavior of the extended library of Cu-based bimetallic electrodes produced via the same method, this seems plausible. For example, Cuenya and co-workers investigated composition controlled Cu_xCo_{100-x} NPs (size of 1.2-21 nm) and showed that HER was favored over CO₂RR.⁴³ Later, they also studied AuCu alloys in the 1.4 to 24 nm size regime and reported again high H₂ FE independently of the size.⁴¹ Contrarily, Yang and co-workers showed at least 40% CO FE under the same conditions for 10 nm AuCu NPs of various compositions prepared using a co-reduction method.^{41,100} As we have seen

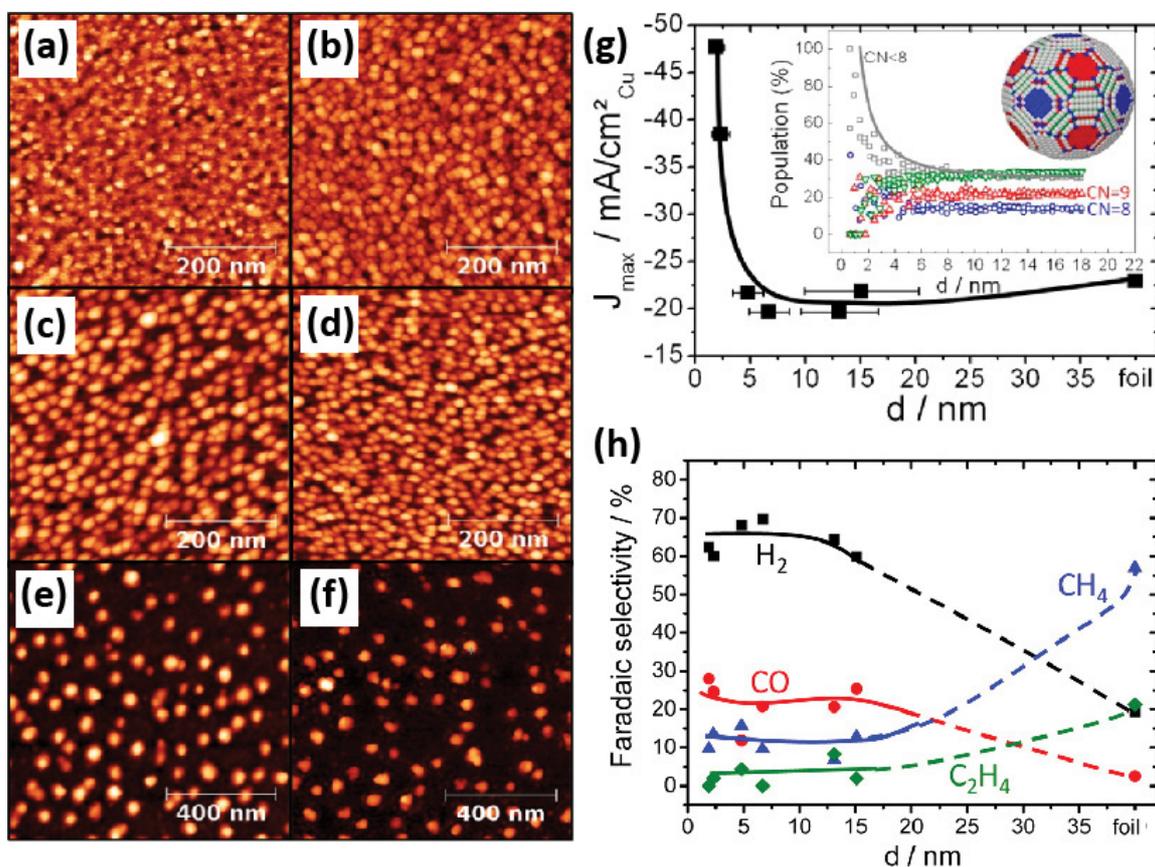


Figure 15. (a-f) AFM images of 2-15 nm Cu NPs on glassy carbon. (g) Enhanced overall activity of Cu NPs as a function of particle size at -1.1 V vs RHE in 0.1 M KHCO_3 . (h) Evolution of the product distribution on Cu NPs as a function of size at -1.1 V vs. RHE in 0.1 M KHCO_3 showing that most of the current enhancement reported goes towards the parasitic HER. Reproduced from ref. ³⁶. Copyright 2014 American Chemical Society.

that adsorbed organic molecules and ligands can dominate the reaction, with size only of minor influence, care should be taken by interpreting these results. Thus, further experiments excluding some of the possible contributing factors should be performed, to precisely evaluate the intrinsic performance of Cu NPs this size regime. Magnetron sputtering under UHV such as reported by Kibsgaard and co-workers is good method for this, although the low loading of NPs makes the accurate quantification of products harder. We would like to point out that much higher deposition rates have been reported for spark ablation (1 g/h for 5 nm NPs).¹⁰¹ Although its application in catalysis is still in its infancy, the high production rates reported and absence of ligands make it an interesting candidate to investigate this size-class further.^{102,103}

From the above-mentioned examples of non-Cu and Cu-based ultras-small particles, it is clear that decreasing the particle size is an effective way to tune the catalytic performance. However, smaller particle size, although enhancing overall reaction rates due to a higher degree of undercoordination,

does not necessarily result in better CO₂RR performance. An intricate balance between adsorption strengths of intermediates determines the selectivity often resulting in volcano-like selectivity trends as competing reaction (i.e., HER) sway the performance. Further, the effect of support and ligation-shell cannot be excluded from performance assessments as they may dominate the reaction kinetics. It is worthwhile to note that although our discussions have been focused on single-element metal catalysts, most of the bimetallic catalysts (e.g., alloys, tandem catalysts) can be devised in this particle regime.^{104,105} In the framework of systematic investigations of structure-performance relationships in combination with composition effects, we see opportunities for these types of studies in the future. Our discussions of single-elemental particles may help as a guideline to place such studies in context.

2.4. Metal cluster catalysts

Below a certain particle size, <1.5 nm for Au for instance, common structural factors useful to determine reactivity of NPs become meaningless.¹⁰⁶ In this regime, metallicity breaks down and clusters behave more like molecules than particles. Localized electron density, e.g., in the form of molecular orbitals, now dictate the reactivity. Clusters, namely, occupy discrete energy levels (**Figure 2**), which are directly related to the number of atoms bonded, their spatial arrangement and charge.^{107,108,109,110} Metal clusters that contain a small number of atoms have shown great advantages in heterogeneous catalysis. For example, the activity and selectivity of the catalytic reaction can be well tuned by precisely controlling the size of the clusters. Furthermore, clusters of a single and well-defined mass can facilitate the understanding of reactivity as it allows for computational studies at the highest level of theory. As early as the 1980s have metal clusters been produced using physical deposition methods, such as thermal evaporation or magnetron sputtering, and applied in catalysis.^{111,112,113} ¹¹⁴ However, few

studies have used such clusters for CO₂RR, possibly due to their low production rates and loading, as well as the consequent difficulties in quantifying reaction products. Metal clusters can also be synthesized through chemical methods, where atomically precise clusters are protected with organic ligands. These materials have found their applications in CO₂RR in the last few years, showing promising catalytic performances, as will be discussed in the following section. Even more recently, metal clusters have also been produced *in situ* from dispersed metal catalysts upon applied cathodic potential of which sparse examples will be discussed as well.

2.4.1. Ligand effect in metal clusters

Metal clusters, either produced colloiddally or SAC-derived are all bonded to some type of ligand. In the case of colloidal clusters, ligands are molecular compounds such as thiols and phosphines, and are necessary to control atomicity (number of atoms bonded) and geometry and ensure colloidal stability. Instead, in the case of SAC-derived clusters, stability originates from ligation sites in the support (often heteroatoms). Without the ligands, agglomeration would occur upon the slightest perturbation, let alone under applied potential. Beyond stability, however, ambiguity exist about the actual role of ligands in reactivity itself as many convoluted effects may be present.

Thiol-capped icosahedral Au_{25} clusters were first synthesized and used for the CO_2 RR by Jin and co-workers.³⁰ An extremely low CO onset potential of -0.193 V vs. RHE was observed, indicating the exceptional intrinsic activity of the Au clusters (i.e., 200-300 mV earlier than for 2 nm Au NPs and polycrystalline Au). Also, near unity FEs could be obtained at more cathodic potentials (-1.0 V vs. RHE), albeit at low partial current densities (0.1 mA

cm^{-2}). The authors argued based on DFT simulations that strong physisorbed CO_2 bonded through the S atoms of the thiol, explained the enhanced reactivity. However, since the reference Au NPs were citrate capped, the effect of the ligand could not be deconvoluted from the reduction in size. In a later study of the same group, icosahedral Au_{25} clusters were compared with rods of the same mass produced using different sets of ligands (**Figure 16**).³⁴ In this way, it became possible to exclude the effect of atomicity and determine instead to what degree ligation affected cluster reactivity. Interestingly, it was shown that the CO production rate was 2.8 times higher for the near-to-spheres than for the rods at -1.17 V vs. RHE (**Figure 16a**). Further, the icosahedra were 1.5 times more selective for CO than the rods. However, in contrast to physisorption via the ligands reported before, adsorption of CO_2 was expected to proceed through a ligand exchange process instead. And CO_2 adsorption was more facile for the near-to-sphere than the rod explaining the difference in rates. Experimental evidence has been reported

that such atomically precise clusters are partially dethiolated when they undergo CO₂RR and that the active site resides on an uncapped Au atom.¹¹⁵ This suggests that the ligand does not play a direct role in the catalysis but the fast dissociation of those ligands does facilitate rapid conversion. On top of that, the type of ligand also determined the geometry of the clusters. And it was shown that a partial negative charge on the near-to-spheres improved the formation of the *COOH intermediate, which enhances the rate further. Note how

the charge influences the geometry similar to what has been observed for Au_{<14} clusters produced with UHV methods.¹¹⁰ Although ligands here are not directly involved in the conversion of CO₂, they do affect the rates of reaction through exchange rates and charge stabilization. Unfortunately, deconvolution of the rates induced by the ligand and the atomicity of the cluster have not yet been reported. And as we will see in the following section, atomicity may have massive impacts.

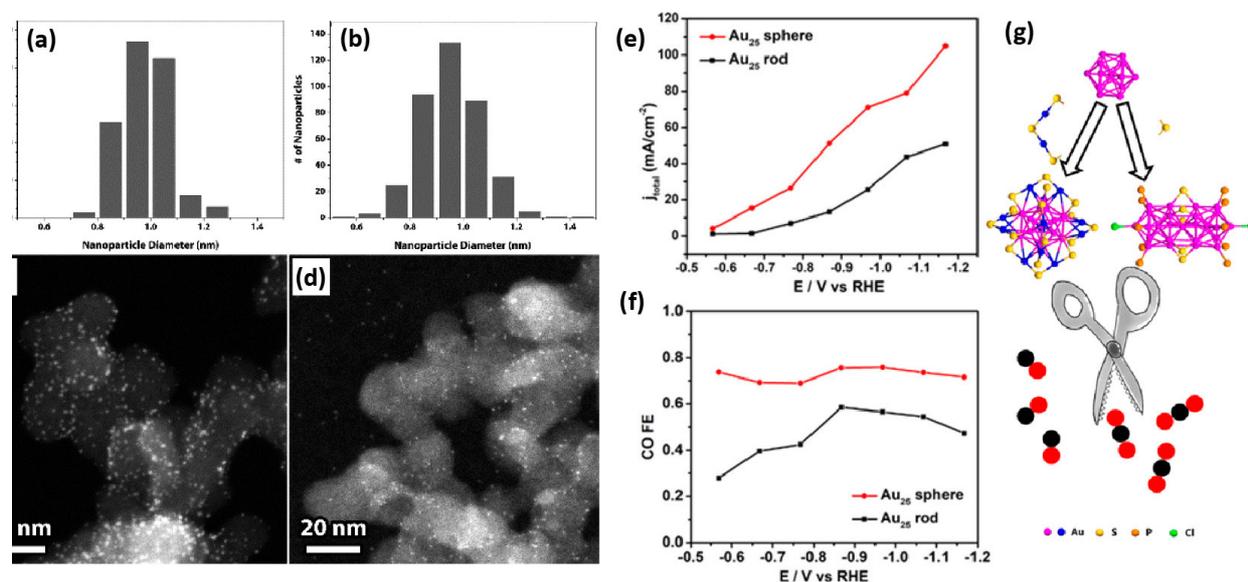


Figure 16. (a-b) Size-distributions of Au₂₅ nanosphere and nanorods, respectively. (c-d) STEM HAADF micrographs of the Au₂₅ clusters supported on carbon black. (e) Total current density of CO₂ reduction as function of potential vs RHE of rods (in black) and spheres (in red) in 0.1 M KHCO₃. (f) Faradaic efficiency of the Au₂₅ cluster pair as a function of potential vs RHE (nanosphere: red, nanorod: black). (g) Atom packing schematic of the conversion of Au nuclei into clusters of nanosphere and nanorod geometry as the result of the ligand shell. Reproduced from ref. ³⁴. Copyright 2018 American Chemical Society.

2.4.2. Atomicity in metal clusters

While both physical deposition and chemical synthesis methods require careful control of synthesis parameters, metal clusters have also been obtained through the dynamic evolution of SACs. Here, the instability of atomically dispersed catalysts is used to produce clusters *in situ*. Fontecave and co-workers, showed that fully oxidized Cu(II)-N-doped carbon SAC (N-C, **Figure 17**) formed metallic Cu clusters of 0.47 ± 0.04 nm under cathodic potential (-1.2 V vs. RHE).¹¹⁶ The *in situ* generated clusters showed an impressive C₂H₅OH FE of 43% at a stable average current density of 16.2 mA cm⁻². Interestingly, the

formation of the Cu clusters was completely reversible as through potential cycling the Cu(II) SAC reformed. Remarkably, other than CO and H₂, no additional products could be detected highlighting how Cu clusters can catalyze reaction pathways with a high degree of specificity. Instability against potential in Cu-hydroxyl SACs was also shown, which interestingly was also C₂H₅OH selective.

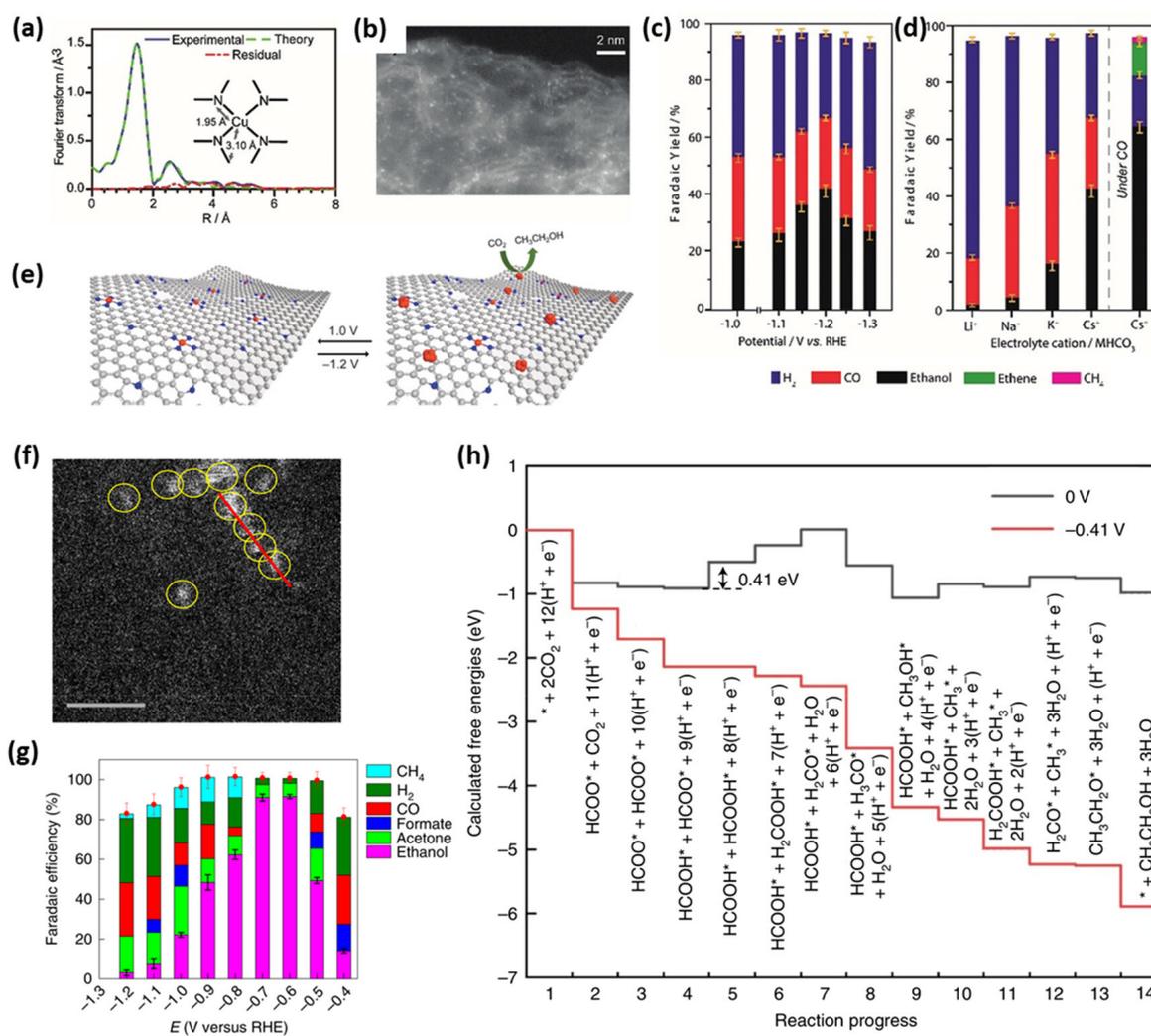


Figure 17. (a) EXAFS data of Cu-N₄-C SACs. (b) Aberration-corrected STEM-HAADF image of the SAC. (c) Faradaic efficiency as a function of potential vs RHE in 0.1 M KHCO₃. (d) Change in FE at -1.2 V vs. RHE in 0.1 M Li-, Na-, K-, CsHCO₃ as well as under CO flow. (e) Schematic showing the in-operando changes of the SAC towards metal clusters as determined by EXAFS explaining the selectivity towards C₂H₅OH. Reproduced from ref. ¹¹⁶. Copyright 2019 Wiley-VCH. (f) HAADF-STEM image of Cu/C-0.4, showing the presence of isolated Cu species marked by yellow circles (Scale bar: 2 nm). (g) The product distribution at different polarization potentials for Cu/C-0.4. (h) DFT simulated reaction pathway of CO₂RR to C₂H₅OH on the supported Cu cluster catalyst at 0 and -0.41V. Reproduced from ref. ¹¹⁷. Copyright 2020 Springer Nature.

Xu and co-workers developed an amalgamation method to obtain atomically dispersed Cu on a hydroxylated-graphene that showed an even better selectivity towards C_2H_5OH (although with a rotating disc electrode, which does not suffer from mass-transport limitations).¹¹⁷ The C_2H_5OH onset potential is, to our knowledge, the lowest ever reported (-0.4 V vs. RHE). Further, the highest FE to date (92%) was achieved at -0.7 V vs. RHE and 1.2 mA cm^{-2} (**Figure 17g**). Fitting of operando EXAFS spectra showed that the initially ligated Cu(II) species had reduced and (reversibly) formed Cu_n (with $n=3,4$) clusters, similarly to what was observed for the N-doped material of Fontecave and co-workers. The authors found through DFT that the HO-ligation sites did not play an active role in the catalytic cycle and, interestingly, that a $HCOO^*$ mediated pathway has an overall lower energy than via $*CO$ (**Figure 17h**). The observation of $HCOO^-$ at the onset potential of C_2H_5OH makes this hypothesis plausible. However, it is in stark contrast with what is known for metallic Cu, as $HCOO^-$ is considered a terminal product.¹⁰

Unfortunately, Fontecave and co-workers did not include DFT calculation in their study. However, the difference in onset potential of 0.6 V suggests entirely different pathways are being catalyzed.

It is known that metal clusters of specific atomicity, differing only by a single atom, can have tremendously different reactivities.¹¹⁸ In the above examples, we possibly see such an event unfold. Using our simplistic model as outlined in **Figure 10** and assuming a 3D geometry of the $0.47 \pm 0.04 \text{ nm}$ clusters reported by Fontecave, we calculate an atomicity of 5. This means that the subtraction of 1-2 atoms from the catalyst resulted in a 0.6 V shift in onset potential. A mere 310 mV off the equilibrium potential (**Table S1**). Strong differences in reactivity upon substitution of 1-2 atoms in colloiddally produced Au clusters have also been reported. For example, by substituting one atom of the Au_{25} near-to-sphere clusters with Pd, not only was the CO FE enhanced to 100% over a 600 mV potential range, an order larger CO partial current density could be achieved as well (35 mA cm^{-2} at -1.2 V vs. RHE).¹¹⁹ Further, substituting two Au atoms

in Au₂₃ with Cd nearly doubled the TOF to CO at the same potential.¹²⁰

Metal clusters provide a new and exciting materials synthesis platform. In example, several orders of magnitude enhanced activities can be achieved with Au_n clusters in the CO₂RR over their bulk metallic counterpart. Further, Cu_n clusters may show enhanced selectivity towards C₂₊ products and specifically oxygenates with respect to their metallic counterparts and are strongly speciating as only specific pathways are catalyzed and the active site is much better defined than for bulk materials. However, to establish the effects of atomicity, charge, geometry and ligand shell on the performance in the CO₂RR, more systematic studies are needed. In the case of SAC-derived clusters, the dynamic nature of these clusters makes it extremely difficult to predict *a priori* what ligation site (density) would lead to what atomicity. Much more

systematic studies are needed in order to gain control over the formation of these clusters and determine the effect of the potential. Lastly, due to the significantly reduced number of bonding electrons in metal clusters with respect to their metallic counterparts, the activity and selectivity of clusters can be modelled at the highest level of theory allowing for theory-guided candidate catalysts selection. For instance, in a combined study by a computational and experimental group, Lee and Jiang and co-workers³³ predicted with DFT and validated experimentally that a CuH catalyst was HCOO⁻ selective at low overpotential but produced H₂ at high overpotential. Such cross-discipline collaborations will become increasingly valuable in this field of research.

2.5. Atomically dispersed catalysts

In the final reduction of the number of atoms comprising an active catalyst, we arrive at isolated metal atoms that are stabilized by the ligands. This type of atomically dispersed catalysts has attracted increasing attention in CO₂RR in recent years. They not only exhibit nearly 100% atom utilization efficiency, but also show high activity, selectivity, and stability. Further, their activity and selectivity can be optimized via tuning of the metal center and the coordination structure.^{121,56,122} However, studies show that SACs behave differently than their bulk and NP forms. This is not surprising as their electronic structure is quite different: NPs have a single valence band, SAC show discrete energy levels (**Figure 6**).⁶⁰ Therefore, the classification of SACs according to the selectivity of their metal centers based on the element is no longer appropriate.

In recent years, various types of SACs have been tested in CO₂RR, including immobilized molecular catalysts, metal organic frameworks (MOFs), metal containing covalent organic frameworks (mCOFs), metal and heteroatom co-doped

carbon materials (M-X-Cs in which M=metal and X=N, O and S etc.), as well as single-atoms anchored on host metals/oxides.^{123,124,125,126,127,128,129,130,131,132,57,133,66,134,59,135,136,137,138,139,140,141,142,143,144,145,146,147,148,149,150,54} Moreover, as a further expansion of the SACs, diatomic catalysts (active sites of two metal atoms close to each other) have also been designed to introduce synergistic effects.^{151,152,153,154} Many excellent reviews regarding synthesis, characterizations, and applications of SACs exist in the literature.^{155,156, 157,158,159,160,161,162,163} As this review focuses on the influence of structural properties of metal catalysts in various size-regimes, in this chapter, we will review the influence of the metal center and the coordination environment on the catalytic performance, as they are the two most important factors that determine the properties of SACs (**Figure 18**). We note, however, that the conductivity of the support can also play a substantial role in performance especially at high current densities.

2.5.1. Effect of the metal center

2.5.1.1 CO selective SACs

With an overview of the published works on SACs for CO₂RR, we find that various types of SACs have been used, and most of them are selective for CO production (**Figure 7 and Figure 18**).^{124,125,126,127,128,129,130,131,132,57,133,66,134,59,135,136,137,138,139,140,141,143,144,145,146,147,148}

Further, even the usually HCOO⁻ selective elements show a tendency towards CO as SACs.¹⁶⁴

The influence of metal centers, organic ligands, supporting materials and reaction conditions have been extensively studied to explain selectivity and activity trends. Herein, we would first like to emphasize the influence of metal centers on the activity of SACs for CO.

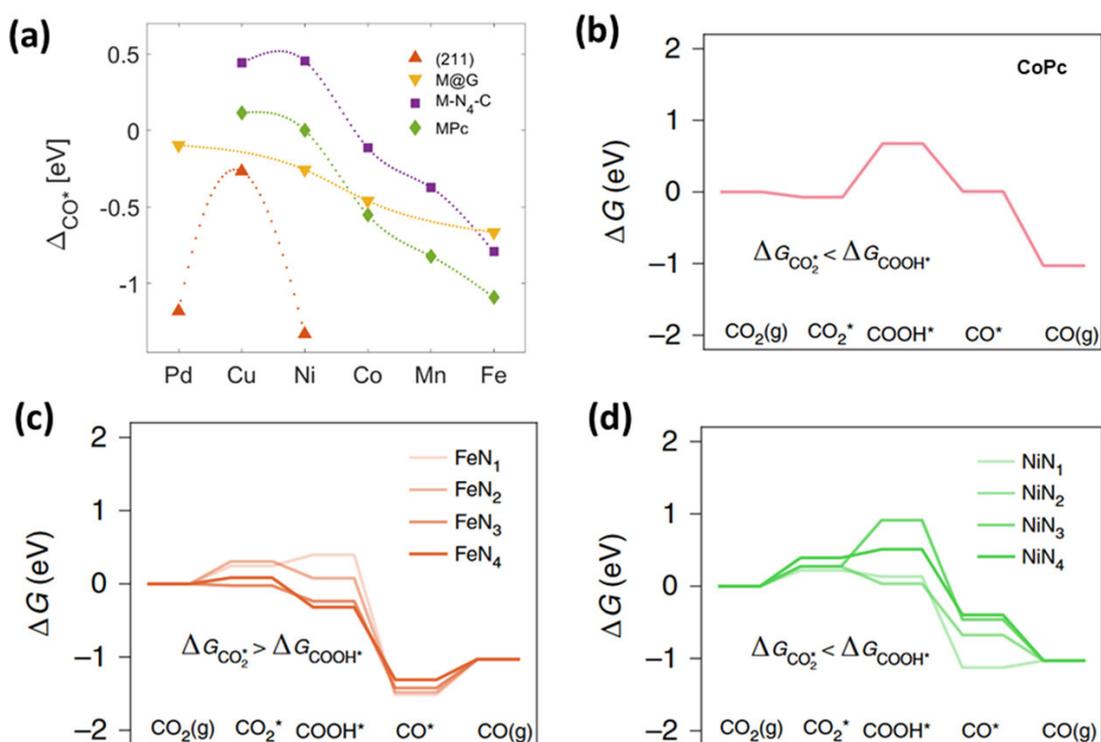


Figure 18. (a) Predicted *CO binding strengths to various electrocatalysts obtained with DFT explaining the strong tendency towards CO production of SACs in the CO₂RR. M@G, M-N₄-C and MPc, denote metal on graphene, metal N-doped carbon with 4 N bonds and metal phthalocyanine, respectively. Reproduced from ref.¹⁶⁰. Copyright 2021 American Chemical Society. Free energy diagram of CO₂ to CO for, (b) CoPc adsorbed on graphene, (c) FeNC, and (d) NiNC with N₁, N₂, N₃ and N₄ the N coordination number. Reproduced from ref.¹⁶⁵. Copyright 2021 Springer Nature.

M–X–C materials are likely the most studied SACs for CO₂RR in the past few years, due to the ease of preparation, high tunability, and high activity and selectivity. Various studies using these types of SACs have investigated the effect of the metal center on catalysts activity and selectivity for CO.^{57,66,142} However, some ambiguity exists on the nature of the most active and selective metal. For example, Strasser and co-workers prepared a series of metal- and N-doped porous carbon materials (M–N_x–C) through pyrolyzing Co, Mn, Fe, Ni and Cu coordinated bipyridine-based polymers.⁶⁶ They found that Mn–N–C and Fe–N–C showed the earliest CO onset potentials, while Ni was more selective and active at higher overpotentials (**Figure 18d**). In contrast, Co–N–C produced mostly H₂ for the entire potential window. The authors performed DFT simulations of CO₂RR and HER pathways using single-site motif M–N₄ as active sites (approximation). Then, they correlated the CO activity to the adsorption energy of key reaction intermediates (*COOH, *CO and *H). The results show that Ni–N₄ adsorbs *COOH, *H and *CO weakly,

and thus requires a high overpotential to produce CO. On the other hand, Ni–N₄ resists *CO poisoning. By contrast, Co–N₄ is energetically favorable for *H adsorption and is, therefore active for HER. Contrarily, Jaouen and co-workers also prepared M–N_x–C catalysts with Mn, Fe, Co, Ni, and Cu but found Co–N–C the most active for CO and least selective for H₂.¹⁴² The authors proposed that the best compromise between *CO and *CO₂[–] binding energies on the Co–N–C site was responsible for the high CO activity, and the competing adsorption of *CO₂[–] and *H determined the selectivity.

The different catalytic behavior with respect to the metal center and the lack of insight in the catalytic mechanism of the above-mentioned works could be explained by possible inhomogeneities in the materials and changes of the catalyst's properties induced by the reaction conditions. Deng and co-workers showed that for well-defined M–N₄ (M=Mn, Fe, Co, Ni and Cu) phthalocyanine-based SACs, DFT could be used to predict the most active metal center.¹⁶⁶ Optimal binding of *COOH and *CO

suggested Co-N₄ to be the most selective. Indeed, when phthalocyanine-carbon paper composite materials were tested for the CO₂RR, an excellent selectivity of 99% was obtained for the Co-N₄ based material. This could form a possible explanation of the ambiguity observed for Co-N-Cs reported by Strasser and Jaouen. In homogeneous molecular catalysts, the active site is well-defined. However, SACs produced via pyrolysis, for example, show various kinds of ligation sites (**Figure 19a**). Observed reactivity is therefore, an ensemble average of the active sites that are present in the material.

Finally, Strasser and co-workers also showed that for the Fe containing composites, small amounts of CH₄ could be observed in the exhaust stream (<1%, **Figure 19b-c**).⁵⁷ This once again showed the relevance of homogeneous catalysts regarding the nature of the active site in SACs, as molecular Fe-based catalyst also show activity towards the production of CH₄ from CO₂.¹⁶⁷ Not much later, Koper and co-workers also observed CH₄ as by-product in the CO₂RR on a SAC but in this case on an immobilized Co porphyrin complex catalyst.¹⁶⁸ Interestingly, the methane pathway showed correlation with adsorbed formaldehyde, which is not an expected intermediate for the production of CH₄ on metallic Cu for instance.²⁶ These studies provided the first evidence that with specific metal centers of SACs, hydrocarbons could be produced as well. We will now turn to the effect of the metal center for the formation of CO₂RR products beyond CO.

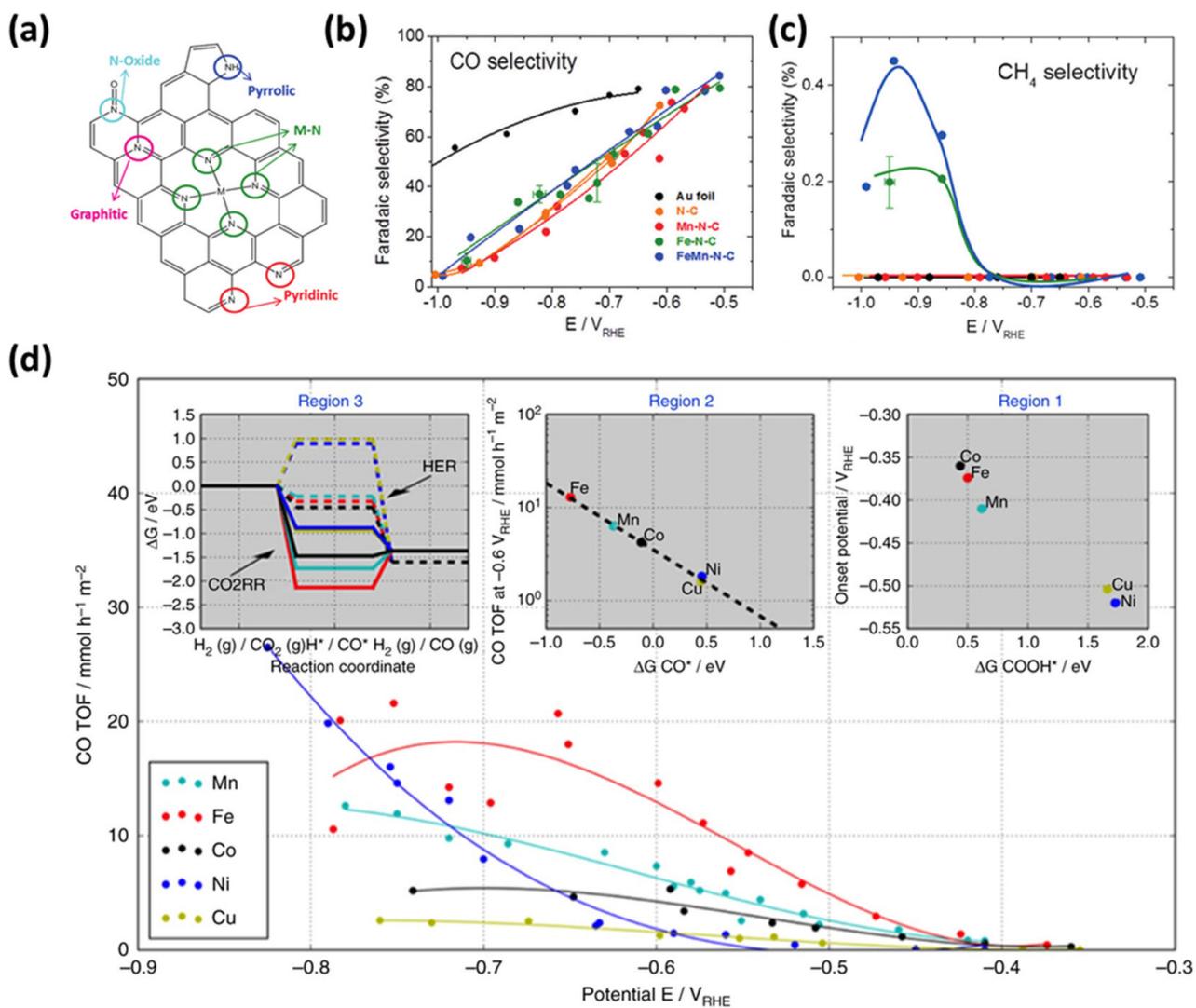


Figure 19. (a) Schematic of the various N-sites present in the M-X-Cs, in which M=Fe, Mn, FeMn. (b) CO FEs as a function of potential for the various M-X-Cs center in which M=Fe, Mn, FeMn. in 0.1 M KHCO₃ (c) FEs of CH₄ for the various electrocatalysts. Reproduced from ref. ⁵⁷. Copyright 2015 Wiley-VCH. (d) CO production turnover frequency (TOF) of the M-N-Cs as a function of potential for the various M-X-Cs in which M= M=Mn, Fe, Co, Ni, Cu. Reproduced from ref. ⁶⁶. Copyright 2017 Nature Springer.

2.5.1.2. C₁ products beyond CO

As discussed previously, the metal center of SACs affects the activity to produce CO, but also includes the possibility to produce further reduced C₁ products, as evidenced by Strasser and co-workers.⁵⁷ In this section, we will discuss how the nature of the metal center may lead to surprising electrochemistry with respect to their bulk counterparts. In a very interesting study by Yang and co-workers, pyrolyzed electrospun carbon nanofibers consisting of single-atom Cu-N-C catalysts achieved a high selectivity for CH₃OH (44% and 41 mA cm⁻², **Figure 20**), a product metallic Cu shows only limited activity for.^{140,169} The absence of the competing CH₄ reaction, which does share intermediates with CH₃OH, was explained using first principle calculations. Therein it was shown that the reduction of the ^{*}COH intermediate to ^{*}CHOH was much more favorable than towards ^{*}C (relevant to the production of CH₄). Further, C-C coupling was deemed unlikely *a priori* due to the absence of Cu-Cu moieties in the material as excluded through XPS. One must note, however, that under applied potential Cu ions can become labile in SAC resulting in the formation of Cu clusters *in situ*, which in effect function as the active catalyst as discussed in the previous chapter. Since the absence of clusters was reported based on ex situ characterization, reversible

cluster formation cannot be excluded as an alternative explanation of the observed performance.

Possibly due to a comparable boiling point of Zn and pyrolysis temperatures required to achieve carbonization, the excellent performance of Zn-N-C in the CO₂RR went unnoticed until 2020.¹⁴⁹ Via a low temperature evaporation-carbonization approach, SACs of Zn supported on N-doped graphite were synthesized and showed a CH₄ selectivity of 85% at -1.8 V vs. RHE with a partial current density as high as -38.5 mA cm⁻². Note that both Zn and partially oxidized Zn cathodes convert CO₂ to CH₄ with FEs <1%.^{42,170} Interestingly, other than CH₄, the only other CO₂RR product observed was CO and the authors invoke a HCOO⁻ mediated pathway to explain its high selectivity. This is a very interesting although controversial claim as HCOO⁻ is generally considered a terminal product.¹⁰ More studies towards the behavior and performance of Zn-based SACs are needed to elucidate such questions. Nevertheless, it is clear that entirely new chemistry can be achieved on the molecule-like active sites of SACs.

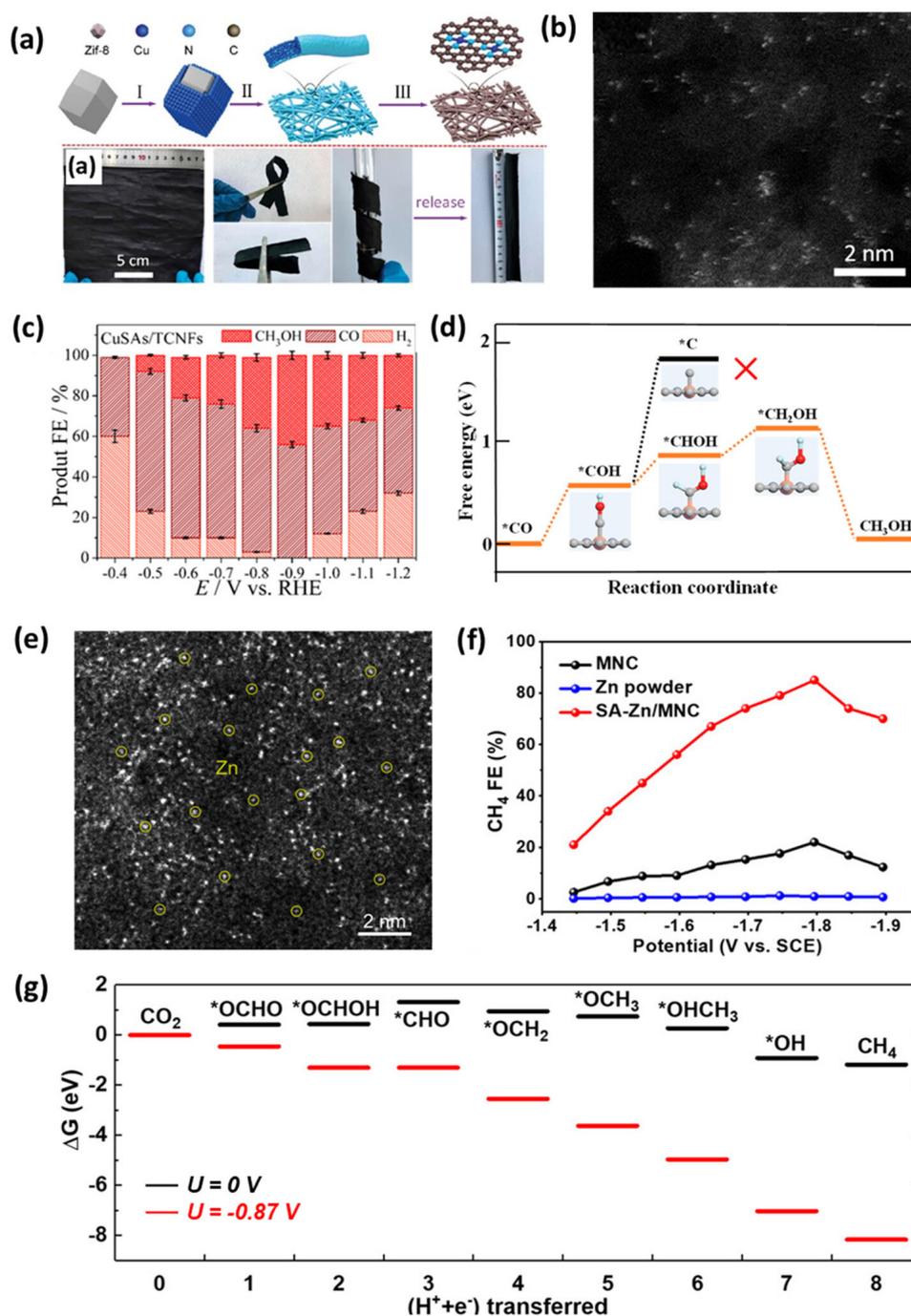


Figure 20. (a) Schematic of the production process of the electrospun ZIF-8 derived porous single-atom Cu catalyst (CuSAs/CNFs). (b) HAADF-STEM images of CuSAs/CNFs. (c) Product distribution as a function of applied potential for CuSAs/TCNFs in 0.1 M KHCO₃. (d) Free energies for conversion of *CO to CH₃OH on Cu-N₄ structure. Orange, gray, dark blue, red, and light blue spheres stand for Cu, C, N, O, and H atoms, respectively. Reproduced from ref. ¹⁴⁰. Copyright 2019 American Chemical Society. (e) HAADF-STEM images of SA-Zn/MNC. (f) FEs for CO₂RR to CH₄ as a function of applied potential for SA-Zn/MNC. (g) Free energy diagrams for CO₂RR to CH₄ on Zn-N₄-graphene structure. Reproduced from ref. ¹⁴⁹. Copyright 2020 American Chemical Society.

2.5.1.3. SACs for C₂₊ products

It is generally understood that in order for C-C coupling to be possible, at least two metal centers need to be in proximity to one another.¹⁷¹ Zheng and co-workers showed that the same is true for Cu-N-C SACs.¹⁴⁷ Where Cu-N-Cs produced at temperatures higher than 900 °C were mostly selective for CH₄, C₂H₄ became the major product when the temperature used was as low as 800 °C. Using EXAFS, it was shown that the relative distance between Cu-N_x species was greatly suppressed by increasing the pyrolysis temperature. The absence of Cu-Cu bonds in either material could be deduced from the same results.

Finally, an opposing view that C-C coupling can take place on single metal centers, can be found in the description of Chen and co-workers of their single-atom Cu anchored on porous N-doped carbon electrocatalyst Cu-SA/NPC, which was selective for acetone (36.7% at -0.74 V vs. RHE and ~3.7 mA cm⁻²).¹⁴⁸ DFT calculation showed that on pyrrolic N-Cu sites, C-C coupling forming the *COCOH intermediate involved an exothermic step, which the authors, therefore determined as facile. STEM-HAADF analysis after electrochemistry showed neither Cu cluster nor particle formation. However, *operando* measurements were not reported and as we saw before, this can prove essential as SACs can reduce reversibly to metal clusters under an applied potential.^{116,117}

2.5.2. Ligation effect

Ambiguity exists in the literature in the determination of the most active metal center in M-X-Cs, which may originate from inhomogeneities in the support material and respective ligation sites. Presently, we discuss studies using M-X-Cs that excellently determine the effect of the ligand showing the strong influence coordination number may have on catalyst performance. In a study by Xie and co-workers, atomically dispersed Co based M-N-Cs with N₂-, N₃- and N₄-coordination were synthesized and their performance assessed.¹⁷² Interestingly, selectivity and activity increased with decreasing coordination number. DFT calculations showed that low coordination resulted in faster electron transfer to form *CO₂⁻ explaining the enhanced rate. This makes sense from a chemical intuition point of view and may remind the reader of the effect of undercoordination in our discussion of NP catalysts. Metal centers coordinated to fewer ligation sites, will have undergone less back bonding interaction with the support. Therefore, it may donate more charge to an adsorbate. Indeed, in another study, the same behavior was

discerned for Ni-containing M-N_x-Cs in which X=2, 3 and 4.¹⁷³ Ni-N₂-C showed the highest selectivity (98% at 10 mA cm⁻²) and the earliest onset potential for CO (-0.6 V vs RHE). Here, DFT identified the formation of *COOH as the potential-determining step,¹⁷⁴ which became increasingly energetically favorable with decreasing coordination number. This offers a roadmap to enhance the catalytic rate in SACs. By actively engineering low number coordination site into the catalyst support, better performances can be achieved.

Overall, it has been clear that M-X-C based SACs can show entirely different reactivities than their metallic counterparts. Explanations for these discrepancies in reactivity have for the most part been based on computational efforts. For M-N-Cs, for example, enlarged adsorbate dipoles due to the discrete and narrow d-states of these molecule like active sites can shift the rate-determining step from CO₂* adsorption found in their transition metal counterparts to *COOH formation strongly accelerating the reaction.¹⁶⁵ More generally, activation barriers insurmountable at



room temperature on metals (>1 eV), can become facile on the SACs. This shows the tremendous potential of these materials. Entirely new pathways could be opened up to the more valuable products of the CO_2RR . With SACs active sites being treatable at the highest level of theory, collaborations between theorists and experimentalists may yield exceptional results. Nevertheless, the lone nature of the metal center, will most likely limit its performance to C_1 products. Metal clusters rather, with multiple metal centers in one active site, can benefit from both worlds: the tremendously rich chemistry of SACs, and the C-C coupling capabilities of metals. Further, such properties can be envisioned for dual-atom catalysts as well although presently only CO selective catalysts have been reported.^{151,152,153,154} We expect major developments in both fields, however.

2.6. Conclusions and perspectives

The CO₂RR powered by renewable electricity can convert CO₂ to valuable chemical and fuels and is therefore a promising strategy for achieving a sustainable global energy economy. Metals have been used as electrocatalysts for CO₂RR for more than three decades, showing distinct selectivity towards a variety of products. Decreasing the size of the metal particle is an effective way to increase the number of atoms exposed to the reactant, thus the activity. Further, with the decrease of the particle size, geometric and electronic structures also change, which in turn influences the catalytic behavior of the metal. As an example, **Figure 21** illustrates the variation of the major products from CO₂RR with the decrease of Cu particle size. Here, we have reviewed representative studies of metal catalysts for CO₂RR and categorized them according to the particle size. We have discussed how key structural factors, including crystal facet, particle size, undercoordination sites, ligands, and support, influence the catalytic behavior of metal catalysts in different size regimes. And determined for each size regime the most relevant structural factors governing the reactivity. This may help researchers determine the parameters that are most relevant to the type of metal catalyst they are interested in or provide direction for catalyst target selection. Moreover, as we have seen

that research groups often operate in only one of the defined size regimes, and that challenges and opportunities differ hugely between these disciplines, we hope our classification system will help researcher effectively communicate their findings between fields.

In brief, it is shown that the crystal facet dominates the activity and selectivity of metal single crystals and nanocrystals with particle size larger than 10 nm. While undercoordination sites start to dominate the performance of particles smaller than 10 nm (but > 1 nm), the role of ligands and support should not be ignored. Finally, for clusters and SACs, their electronic structure is distinct from bulk metals, and the catalytic performance are mainly determined by the ligands/support and the number of atoms. Although much progress has been made in understanding the structure-performance relationships and finding efficient electrocatalysts for CO₂RR, some significant challenges remain in the field both from fundamental and applied perspectives. Now we discuss some of the challenges and opportunities researcher may want to focus on.

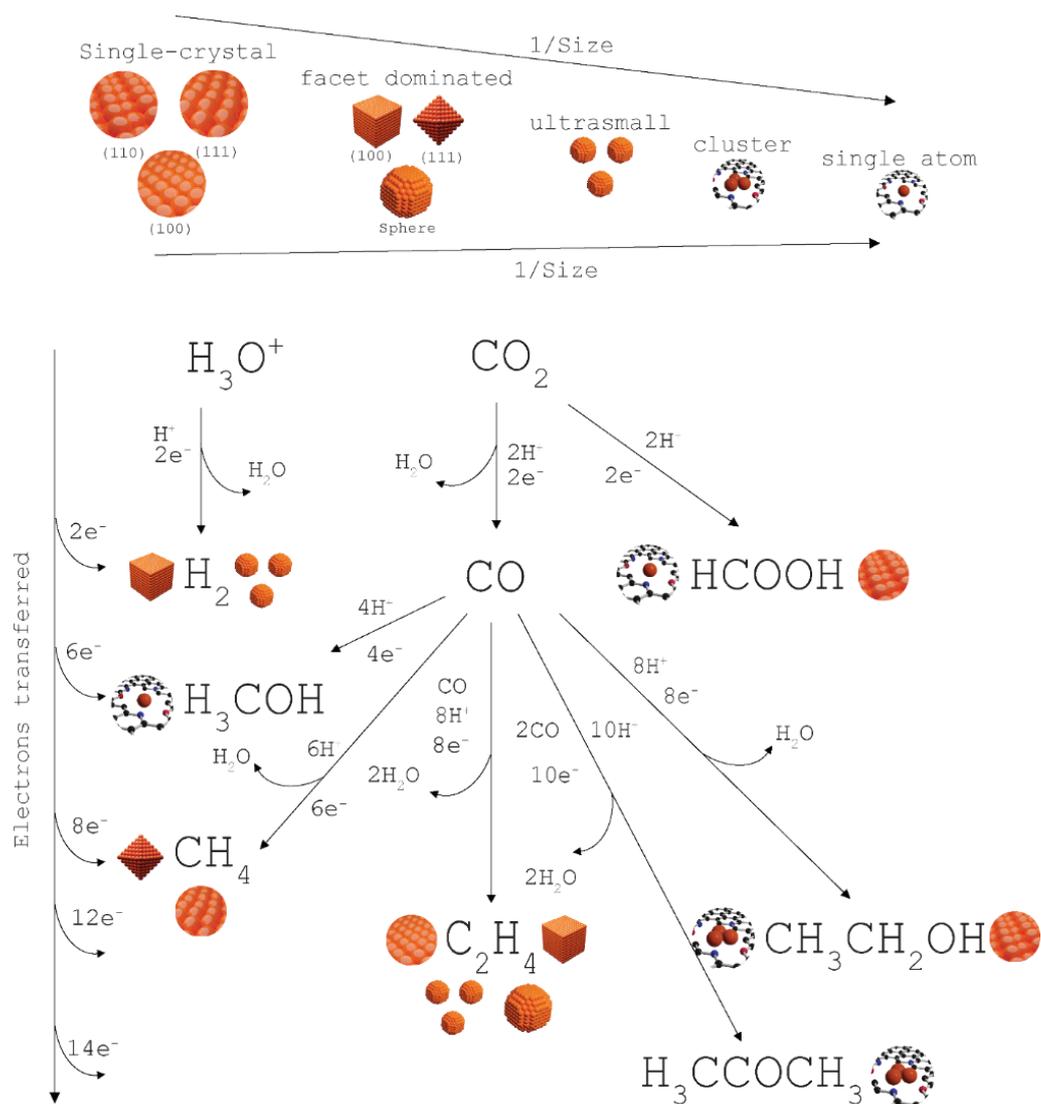


Figure 21. Overview of the major products obtained on various Cu-based electrodes in the different size regimes of the CO₂RR.

2.6.1. Deconvolution of ligand/support effects from chemical nature of the active site

Despite the large number of studies reported for size-selected catalysts spanning multiple size regimes, the non-homogeneity of catalysts production methods and the presence of other often overlooked factors (e.g., effects of the ligand and support), still leaves us without a unified theory to explain and predict catalytic performance. Only by fully dissecting and deconvoluting the intricacy of the parameters governing the CO₂RR within a given synthesis platform, will it be possible to not only qualitatively but also quantitatively compare between them. This calls for more benchmark studies with precise control over the structural factors influencing the performance. Researchers may want to produce metal catalysts of different sizes via the same synthesis method

and stabilize them using different types of conductive supports such as (heteroatom doped) carbonaceous supports (e.g., graphene, reduced-graphene oxide, carbon nanodots, carbon black etc.), MOFs, COFs and metal oxides and determine catalyst performance in relation to the support and or ligand. Further, one may want to include control experiments of particle systems of the same size but using different synthesis methods to elucidate the role of synthesis parameters.

2.6.2. Dynamic nature of the catalysts demands *in situ* and *in operando* characterization of the active site

For cross-discipline, comparative studies to become fully reliable, it is of utmost importance that structure-performance relationships are assessed under practically relevant conditions. As shown in several examples, electrocatalysts greatly undergo rearrangement under laboratory testing conditions. For example, Cu single crystal have been shown to significantly change their morphology under applied potential and over time, which has further been correlated to changes in performance. Similarly, for Cu nanocrystals, applied potential and the binding of adsorbed species progressively damaged particles and resulted in loss in product selectivity. Also, the dramatic switch from CO to H₂ selectivity for Ag NPs <5nm could potentially be assigned to rapid agglomeration under reaction conditions. It is therefore, of utmost important to better understand restructuration processes. Thus, more effort must be invested in the use and further development of *in situ* and *operando* techniques to determine the dynamic nature of the catalysts and its effect on determined structure-performance relationships and long-term stability. This must include both inhouse-developed techniques as well as at large scale research

facilities. For example, performance tests of SACs and or clusters should include *in situ* and preferably *operando* XANES and EXAFS studies to probe the chemical nature of the catalyst. This may involve oxidation state, coordination number and bond length to couple chemical structure with CO₂RR activity. Further, *in situ/operando* IR and Raman spectroscopy could offer insight in the transient nature of the catalyst (e.g., adsorbed species and phase) and reaction intermediates relevant in CO₂RR towards value added chemicals. The use of shiners (plasmonic nanoparticles made electrochemically inactive by surface modifications) can help to enhance Raman scattering in case of low signal strength. Further, corrosion of the electrodes may start to play a role during prolonged electrolysis, *in situ/operando* monitoring of the electrolyte using analytical techniques such as inductively coupled plasma mass spectrometry to determine ion contaminations could prove of value as well.

2.6.3. Theory-guided catalysts design

With structure-property relationships well-established and benchmarked, it should become possible to build up unified reaction mechanisms across the size regimes in the CO₂RR.¹⁶⁵ Having overarching mechanistic insights conjoining several size regimes would be of tremendous value to catalyst candidate selection as theory could guide performance-optimization *in silico*. Incorporation of multi-scale modelling at the device level would be a prerequisite to translate such computational studies to real-world applications, however.

A great opportunity lies here for the incorporation of artificial intelligence (AI) in reaction parameter optimization.^{85,175,176} The autonomous learning capabilities of AI based-algorithms offer improved predictability at a fraction of the (computational) cost. Stronger ties between experimentalists and theorists could reap the benefit of symbiotic efforts in which theory guides catalysts design and experiment offers data for the improvement of the predictive power of the algorithm.

2.6.4. Reactor and electrolyte design

For the large part, our discussions have considered performance tests in the conventional H-cell and in aqueous electrolyte, as most studies have evaluated the performance of catalysts under such conditions. However, due to the low solubility of CO₂ (350 ppm in water), its local concentration at the catalyst surface will be limited. This limits the partial current densities <100 mA cm⁻², which are far from industrially relevant (> 1 A cm⁻²). Further, the low solubility may also result in the CO₂RR becoming mass-transport limited, which may in turn affect performance parameters such as selectivity. Thus, the catalytic behavior of metal catalysts in different size regimes will require validation at more industrially applicable current densities, i.e., in flow cell or membrane electrode assemblies. Further, to achieve unitary selectivity's and keep energy losses at a minimum, the parasitic HER will need to be suppressed in order for CO₂RR electrolyzer technology to reach market maturity. This may be achieved by introducing hydrophobic polymers and or molecular adsorbates at the catalyst interface, reducing the local proton flux and increase CO₂/CO concentration.^{95,177} Further, beyond

catalyst design and interface modification, reactor and electrolyte design may be used to this affect as well. High-pressure devices that enhance the CO₂ concentration at the catalyst surface can play an important role herein. Early work from the last century in this direction by Sakata and co-workers have shown promising results in aqueous electrolyte.^{178,179} High CO₂ local partial pressures may as well be achieved by increasing its relative solubility by switching to non-aqueous electrolyte, i.e., ionic liquids. Also, since cations such as Na⁺, K⁺, Cs⁺ have shown to be essential in the catalytic CO₂ reduction and influences the selectivity in aqueous electrolyte, molecular cation engineering could be considered to tune selectivity towards desired products further.¹⁸⁰ Finally, issues associated with liquid electrolyte based-devices such as carbon losses and thus low conversion due to formation and cross-over of CO₃²⁻ to the anode side, can be solved by switching to an all solid-state device as has been reported by Wang and co-workers.¹⁸¹

2.6.5. Scalable synthesis

Finally, leaps have been taken in the synthesis of various electrocatalysts of well-defined structure ranging from wet-synthesis (i.e., colloidal) to production of aerosols and physical deposition (i.e., magnetron sputtering). However, other than some SACs and a handful of atomically-precise clusters, most catalysts are produced with a broad distributions of sizes and/or geometries and/or active sites making it hard to formulate unifying postulations.

Therefore, more precise, scalable

production of particles and clusters could unlock a treasure trove of new information regarding performance optimization, as the most active and selective candidates can be identified and selected. In this way, cost-efficient electrocatalyst for all the relevant products of the CO₂RR, which in the near-future may start uprooting the petroleum industry, can be unveiled with the speed necessary to tackle one of the biggest challenges mankind faces: the energy transition.

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2.8. Supporting Information

Half-reaction	E^0 [V vs. RHE]	Product and named-reactions
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	1.23	Oxygen evolution reaction (OER)
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0	Hydrogen evolution reaction (HER)
$x\text{CO}_2 + n\text{H}^+ + ne^- \rightarrow \text{product} + y\text{H}_2\text{O}$		CO_2 reduction reaction (CO_2RR)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.12	Formic acid
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.10	Carbon monoxide
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + 6\text{e}^-$	0.03	Methanol
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{C} + 2\text{H}_2\text{O}$	0.21	Graphite
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	0.17	Methane
$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow (\text{COOH})_2$	-0.47	Oxalic Acid
$2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	0.11	Acetic Acid
$2\text{CO}_2 + 10\text{H}^+ + 10\text{e}^- \rightarrow \text{CH}_3\text{CHO} + 3\text{H}_2\text{O}$	0.06	Acetaldehyde
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	0.09	Ethanol
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	0.08	Ethylene
$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	0.14	Ethane
$3\text{CO}_2 + 16\text{H}^+ + 16\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{CHO} + 5\text{H}_2\text{O}$	0.09	Propionaldehyde
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	0.10	Propanol
$4\text{CO}_2 + 24\text{H}^+ + 24\text{e}^- \rightarrow \text{C}_4\text{H}_9\text{OH} + 7\text{H}_2\text{O}$	0.13	Butanol

Table S1. Table of CO_2RR products, other relevant half-reactions and their equilibrium potentials.^{5,6,7}

The equilibrium potentials of the most valued products of the CO_2 reduction reaction listed here comprise the cathodic side of the redox reaction and are reported versus the reversible hydrogen electrode. Therefore, by definition, the equilibrium potential of the hydrogen evolution reaction is zero. In the main text, the anodic reaction was in all cases the oxygen evolution reaction. Cell voltages (without overpotentials) can be determined from:

$$E_{cell}^0 = E_{red.}^0 - E_{ox.}^0$$

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Note S3. Geometrical model: cube, octahedra, truncated octahedra

S3.1. Geometrical model of the cube

In order to determine the relative contribution of the facet, edge- and corner sites as well as the bulk atoms to the total number of atoms a particle consist of, we first defined the particles mass, which for a cube is given by:

$$m_{cube} = \rho \cdot l_{edge-length}^3$$

With ρ the density of the bulk and $l_{edge-length}$ the particle edge-length. This then, allows to determine the number of atoms based on the mass via:

$$Atoms_{mass} = \frac{m_{cube} \cdot N_A}{MW}$$

in which N_A is Avogadro's number and MW the molecular weight. Alternatively, one can calculate the total number of atoms based on the volume and the volume of the unit cell:

$$Atoms_{volume} = \frac{l_{edge-length}^3 \cdot n_{atoms}}{l_{unit\ cell}^3}$$

With n_{atoms} the number of atoms in the unit cell and the lattice constant (FCC). The number of atoms calculated based on the mass and the volume match for the first two significant digits. Since it is uncertain if the bulk density is a reliable quantity on the nanoscale, we have opted to use the volumetric atom number instead.

To determine the number of surface atoms, we first defined a subsurface, which comprises the V_{cube} but with one monolayer of atoms subtracted (see Figure S1 for a spherical representative schematic):

$$V_{subsurface} = (l_{edge-length} - 4r_{covalent})^3$$

in which r_{covalent} is the metal-metal bond length. In here the constraint is applied that and that only a complete monolayer can be removed at a time. The number of surface atoms then becomes:

$$Atoms_{\text{surface}} = \frac{(V_{\text{Cube}} - V_{\text{subsurface}}) \cdot n_{\text{atoms}}}{l_{\text{unit cell}}^3}$$

With

$$Atoms_{\text{bulk}} = Atoms_{\text{volume}} - Atoms_{\text{surface}} = Atoms_{\text{subsurface}}$$

Since a cube consists of 6 equal faces, the number of (100) facet atoms become:

$$Atoms_{\{100\}} = \frac{6 \cdot (l_{\text{edge-length}} - 4r_{\text{covalent}}) \cdot r_{\text{covalent}} \cdot n_{\text{atoms}}}{l_{\text{unit cell}}^3}$$

And as the number of corners remain constant i.e. 8, the number of edge sites becomes:

$$Atoms_{\text{Edge}} = Atoms_{\text{surface}} - Atoms_{\{100\}} - Atoms_{\text{corners}}$$

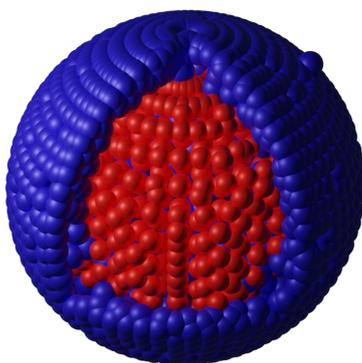


Figure S2. Ball model describing the subsurface approach to the determination of the number of surface atoms. The surface atoms in the geometrical model, here depicted in blue, consist of a single monolayer.

S3.2. Geometrical model of the Octahedra.

In order to determine the relative contribution of the facet, edge- and corner sites as well as the bulk atoms to the total number of atoms a particle consist of, we first defined the particles mass, which for a cube is given by:

$$Atoms_{volume} = \frac{8\sqrt{2} \cdot l_{edge-length}^3 \cdot n_{atoms}}{l_{unit\ cell}^3}$$

and

$$Atoms_{subsurface} = \frac{8\sqrt{2}(l_{edge-length} - 2r_{covalent})^3 \cdot n_{atoms}}{l_{unit\ cell}^3}$$

and

$$Atoms_{(111)} = \frac{3\sqrt{3} \cdot (l_{edge-length} - 2r_{covalent})^2 \cdot r_{covalent} \cdot n_{atoms}}{2 \cdot l_{unit\ cell}^3}$$

and

$$Atoms_{(100)} = \frac{(l_{edge-length} - 2r_{covalent})^2 \cdot r_{covalent} \cdot n_{atoms}}{l_{unit\ cell}^3}$$

S3.3. Geometrical model of the Truncated Octahedra

The geometrical model of the truncated octahedra was derived following the same logic as for the cube. We will, therefore, only list the changes respective of the geometry.

$$Atoms_{volume} = \frac{8\sqrt{2} \cdot l_{edge-length}^3 \cdot n_{atoms}}{l_{unit\ cell}^3}$$

and

$$Atoms_{subsurface} = \frac{8\sqrt{2}(l_{edge-length} - 2r_{covalent})^3 \cdot n_{atoms}}{l_{unit\ cell}^3}$$

and

$$Atoms_{(111)} = \frac{3\sqrt{3} \cdot (l_{edge-length} - 2r_{covalent})^2 \cdot r_{covalent} \cdot n_{atoms}}{2 \cdot l_{unit\ cell}^3}$$

and

$$Atoms_{(100)} = \frac{(l_{edge-length} - 2r_{covalent})^2 \cdot r_{covalent} \cdot n_{atoms}}{l_{unit\ cell}^3}$$

Chapter 3

Research Objectives

3.1. Objectives of the Thesis

Based on the comprehensive critical review of experimental data on the CO₂RR on metal catalysts spanning well-over three decades as discussed in Chapter 2,¹ and in particular from Figure 7 (reprinted here for reasons of clarity), it can be concluded that for the production of C₂₊ products and especially liquid fuels, the sole practical catalyst to consider is Cu. All other pure elements produce mostly H₂, CO, CH₄ or HCOO⁻. As the aim of the thesis is to improve upon electrocatalyst design for enhanced selectivity towards liquid fuels, we narrow our scope of potential catalyst candidates to Cu-based species. This brings us to the second observation. In the size regime >10 nm, the facet dominated regime, barely any

Cu alloys have been reported (i.e. others, mostly limited to Cu-Au and Cu-Pd). This means that the facet effect, in combination with the electronic effect upon the alloying of Cu with other components, is poorly understood. Therefore,

Objective 1:

Produce catalysts of Cu-X alloys that are facet controlled to study the effect of the facet in combination with the electronic effect of alloying in the CO₂RR with the aim to enhance the selectivity towards liquid fuels.

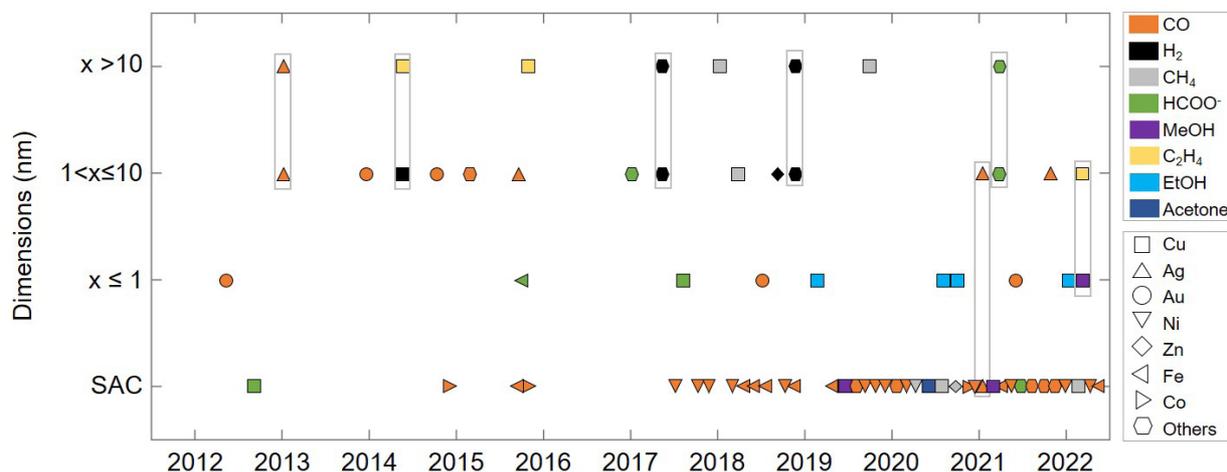


Figure 7. The most common products of CO₂RR for typical metal catalysts in different size regimes: single-crystal and facet dominated nanoparticle (>10 nm), ultra-small particle (1<x≤10 nm), cluster (≤1 nm), and SAC. The metal utilized to obtain the results is indicated by shape, and the product is indicated by color. The ‘others’ series includes Cu alloys and other metals. Each point represents a published study, where studies covering different size regimes are included in the gray box. For a list of the publications, see Note S2 of the Supporting Information. Note that publications in Figure 7 have been selected for their investigation of metal catalysts of different sizes using the same synthesis technique. Further, to highlight the differing performance of metal catalysts versus their SAC counterparts, we have included a selection of those as well.

Cu-X candidate selection, was then inspired by computational efforts of collaborators of this work, e.g. Figure 22.²

Especially, the bimetallic Cu-Ag system is of interest due to the fact that A) it has a promising high predicted selectivity of CO₂RR over HER (Figure 22b, abscissa) as well as a promising high activities predicted for CORR, i.e., C-C coupling (Figure 22b, ordinate) in comparison to pure Cu and B) no facet controlled Cu-Ag system in this size regime has been reported due to the

immiscibility of Cu and Ag making it an extremely challenging system to produce.³ Therefore, Objective 1 was narrowed further,

Objective 1.1:

Produce catalysts of Cu-X (with X = at least Ag) alloys that are facet controlled to study the effect of the facet in combination with the electronic effect of alloying in the CO₂RR with the aim to enhance the selectivity towards liquid fuels.

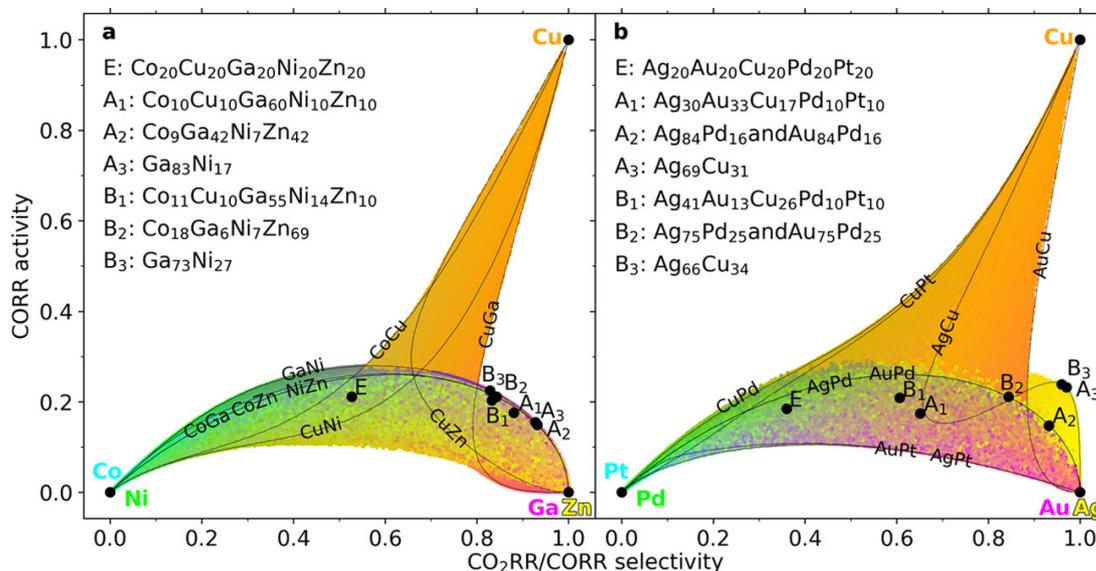


Figure 22. Selectivity vs activity plots of Cu based alloys of up to five components as based on predicted values via a supervised machine algorithm trained with adsorption energies of key intermediates, H* and CO*. Reprinted with permission from ref. ²

From the fact that no procedure exists that offers insight in the composition distribution of multimetallic nanoparticles with ensemble representative statistics as current state of the art either offers ensemble averages, i.e. via inductively coupled plasma mass spectrometry or optical emission spectroscopy, X-ray diffraction, X-ray absorption spectroscopy etc., or the composition of a single particle via means of electron microscopy or diffraction, an information gap immerses: knowledge of the composition on the nanoscale, cannot be extrapolated to the bulk. Therefore,

Objective 2:

Develop a methodology to determine the composition distribution of multimetallic nanoparticles at the single particle level of detection but with ensemble representative statistics to correlate nanoscale characteristics (such as composition fluctuations) to bulk phenomena such as catalysis.

Following the comprehensive review and in particular Figure 7,¹ another conclusion can be drawn. In the size regime <1 nm, a disproportionally large degree of high liquid

fuel selectivity has been reported on Cu cluster catalysts and with a limited number of systems investigated. Further, strong correlation with the product selectivity and the cluster atomicity (number of atoms bonded) has been observed. Further, no bimetallic Cu-based cluster system has been reported to date. Finally, the effect of the support has not yet been fully deconvoluted from other effects in cluster electrocatalysis and remains unknown. Therefore, finally,

Objective 3:

Develop a synthesis process to produce Cu-X (with X = at least Ag) clusters functionalized on various carbonaceous supports to study the effect of cluster atomicity, composition and support effect in the CO₂RR with the aim to enhance the selectivity towards liquid fuels.

3.2. Overview of the research work

Based on the previous objectives outlined, a brief overview of the research work in the present thesis is provided. First, a discussion on the newly developed methodology to determine ensemble representative composition distributions of multimetallic nanoparticles based on single-particle inductively coupled plasma mass spectrometry will follow in Chapter 4.⁴ Thereafter, the low-temperature non-equilibrium synthesis developed presently to produce multimetallic facet-controlled nanoparticle alloys, which were used as model electrocatalyst in CO₂RR towards liquid fuels will be discussed in Chapter 5. And finally, the developed synthesis procedure to produce Cu-Ag clusters, which were used to electrocatalytically convert CO₂ to acetaldehyde, will be discussed in Chapter 6.

3.3. References

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Chapter 4

High-throughput sizing, counting and elemental analysis of anisotropic multimetallic nanoparticles with single-particle inductively-coupled plasma mass spectrometry

Post print version: this section has been published as a full-length article in *ACS Nano*, 2022, 16, 8, 11968-11978

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Edit: caption numbers of figures, tables, and equations were edited to match the thesis **chapter number**.

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Abstract

Nanoparticles (NPs) have wide applications in physical and chemical processes, and their individual properties (e.g., shape, size, and composition) and ensemble properties (e.g., distribution and homogeneity) can significantly affect the performance. However, the extrapolation of information from a single particle to the ensemble remains a challenge due to the lack of suitable techniques. Herein, we report a high-throughput single-particle inductively-coupled plasma mass spectrometry (SP-ICP-MS) based protocol to simultaneously determine the size, count, and elemental make-up of several thousands of (an)isotropic NPs independent of composition, size, shape, and dispersing medium with atomistic precision in a matter of minutes. By introducing highly diluted nebulized aqueous dispersions of NPs directly into the plasma torch of an ICP-MS instrument, individual NPs are atomized and ionized, resulting in ion plumes that can be registered by the mass analyzer (typically quadrupole, sector-field, or time-of-flight tube). Our proposed protocol includes a phase transfer step for NPs synthesized in organic media, which are otherwise incompatible with ICP-MS instruments, and a modeling tool that extends the measurement of particle morphologies beyond spherical to include cubes, truncated octahedra, and tetrahedra, exemplified by anisotropic Cu NPs. Finally, we demonstrate the versatility of our method by studying the doping of bulk-dilute (<1 at. %) CuAg nanosurface alloys as well as the ease with which ensemble composition distributions of multimetallic NPs (i.e., CuPd and CuPdAg) can be obtained providing different insights in the chemistry of nanomaterials. We believe our combined protocol could deepen the understanding of macroscopic phenomena involving nanoscale structures by bringing about a statistics renaissance in research areas including, amongst others, materials science, materials chemistry, (nano)physics, (nano)photonics, catalysis, and electrochemistry.

Keywords

Nanoparticle, Single-particle ICP-MS, multimetallic, size, shape, composition, protocol

4.1. Introduction

The size and composition of nanoparticles (NPs) have shown to play an important role in a variety of physical and chemical processes, including light-matter interactions, magnetism, catalysis, etc.^{1,2,3,4,5,6} To determine structure-property relations for such phenomena, the size and composition of the NP must be accurately and precisely described. Advancements in electron tomography using aberration-corrected microscopes have allowed for an exact 3D description of NPs with each individual atom accounted for.⁷ However, at least eight orders of magnitude separate a single particle from its bulk powder. Therefore, the sample space that can reasonably be attained with high resolution electron microscopes (EM) is too low for statistically sound extrapolation to the bulk. An information gap immerses.^{8,9}

More crudely but with better statistics, NPs can be sized through the production of low resolution EM images and subsequent automated edge-length analysis.^{10,11} Several commercial and open-source image processing software exist that can be of aid herein.^{12,13,8}

However, exact determination of atomicity using such approaches is impossible as the resolution required lies outside the information limit. Further, the success of automated sizing is often frustrated by tedious sample preparation steps and the large quantities of micrographs needed for reasonable statistics.^{8,9} In the present study, we propose the use of a methodology complementary to EM that allows to determine atomicity, composition, size, and number concentration of inorganic NP dispersions independent of element and shape with ensemble-representative statistics in a single experiment, based on single-particle inductively-coupled plasma mass spectrometry (SP-ICP-MS).^{14,15,16,17,18}

ICP-MS is routinely used to determine the concentration of elements in their ionic form. In the framework of nanomaterials, this entails the digestion of particulate matter using strong acids such as concentrated nitric acid (HNO_3), hydrochloric acid (HCl), or aqua regia yielding dissolved ionic solutions of the respective materials. The MS determines the ion intensities of a

defined mass to charge ratio for each of the analytes and correlates it to the absolute concentration based on the external calibration curve prepared using standard solutions of the analytes at known concentrations.¹⁹ Such an approach allows for the determination of average elemental make-up, synthesis yields, dispersion concentrations etc., but is insensitive to the homogeneity of the ensemble. For

an ICP-MS instrument with a quadrupole mass analyzer, an intensity reading is acquired every defined time interval, known as dwell time or integration time, and averaged over the total acquisition time. Instead, in single-particle-ICP-MS, undigested NP dispersions are nebulized and introduced to the plasma torch directly, after which the individual particles become desolvated, vaporized, atomized and ionized, and arrive at the mass analyzer

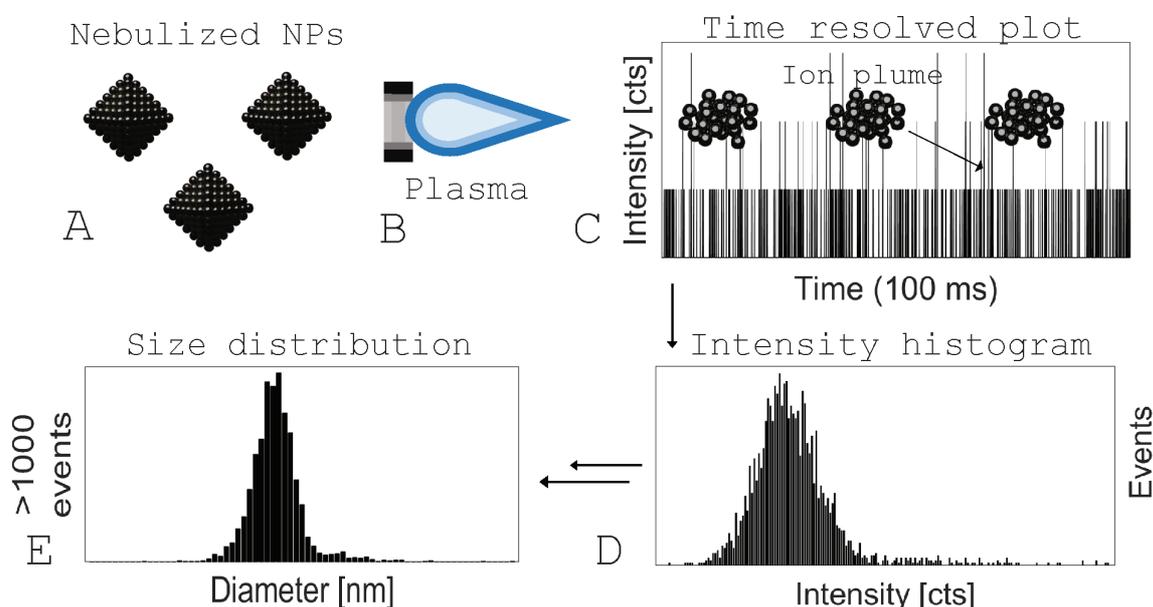


Figure 23. Schematic diagram of the general approach for obtaining size distribution of NP dispersions using SP-ICP-MS. (A) Nebulized NPs formed after nebulization of the sample dispersions. (B) Plasma torch of the ICP-MS instrument used for the desolvation, vaporization, atomization, and ionization of the particles present in the aerosol. (C) SP-ICP-MS raw data containing both background signal (e.g., dissolved ions) and particle events (ion plumes). A snapshot of 100 ms is depicted for representation. (D) Histogram of the raw data obtained via a sorting algorithm after background subtraction equating the intensity to the number of observations (events). (E) Final solution of SP-ICP-MS data processing pipeline, e.g., size distributions.

as discrete ion packages, or ion plumes, retaining the information of the elemental make-up of each individual particle (**Figures 23A, B**).²⁰ Intensity spikes above the background herald the arrival of an ion plume or particle event at the detector. This is distinctively different from dissolved ion intensities, or background signal, which remain constant. To distinguish between these discrete particle events and the dissolved ions, dwell times much shorter than in conventional ICP-MS are needed (μs to ms). Each individual acquisition of the intensity read-out is then plotted against the acquisition time representing the SP-ICP-MS raw data (**Figure 23C**). A series of steps (**Figure 23D**) have to be executed before raw SP-ICP-MS data can be transformed into a meaningful data-set such as a NP size distribution (**Figure 23E**).^{14,16}

Traditionally, SP-ICP-MS has been used to determine particle number concentrations and size distributions of undefined, crude dispersions relevant to environmental research, health and/or food sciences, limited to metal oxides and noble metals such as Au, Ag, and Pt.^{15,17,20,21,22,23,24,25,26}

Recently, some more complex analytes (e.g., TiNbCN and AuAg) have been studied as well albeit of undefined morphology or isotropic in nature.^{27, 28} Moreover, due to the incompatibility of ICP-MS with organic solvents, samples analyzed are produced or dispersible in water alone. Herein, we show the capabilities of SP-ICP-MS to determine the size, count and composition of transition metal (an)isotropic (multi) metallic NPs of well-defined size and shape, including but not limited to spheres, cubes, truncated octahedra and tetrahedra, synthesized in organic media using our in-house developed syntheses procedure (**Figure 24**). We further demonstrate that the high sensitivity of the quadrupole mass analyzer allows to quantify the atomicity of bulk-dilute (<1 at. %) anisotropic CuAg nanosurface alloys (NSA), corroborated with X-ray photoelectron spectroscopy (XPS), offering a roadmap for the study of NP doping with reliable statistics using SP-ICP-MS. Finally, by extending upon our in-house developed syntheses, we produce CuPd and CuPdAg cubic multimetallic NPs and use a time-of-flight (TOF) ICP-MS to show

that the composition of NP ensembles can be studied with ease. We further verify these results with scanning transmission electron microscopy energy dispersive X-ray spectroscopy (STEM-EDX). We aim at providing a method to the reader to quantify (an)isotropic inorganic NP dispersions complementary to EM. We believe that this method can also be applied to a variety of materials, including semiconductors (e.g., CdSe, CsPbBr₃, InP, etc.), upconversion nanocrystals (e.g., NaYF₄, NaGdF₄, NaLuF₄, etc.), metal oxide (e.g., Al₂O₃, TiO₂, ZnO₂

etc.), metal organic frameworks (e.g., ZIF-8, HKUST-1, UiO-66, etc.) and finally, metals and alloys (e.g., Mn, Co, Ni etc.). Therefore, a complete description of the instrument calibration and data processing pipeline is provided in the following section.

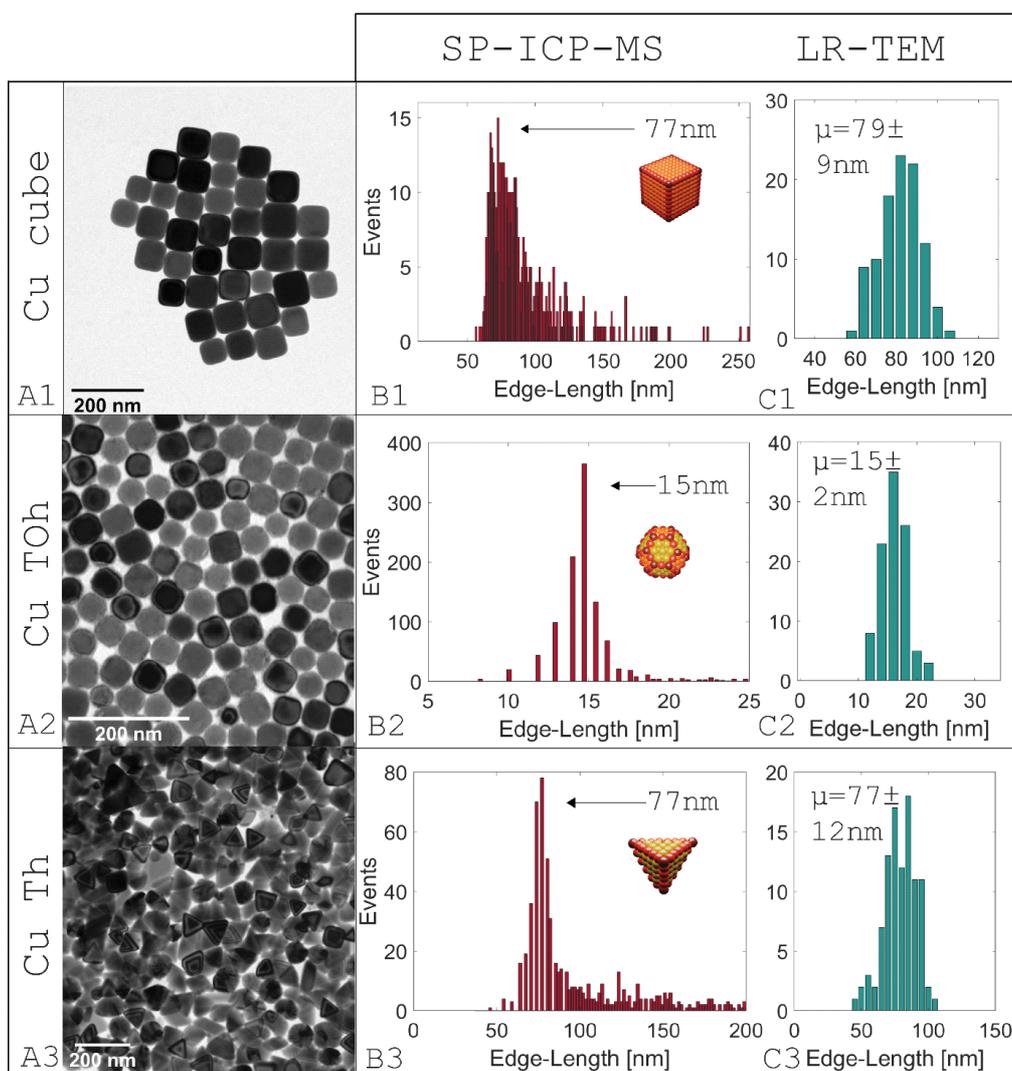


Figure 24. (A1-A3) Low resolution transmission electron microscopy (LR-TEM) micrographs of cubic (C), truncated octahedral (TOh), and tetrahedral (Th) Cu NPs synthesized using a phosphine-derivative mediated wet-chemical procedure. (B1-B3) Size distributions of the C-, TOh- and Th-Cu NPs obtained using SP-ICP-MS. The particle most frequently observed has an edge-length of: 77, 15 and 77 nm, respectively. Edge-length is defined as the center-to-center distance between two corner atoms of a particle (depicted in deep red in the ball models in the inset). The total number of particles observed in a single experiment was as high as 1100 for a measurement of 100 s duration with a dwell time of 50 μ s. Excellent agreement exists between the SP-ICP-MS and LR-TEM (C1-C3) measurements. Aggregates in the sample that are missed by the LR-TEM can be observed (events at the far end of the distributions in (B1-B3), giving a more complete picture of the ensemble. (C1-C3) Size distributions of 100 C-, TOh- and Th-Cu NPs using particle counting of LR-TEM micrographs.

4.2. Instrument calibration and data processing

As described in the introduction, SP-ICP-MS raw data consist of a signal intensity as a function of time (**Figure 25A**). This includes a background/dissolved analyte signal and particle events evidenced by intensity spikes above the background. In order to extract all particle events, background subtraction has to be performed, which is achieved mathematically and iteratively (see **Methods**). All extracted particle events are then grouped and sorted based on their respective intensity values and reported as events-versus-intensity histograms (**Figure 25B**).²⁹ The total number of events is a direct measure of the number of particles that have reached the detector, which can be converted into a number concentration using Eq. 1:

$$N = \frac{f}{tQ\eta_t} \quad (1)$$

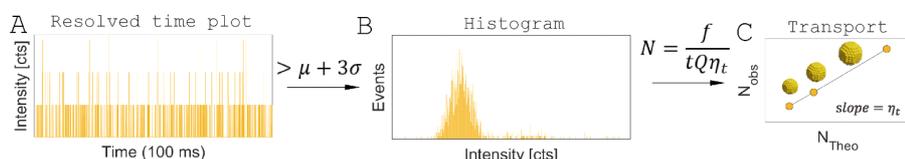
in which N is the NP number concentration (mL^{-1}), f the total number of events, t the total acquisition time (min), and Q the sample flow rate (mL min^{-1}), which can be estimated from the mass change of an arbitrary volume of water consumed by the instrument as a function of time. The dimensionless quantity η_t , known as the transport efficiency, is introduced to account for the fraction of particles originally introduced that can actually be detected and is generally $<10\%$.^{14,16} This is due to losses associated with the generation of the aerosol, which is instrument and size dependent.³⁰ Therefore, sets of known particle size and concentration are introduced and their observed number concentrations are determined (**Figure 25C**). Calibration can then be performed using Eq. 2:

$$N_{obs} = \frac{f}{Qt} = \eta_t N_{Theo} \quad (2)$$

in which N_{obs} is the observed particle number concentration and N_{Theo} the theoretical particle number concentration. Alternatively, calibration can also be performed based on the particle size but requires an additional external calibration step.^{14,16} Often used calibrants are monodisperse isotropic Ag and Au NPs, which can be purchased from various sources and of which the latter is used presently (see **Methods, Figure S1** and **S2**). In theory, any set of

well-defined, monodisperse particles with known characteristics can be used for the calibration. Ideally, one would use standard dispersions of the same element as well as the same matrix as the analyte. However, commercial availability is limited. Therefore, we are working on sets of synthesized NP calibrants to match our analyte and determine its effect, if any, which is the subject of a later work.

Instrument calibration



Data processing

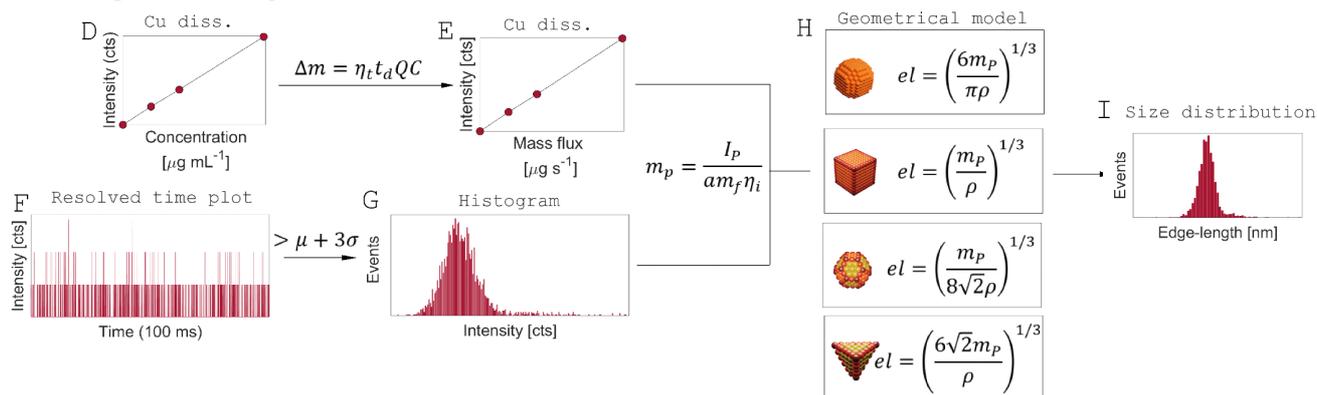


Figure 25. (A) Time resolved plot of the SP-ICP-MS raw data of a calibrant (yellow). Only 100 ms is depicted for clarity. (B) Intensity-versus-events histogram of a calibrant (yellow). (C) Transport efficiency (η_t) calibration curve of particle dispersions of known size and number concentration (in the present study Au NP (see **Methods, Figure S1** and **S2**)). (D) Dissolved standard solutions calibration curve (Cu in the present study). (E) Converted $\mu\text{g s}^{-1}$ calibration curve of the dissolved ion standards (Cu in the present study). (F) Time resolved plot of the SP-ICP-MS raw data of an analyte (red). (G) Intensity-versus-events histogram of an analyte. A snapshot of 100 ms is depicted for representation. (H) Various geometrical models to extract dimensional parameters such as edge-length including but not limited to spheres, cubes, truncated octahedra and tetrahedra. (I) Final solution of the SP-ICP-MS data processing pipeline representing a NP size distribution.

With the instrument calibrated and η_t obtained, one could directly measure the number concentration of a given unknown NP dispersion. However, in order to determine the mass of the particles counted, another calibration is required. As mentioned before, in ICP-MS, the dissolved analyte concentration of an unknown solution is determined by comparing its average intensity to the intensity measured of solutions of known concentrations. However, SP-ICP-MS intensities are detected at discrete intervals. Therefore, to relate such a discrete intensity to an ion plume mass, the average concentration of the calibration curve ($\mu\text{g mL}^{-1}$; **Figure 25D**) needs to be converted into the amount of material detected at any given dwell time ($\mu\text{g s}^{-1}$; **Figure 25E**). This can be achieved according to Eq. 3:

$$\Delta m = \eta_t t_d QC \quad (3)$$

in which t_d is the dwell time (or integration time) and C the dissolved ion concentration. The slope of the converted calibration curve (a) then relates the intensity of the ion plume (I_p) to the particle mass (m_p) through Eq. 4:

$$m_p = \frac{I_p}{am_f \eta_i} \quad (4)$$

in which η_i is the ionization efficiency, the dimensionless parameter that allows for a correction factor for materials that ionize poorly. Partial ionization is strongly mass dependent both relative and absolute, and has been determined for Au to occur for particles >150 nm.^{20,31} Further, partial ionization may also play a role for metal oxides for their generally high boiling points.^{20,31} As the materials investigated in this study (i.e., Cu, CuAg, CuPd, and CuPdAg NPs) have lower melting points and ionization potentials than Au and are smaller than 150 nm in size, it is reasonable to assume an ionization efficiency of 100%.

Another parameter m_f , the mass fraction, or the contribution of the element analyzed to the total particle mass, is introduced for modelling purposes. For example, only metal species in metal oxides can be detected by ICP-MS and this can be accounted for by a corresponding m_f value.

With the particle mass in hand, the events per intensity histogram of the analyte can be converted into a size distribution of a specific particle geometry by using a dimensional descriptor such as the edge-lengths (el). This includes but is not limited to spheres (Eq. 5), cubes (Eq. 6), truncated octahedra (Eq. 7), and tetrahedra (Eq. 8):

where ρ is the density.

$$el_{Sph} = \left(\frac{6m_p}{\pi\rho} \right)^{\frac{1}{3}} \quad (5)$$

$$el_{Cu} = \left(\frac{m_p}{\rho} \right)^{\frac{1}{3}} \quad (6)$$

$$el_{TOh} = \left(\frac{m_p}{8\sqrt{2}\rho} \right)^{\frac{1}{3}} \quad (7)$$

$$el_{Th} = \left(\frac{6\sqrt{2}m_p}{\rho} \right)^{\frac{1}{3}} \quad (8)$$

4.3. Results and Discussion

4.3.1. NP concentration optimization

In order to have the most accurate measurement, it is adamant that each particle event can be distinguished from the background. If the ionic contribution to the signal is too high (e.g., a residual from the synthesis), NPs having intensities similar or below that of the dissolved analyte cannot be identified by the algorithm. However, since the intensity of each particle is fixed and the intensity of the dissolved analyte is concentration dependent, sample dilution can help detect the smaller particles in the ensemble as well (for particles above the limit of detection (LOD)).^{32,33} To evaluate the effect of NP concentration on the results, in **Figure 26**, a suspension of 15 nm TOH-Cu NPs at a concentration of 10^5 mL^{-1} was analyzed by SP-ICP-MS as well as their 3- and 6-fold dilutions. The measured most frequent size was: 29 nm (**Figure 26A, Table S1**), 23 nm (**Figure 26B, Table S1**) and 15 nm (**Figure 26C, Table S1**), respectively. The latter one portrays the complete distribution whereas for the former two only a portion of the ensemble can be observed. This shows the dissolved analyte concentration cap. Above it, the background signal is too

high to extract the full distribution. Diluting further, on the other hand, will result in progressively lower numbers of events as less and less intervals will contain a particle event. Of course, this could be off-set by extending the measurement time but this is rather impractical: for every additional second measured, with $t_d = 50 \mu\text{s}$, 2×10^4 data points are added to the data file. Therefore, there exists an optimized dissolved analyte to particle concentration that yields good statistics with the least amount of data, but excludes the loss of information due to a too high ionic background. For the Cu NPs reported here and using the instrument settings as outlined in the **Methods** section, this optimal concentration lies between 10,000-20,000 mL^{-1} . However, this value can vary strongly between particles of different elements and depends on both the chemical nature of the NPs, their size, the instrument and its corresponding settings and finally the synthesis procedure used (e.g., for Au NPs of 30-100 nm used presently this value is $\sim 50,000 \text{ mL}^{-1}$ for $t_d = 50 \mu\text{s}$ on a quadrupole based ICP-MS instrument).^{34,29} Preparing dilution series as

in **Figure 26** can be of tremendous value to calibrate a measurement when optimal number concentrations are unknown. It is worth noting the difference in events between **Figure 26A, 4B** and **4C**. When the dissolved analyte concentration is too high, only the tail of the distribution can be extracted resulting in a low number of events. Once the ionic background intensity

falls below that of the smallest particle of the ensemble, the total number of events goes up by at least an order of magnitude. This change in NP events can be used as a handle to find the optimal concentration.

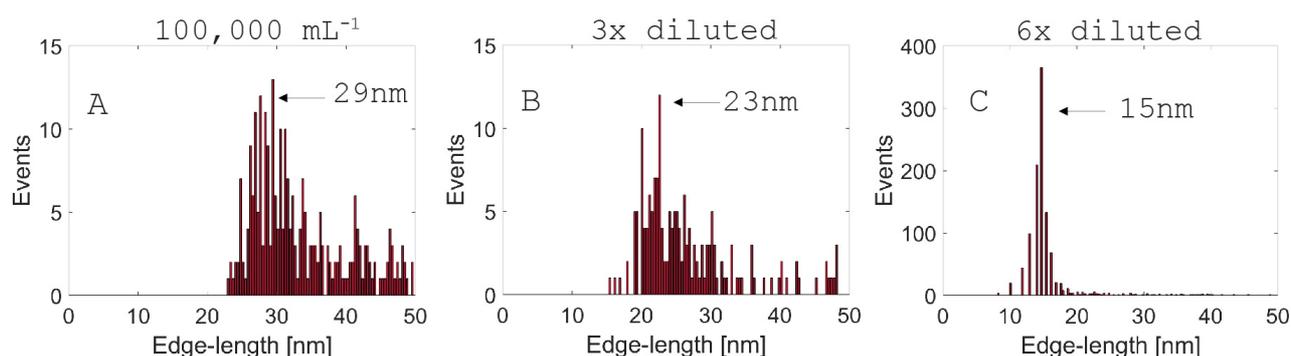


Figure 26. Size distributions of a dilution series of TOh-Cu NPs. (A) NP number concentration (N): 10^5 mL⁻¹, (B) NP number concentration (N): $1/3 \times 10^5$ mL⁻¹, (C) NP number concentration (N): $1/6 \times 10^5$ mL⁻¹. Shift of the average size, thus mass, to lower values. upon dilution highlights the significant effect of the dissolved analyte concentration on data quality. If the dissolved analyte concentration is too high, ion plumes derived from initial particles of intensities close to the dissolved analyte cannot be distinguished from the background. Optimization and calibration of N is instrumental to correct distribution determination. This feature perseveres even with an independent instrument calibration used (**Figure S3**). The gain in the number of events is evidence that all particle events can be extracted.

4.3.2. Reliability of the method

To determine the reliability of the technique to provide reproducible size distributions (as it is still one of the main means to show ensemble (in)homogeneity),^{10,11} we prepared two dilution series of the same NPs (TOh-Cu, **Figures 26A-C** and **S3A1-C1**) but used independent standards for the instrument calibration of η_t (**Figures S1** and **S2**). By using the same mass s^{-1} calibration curve for both dilution series (**Figure S4**), we ensured that any changes to the size distribution that originated from inaccuracy in the determination of the η_t , which is expected to introduce the largest error,¹⁴ are taken into account. When the particle concentration reaches its optimal value, a perfect match in the particle mass is obtained with the edge-length of the TOh-Cu NPs determined at 15 nm in both cases, independently of calibrant used (**Figures 26C** and **S3C1**). With a well-calibrated instrument, precise and accurate size distributions can be obtained reproducibly, independent of particle size and shape (for particles above the LOD) as equally agreeing results could be obtained for the Th-Cu NPs (**Figures S3A2-C3** and **S4**).

We further investigated the accuracy and precision of SP-ICP-MS to determine NP number concentrations as they are of interest to study colloidal stability, nanoparticle sintering and catalytically active surface area estimation, amongst others.^{35,36,37,38} We prepared six independent dilutions of C-, TOh-, and Th-Cu NPs, based on a three-fold dilution series, and measured the particle concentrations (**Table S2**). With an uncertainty of the measurement of only 4% (estimated through error propagation of the dilution series based on manufacturer reported uncertainties at 2%, **Table S2.2**), SP-ICP-MS allows for number concentration determinations with high precision. Further, it reveals a consistently lower particle concentration (~10%) than estimated based on LR-TEM particle counting. This is most likely a result of aggregates in the sample, however.

4.3.3. Applications

Beside the size and the particle number concentration, SP-ICP-MS can be used to quantify different elements within a particle ensemble.⁴⁰ Due to the short dwell times needed for SP-ICP-MS, TOF mass analyzers are required to obtain a full elemental spectrum in a single dwell/integration time.^{18,20,41,42} Very recently, a SP-ICP-MS method has been established to simultaneously measure two elements by extending the signal duration through the introduction of a collision cell.²⁸ This limits the LOD, however. Alternatively, one may perform sequential spectral analysis.²⁰ Using a galvanic exchange reaction, we were able to synthesize anisotropic CuAg NSAs (C-CuAg, **Figure 27A1, A2** and TOH- and Th-CuAg **Figure S5**). With the Ag and Cu distributions obtained via SP-ICP-MS, followed by a subsequent subsurface based modelling step, we were able to determine the ensemble average surface composition of our anisotropic particles (**Figure 27C1-C2**). We deduce that 0.59 monolayer of Ag has been deposited in the case of the C-CuAg NSA. Further, we show that Ag at. % is normally distributed around

the mean (max. Ag 9 at. %, **Figure 27C2**). Our method offers the same information as for dopant distributions that have been studied for bulk materials, e.g., n-type semiconductors.^{43,44,45} We further confirmed these results with the good agreement of those obtained from XPS by comparing the estimated penetration-depth to the inelastic mean free path information depth (error <5%, **Figure S6** and **Table S3**).⁴⁶

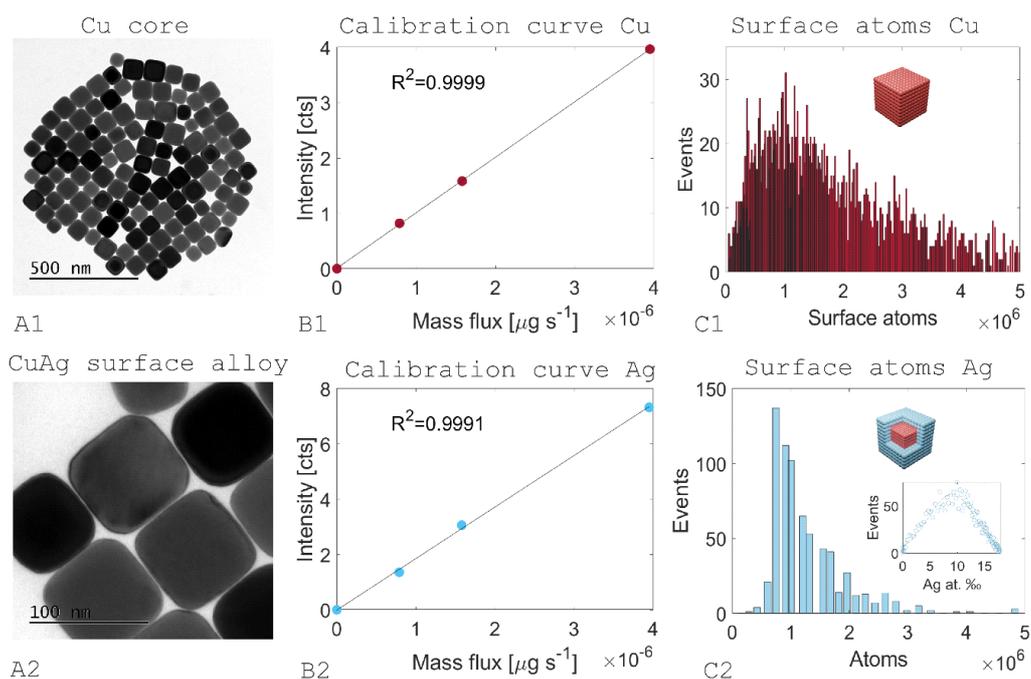


Figure 27. SP-ICP-MS as a method to characterize anisotropic NSAs.³⁹ The C-Cu NPs synthesized in the present study were coated with an ultrathin shell of Ag using a galvanic exchange reaction (see **Methods**). (A1-A2) LR-TEM micrograph of the Cu cubic core and the CuAg cubic NSA, respectively. (B1-B2) Cu and Ag mass flux calibration curve used to convert the intensity measured to the mass of the particle. (C1) Using a subsurface distribution model (**Note S2**), the Cu particle mass distribution obtained with SP-ICP-MS can be converted into an ensemble distribution of surface atoms. (C2) Distribution of Ag atoms obtained via SP-ICP-MS. By taking the ensemble average, we deduce that 0.59 monolayer of Ag has been deposited. Inset shows the normally distributed doping concentration of Ag by superimposing the Cu and Ag spectra, respectively.

While sequential analysis suffices for simple bimetallic samples, experiment and data treatment quickly becomes tedious for more complex systems (e.g., high-entropy alloys⁴⁷). Further, data treatment requires assumptions and preexisting knowledge of the sample, e.g., that each particle contains all elements. Therefore, we further extended upon our galvanic replacement reaction to produce next to C-CuAg NSAs, C-CuPd and C-CuPdAg anisotropic multimetallic NPs to show the capabilities of TOF mass analyzers to determine the elemental make-up of every *single* particle simultaneously and its advantage over quadrupole mass analyzers for, e.g., doping studies (**Figure 27**). As a benchmark, we first sized C-Cu NPs using SP-ICP-TOFMS to determine the reliability of the method and alternative calibration procedure using monodisperse microdroplets of element solutions, which showed an excellent match with LR-TEM (**Figure S7**). Further, we confirmed the normal distribution of Ag in the C-CuAg NSA (**Figure 28C1**) and determined that in the case of CuPd, a positive skew followed with an order larger Pd content (**Figure 28C2**). We invoke differences in standard reduction potentials of both metals to explain the difference in reactivity (+0.7996 and +0.915 V for Ag(I) and Pd(II), respectively). We could verify the presence of Ag and Pd in the respective bimetallic systems using STEM-EDX, which showed a core-shell like morphology for C-CuPd NPs, corroborating

the higher average Pd content determined with SP-ICP-TOFMS (**Figure 28B1-B2**). Moreover, by reintroducing C-CuAg NSAs in the Pd-precursor reaction mixture, we were able to synthesize C-CuPdAg NPs as well (**Figure 28A3-C3**). Interestingly, it could be deduced that Ag had corroded instead of the expected Cu alone (+0.52 V, **Figure S8**). This can be explained by the more facile etching of Ag in the presence of Cl⁻ ions. Further scrutiny of the SP-ICP-TOFMS data pointed towards the presence of bimetallic AgPd NPs in the ensemble as well albeit of low occurrence. After reexamination of the sample with STEM-EDX, these particles could eventually be observed likewise (**Figure S9**). Finally, we show that using SP-ICP-TOFMS it is possible to distinguish bimetallic physical mixtures (CuAg + CuPd) from multimetallic NPs, which would not have been possible using a quadrupole mass analyzer (**Figure S10**). With the TOF instrument used presently, any ion within the range of 7-175 *m/z* can be observed simultaneously (**Table S4**).⁴⁸ This includes most of the elements of the periodic table. However, not all elements can be observed with equal sensitivity. For a list of elements that can be quantified with SP-ICP-TOFMS and their reported LODs if any, we direct the reader to the SI (**Table S5**).

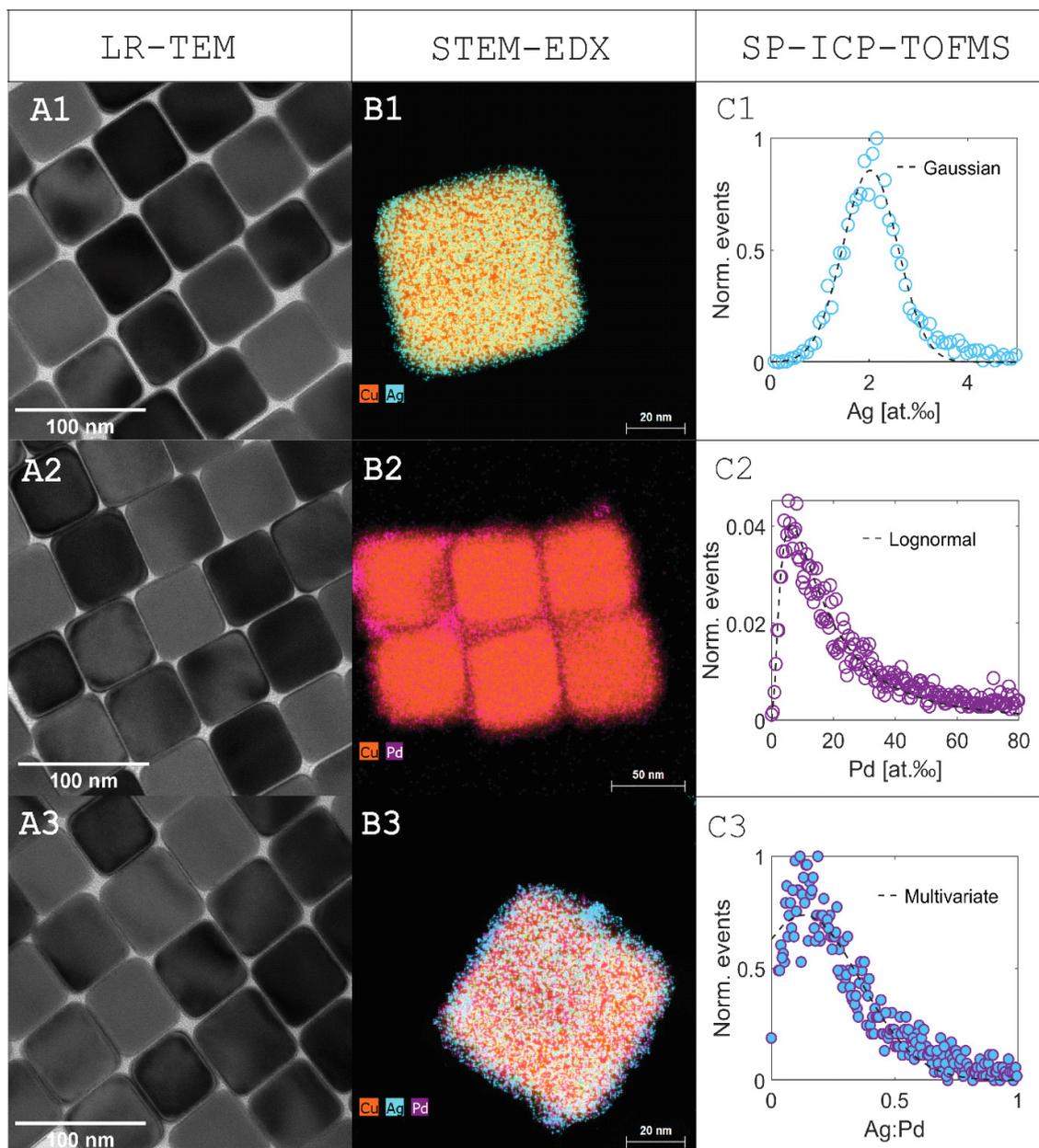


Figure 28. (A1-A3) TEM micrographs of the C-CuAg, C-CuPd, and C-CuPdAg multimetallic NPs, respectively. (B1-B3) STEM-EDX elemental maps of C-CuAg, C-CuPd, and C-CuPdAg NPs. (C1-C3) Normalized composition distributions of C-CuAg, C-CuPd, and C-CuPdAg multimetallic NPs obtained with a TOF mass analyzer. The C-CuAg and C-CuPdAg distributions were normalized by the number of events. The C-CuPd distribution was normalized so that the probability density function integral equaled to one. (C1) The C-CuAg distribution shows that Ag is normally distributed around the mean, corroborating the results obtained using the quadrupole (Gaussian fit: $R^2 = 0.9723$, see **Note S4**). The maximum lies at ~ 2.2 Ag at. %, a four-fold reduction with respect to the SP-ICP-MS determined composition distribution (**Figure 5C2**), which can be explained by the higher number concentration at a fixed mass loading (see **Figure S7** and **S11**). (C2) The C-CuPd is lognormally distribution evidenced by the positive skew ($R^2 = 0.9816$, see **Note S4**). (C3) The C-CuPdAg distribution shows against a normal distribution ($R^2 = 0.9467$, see **Note S4**).

4.4. Conclusion

The high-throughput, element discriminative, dispersing media indiscriminate, size and shape independent NP dispersion quantification and characterization protocol, based on SP-ICP-MS, is a powerful tool that may help to bring about a statistics renaissance in the nanomaterial's science world. With this approach, nanoscale structures relevant to bulk phenomena can be quantified and characterized with ease and with ensemble-representative reliability. With four shapes of NPs (Au spheres and Cu

cubes, truncated octahedra and tetrahedra) and three Cu-based surface-alloy NPs (CuAg, CuPd and CuPdAg) as successful examples, we believe that the protocol can be applied to more complex structures and other inorganic nanomaterials in the future. We hope this method finds use in, amongst others, materials science, materials chemistry, (nano)physics, (nano)photonics, catalysis and electrochemistry.

4.5. Methods

4.5.1. Chemicals

The following chemicals and solvents were acquired from Sigma-Aldrich: copper bromide 99.99% (CuBr), palladium chloride 99% (PdCl₂), nitric acid 70% (HNO₃), trioctylphosphine oxide 99% (TOPO), trioctylphosphine 99% (TOP), oleyl amine 70% (OLAM), polyvinylpyrrolidone (PVP, MW ~55,000), dichloromethane (DCM), and dimethyl formamide (DMF). Anhydrous

ethanol 95% was purchased from ACROS organics (EtOH) and anhydrous toluene (99.8%) from Alfa Aesar. Silver nitrate 99.9995% was obtained from Puratrem (AgNO₃). All chemicals were used as received without any further purification. All aqueous solutions were prepared with di-ionized (DI) water with a resistivity of 18.2 MΩ cm⁻¹.

4.5.2. Synthesis of anisotropic copper crystals

Cu NPs of three different morphologies were synthesized using a reflux set-up under inert conditions. For the C-Cu synthesis, adapted from Guo et al and Lojudice et al,^{49,50} 0.45904 g CuBr and 1.78 mL TOP stored in a glove box, were mixed with 9 mL of degassed OLAM and sonicated for 10 min to form a transparent, pale yellow solution. Meanwhile, 50 mL of OLAM (70 %) were added to a 250 mL three-necked flask and degassed under vacuum. The flask was purged with N₂ after the bubble formation has stopped. Using a clean syringe, the reaction mixture was then quickly added to the flask. The mixture was heated to 80 °C using a heating mantle and kept at that temperature for 30 min while using a low vacuum to dry the solution. The yellow transparent reaction mixture was purged with N₂ and the temperature was quickly increased to 270 °C and kept for 1 hour. At 270 °C, the reaction mixture turned red, indicating nucleation. After the solution had cooled to room temperature, the reaction mixture was transferred to the glove box and washed with toluene using centrifugation (7,500 rpm for 5 min). The C-Cu pellet was

redispersed in 5 mL of toluene. For TOh-Cu, the reaction was carried out at 260 °C instead, all other conditions were kept the same. For the Th-Cu, 0.23908 g CuBr and 3.12417 g dry TOPO were dissolved in 5 mL degassed OLAM using ultrasonication (10 min), yielding a pale-yellow translucent solution. This was then quickly added to 34 mL OLAM in a three-necked flask under inert atmosphere using a syringe. Then, the temperature was raised to 80 °C under vacuum, kept for 30 min, and raised further to 180 °C to cause boiling. The pale-yellow solution turned to a deep gold color. At this point, a N₂ purge was applied and the temperature was further raised to 260 °C upon which the solution turned translucent black, indicating nucleation. The reaction was continued for 1 h to yield a purple dispersion, which was then washed using toluene.

4.5.3. Synthesis of multimetallic NPs

The synthesis of the multimetallic NPs was inspired by the protocol from Lee et al.⁵¹ 4 mg of NPs dispersed in toluene were added to a 10 mL glass vial to which 3.5 mL of degassed OLAM were carefully added, without disturbing the NP film. Additionally, 0.5 mg of dry AgNO₃ or PdCl₂ were added to 1.5 mL of degassed OLAM and heated at 50 or 80 °C using an oil bath until dissolved. AgNO₃ or PdCl₂ in OLAM was then carefully added to the reaction vial, which was then

allowed to react at 80 °C for 60 s with C-Cu and TOh-Cu, or 50 °C for 300 s with Th-Cu, after which the reaction was quenched with toluene. This yielded the Th- and TOh-CuAg and C-CuAg/Pd. For the synthesis of C-CuPdAg, 4 mg of C-CuAg rather than C-Cu NPs were used instead. All other parameters were kept the same. The coated crystals were washed with toluene and stored in a glovebox.

4.5.4. Preparation of aqueous dispersions

100 µL of the (multi)metallic anisotropic nanoparticle dispersions at concentrations of 2-20 mg mL⁻¹ were ligand exchanged by washing with DMF (1 mL, 5,000 rpm and 2 min) in three-fold and dispersed in 100 µL DMF using the protocol of Johnson et al.⁵² An aliquot equivalent of 100,000 mL⁻¹ over a 3-step dilution series was added to deionized water, which was used for sampling.^{53,54}

4.5.5. Characterization

Electron microscopy (EM). LR-TEM images were acquired with a FEI Tecnai Basic Spirit operated at 120 kV in bright field mode. The microscope was equipped with a Gatan charge-coupled device (CCD) camera and Digital Micrograph for imaging. Samples were drop-casted on ultrathin 400 mesh carbon film Au grids from Ted Pella Inc., which were washed with ethanol before and after drop-casting. Size distributions were obtained through edge-length analysis using the FIJI ImageJ software package of at least 100 unique particles. Scanning transmission electron microscopy high-angle annular dark-field (STEM-HAADF) micrographs and EDX elemental maps were obtained using a FEI Tecnai Osiris operated at 200 kV. The high-resolution TEM is outfitted with a X-FEG field emission gun reaching a brightness of $1.8 \times 10^9 \text{ A cm}^{-2} \text{ srad}$ at 200 kV and when operated in scanning mode optimized for EDX, has a probe size of 1.0 nm with a current of 1 nA. The silicon drift Super-X EDX detectors in combination with the Bruker Esprit imaging software were used to acquire and analyze the EDX elemental maps.

X-ray photoelectron spectroscopy (XPS). XPS was performed with a Kratos Axis Supra system, using a monochromated Al K_{α} (1486.61 eV) X-ray source at a nominal power of 225 W. The samples were drop-casted on gold foil in a N_2 glovebox and transferred for measurement without exposure to air. No charge compensation was required and the binding energies (BEs) were referenced to Au $4f_{7/2}$ at 83.95 eV. A pass energy of 20 eV was used for acquiring all core-level and Auger electron spectra.

Inductively coupled plasma - optical emission spectroscopy (ICP-OES). The concentration of the NP solution was determined with an Agilent 5110 ICP-OES with a VistaChip II CCD camera. The NPs were digested overnight in 2% HNO_3 and filtered with 0.4 μm pore size Ultrapore nylon filters. The calibration curves were obtained through the preparation of a dilution series of elemental standards obtained from Sigma Aldrich.

Inductively-coupled plasma mass spectrometry (ICP-MS). Particle sizing, counting and elemental analysis of the C-, TOh- and Th-Cu NPs as well as C-, TOh- and Th-CuAg NSAs was achieved with a NexION 350D ICP-MS instrument from PerkinElmer operated in continuous data acquisition mode. An icpTOF instrument of TOFWERK AG, Thun, Switzerland equipped with an orthogonal-acceleration TOF mass analyzer was used to size C-Cu and determine the composition of C-CuAg, C-CuPd, and C-CuPdAg NPs. For a comparison of the operating conditions of both ICP-MS instruments see **Table S6**. Particles were extracted from the raw data using both commercial software from Perkin Elmer (Syngistix) and TOFWERK AG (TofPilot) as well as via an in-house developed MATLAB script (see **Table S7**). In the case of Syngistix and our MATLAB script, data processing, e.g., particle event extraction, was achieved by averaging over all intensities (counts) and determining the standard deviation (σ). A particle event is defined as any intensity 3σ above the average of all intensity counts (raw data).^{30,55} This is done iteratively. After

the first set of particle events has been collected, which are all the intensities (counts) above the determined threshold, the average and the σ of the new data-set (remaining intensity counts) is determined and the process is repeated until no signal $>\text{average} + 3\sigma$ remains. TofPilot performs iterative signal/background separation every 1000 data points instead.^{56,57} This allows for corrections in fluctuations of the dissolved signal. The average and σ are determined for each data subset with the threshold of a particle event defined as $>\text{average} + (3.29\sigma) + 2.72$ reducing false positives. Alternative methods to reduce false positives exist as well, which may offer better results under certain conditions.^{58,59} Calibration of the transport efficiency (η_t) of the NexION 350D ICP-MS instrument was achieved in parallel with Au NPs standards of 61, 78 and 98 nm purchased from NanoComposix as well as 30, 50 and 80 nm purchased from PerkinElmer at number concentration of $\sim 50,000 \text{ mL}^{-1}$ (**Figures S1 and S2, Table S8**). After Au NPs standards introduction, the instrument was rinsed with 1% HCl for 30 s and 2% HNO_3 after

Cu, CuAg, CuPd and CuPdAg NP sampling. After rinsing with acid, i.e., before sample introduction, the sampler was rinsed with DI water. Dissolved metal calibration curves were obtained from elemental standards purchased from Sigma Aldrich. For the icpTOF instrument, calibration was achieved using an online droplet calibration method with a microdroplet generator described by Hendriks et al.⁵⁴ Monodisperse microdroplets of Cu, Pd, and Ag were used as calibrants and introduced into the NP aerosol flow in calibration run. Construction of the composition distributions was achieved in-house (see **Note S2**). The most abundant mass was used in all cases but inspected for false positives using all other isotopes and their

respective LODs (See **Table S9** and **S10** for the LODs of the quadrupole and time-of-flight based methods respectively). For complex media, or highly concentrated salts such as phosphate buffered saline (PBS), matrix effects, such as spectral overlap and intensity changes, may significantly affect sizing and or composition determination accuracy.^{53,54} Since in the present study only aqueous dispersions were used, matrix effects were of lesser concern. Further, the calibration method used in this work ensures that the analyte and calibrant experience the same plasma conditions, thus allowing for matrix-independent mass quantification.

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4.7. Supporting Information

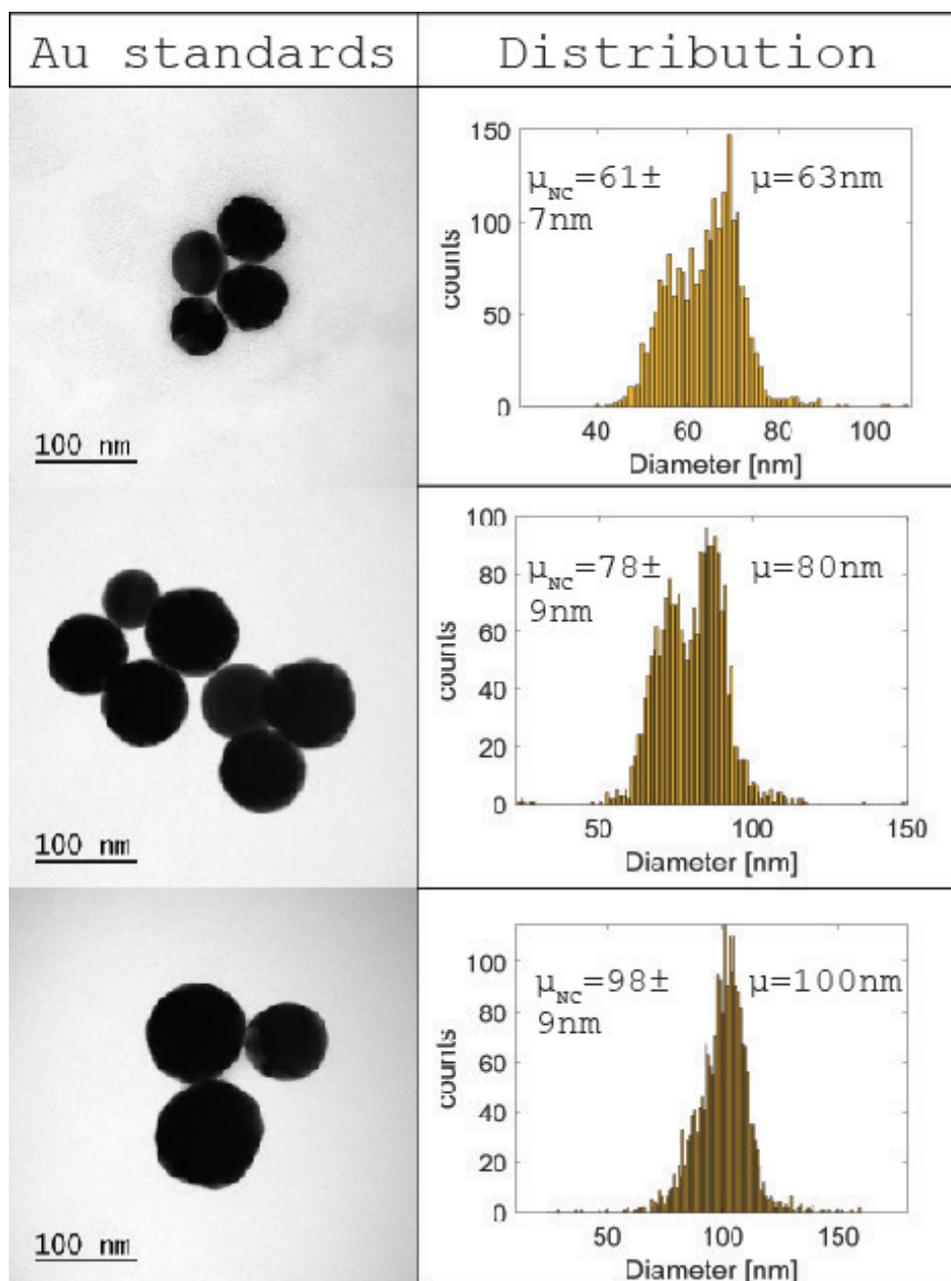


Figure S1. NanoComposix Au standard particle suspensions. The experimental mean (μ) obtained via SP-ICP-MS matches the certified mean (μ_{NC}) in all instances within error of measurement. Particle concentration was 50,000 mL⁻¹.

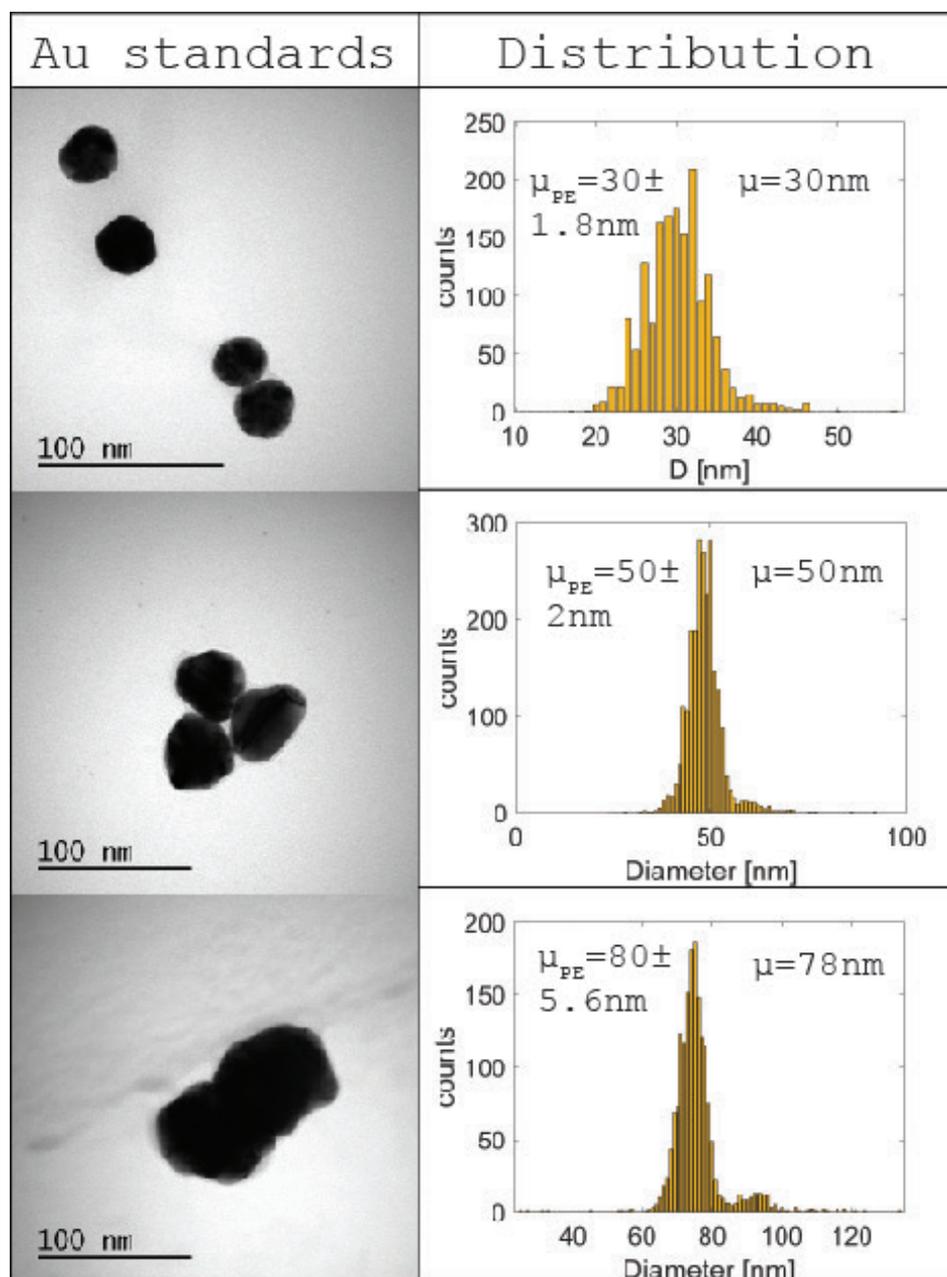


Figure S2. PerkinElmer Au standard particle suspensions. The experimental mean (μ) obtained via SP-ICP-MS matches the certified mean (μ_{NC}) in all instances within error of measurement. Particle concentration was 50,000 mL⁻¹.

TOh	Particle concentration (NPs mL ⁻¹)	Most frequent size (nm)	Particle size mean (nm)	Dissolved. Concentration (µg L ⁻¹)	η _t (%)	R ²
Stock	100000	32.3	42	3.1	3.46	0.9997
3×	33333	18.3	30.6	0.94	3.46	0.9997
6×	16667	15.4	19.3	0.35	3.46	0.9997

TOh_2	Particle concentration (NPs mL ⁻¹)	Most frequent size (nm)	Particle size mean (nm)	Dissolved Concentration (µg L ⁻¹)	η _t (%)	R ²
Stock	100000	29.4	41.8	3.1	4.11	0.9997
3×	33333	22.6	32.4	0.90	4.11	0.9997
6×	16667	14.7	16.33	0.31	4.11	0.9997

Table S1. Results of the TOh-Cu NP suspension of 10⁵ mL⁻¹ (15 ±2 nm) and its dilution series. Particle extraction achieved with Syngistix. Geometrical fitting performed in-house.

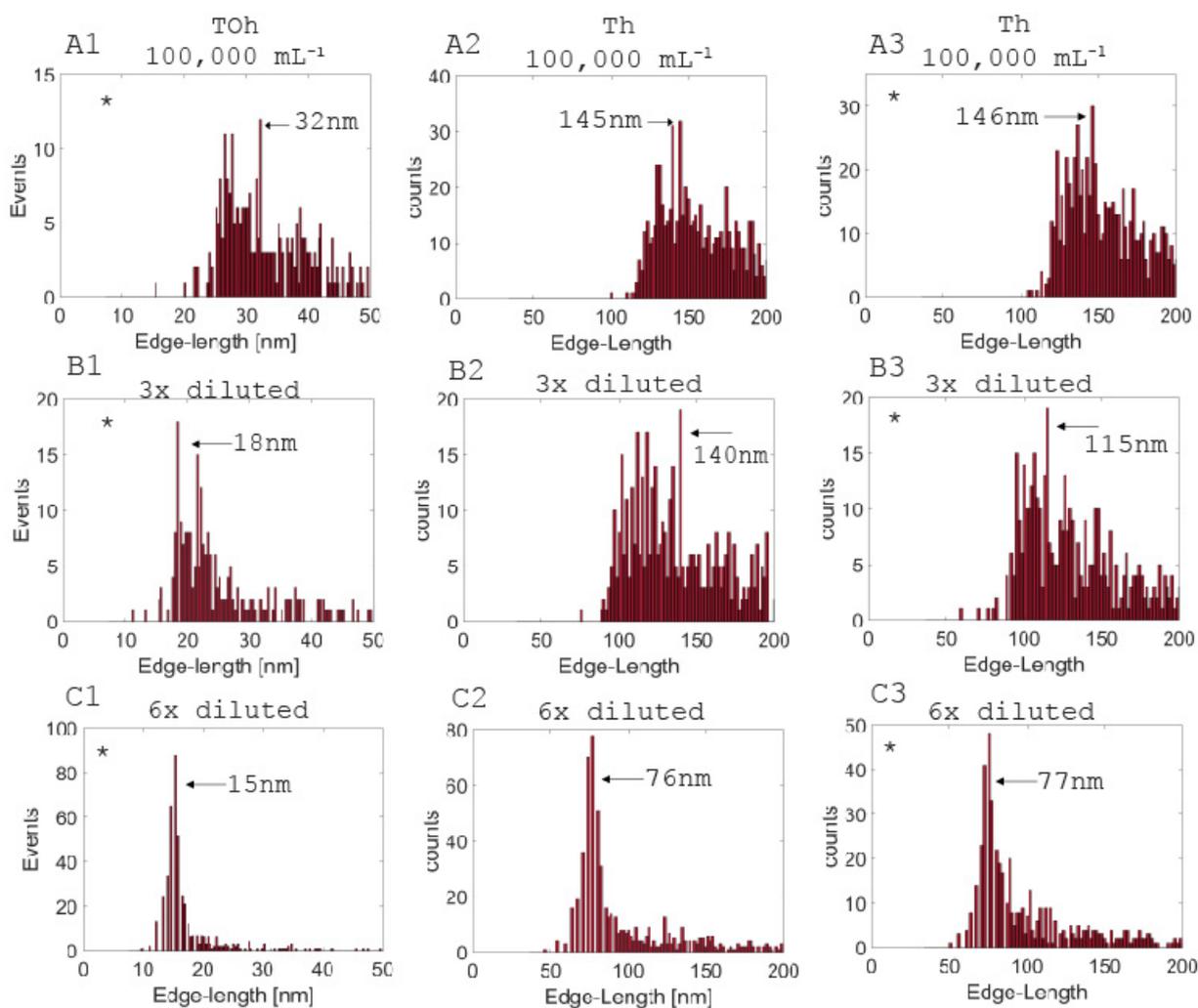


Figure S3. Dilution series of TOh and Th-Cu NPs using calibrants from **Figure S1** and **S2**. A1-A3) NP number concentration (N): 10^5 mL^{-1} , B1-B3) NP number concentration (N): $1/3 \times 10^5 \text{ mL}^{-1}$, C1-C3) NP number concentration (N): $1/6 \times 10^5 \text{ mL}^{-1}$. A1-C1) dilution series of TOh Cu NPs complementary to **Figure 4** in the main text. A2-C3) dilution series of Th Cu NPs. Expected size based on LR-TEM particle counting was $77 \pm 12 \text{ nm}$. Difference in total number of events between the six-fold diluted measurements with calibrants **Figure S1** and **S2** for the TOh in the main text and for the Th arrive from particle aggregation.

Note S1. Considerations of the distribution of the dilution series.

Figure S3 shows that with both calibrants we achieve the same results at appropriate dilution. We have not used the average of all 6 NP standards (**Figure S1** and **S2**) as we explicitly wanted to determine if we could quantify correctly with different standards. Further, the coefficient of variability for the 61, 78 and 98 nm Au spheres measured with SP-ICP-MS for instance (12%, 13% and 11%) matches the manufacturers well (11%, 12% and 9%, respectively). Nevertheless, as seen in **Table S1**, the change to the transport efficiency (~15%) between both sets is actually reflected in the assigned mass. In example, the most frequently observed particle had about a ~13% lower mass when determined with the particle set in **Figure S2** than when obtained with those in **Figure S1**. However, this translates only to a difference in edge-length of 0.7 nm (~5%). Therefore, we conclude that within the error of measurement, correct sizing can be achieved independently of the calibrant used.

We would like to point out the difference in events between the particles observed in the 30-40 nm range (<10, **Figure 4** and

Figure S3A1-B1) and the smaller particles that can only be observed upon sufficient dilution (>100, **Figure 4** and **Figure S3C1**). Some of the 30-40 nm particles are actually still present in the final distribution. However, due to their low number of events, their contribution is easily overlooked due to different y-axis scale. Nevertheless, their frequency actually goes down when the dilution factor is increased. We explain that with the following. We argue, namely, that with a high ionic background, the smaller particles are not only 'invisible', observable particle size also shift to higher values. The reason for this is that it becomes harder and harder for the algorithm to correctly assign particle events when the ionic background is high. As a result, the degree of false positives increases. This leads to two sorts of artifacts. The creation of false particles and the addition of background signal to real particle events. The latter, in which mass is added to existing particles, explains the decrease in frequency upon reduction of the background signal.

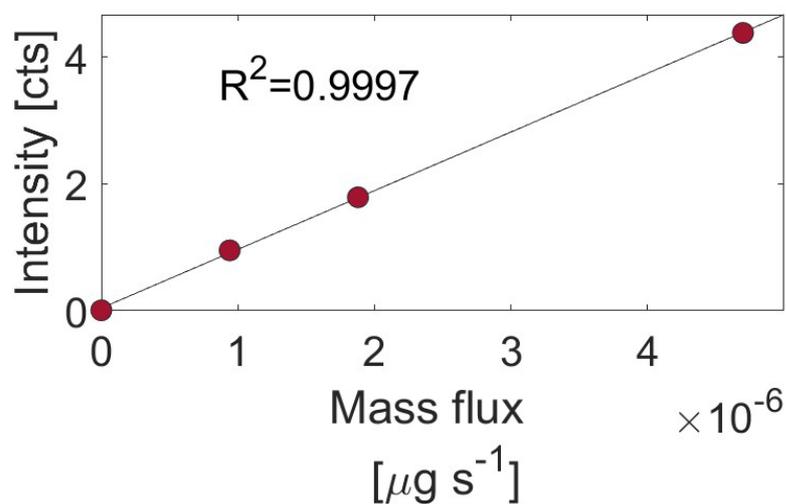


Figure S4. Cu dissolved standard calibration curve.

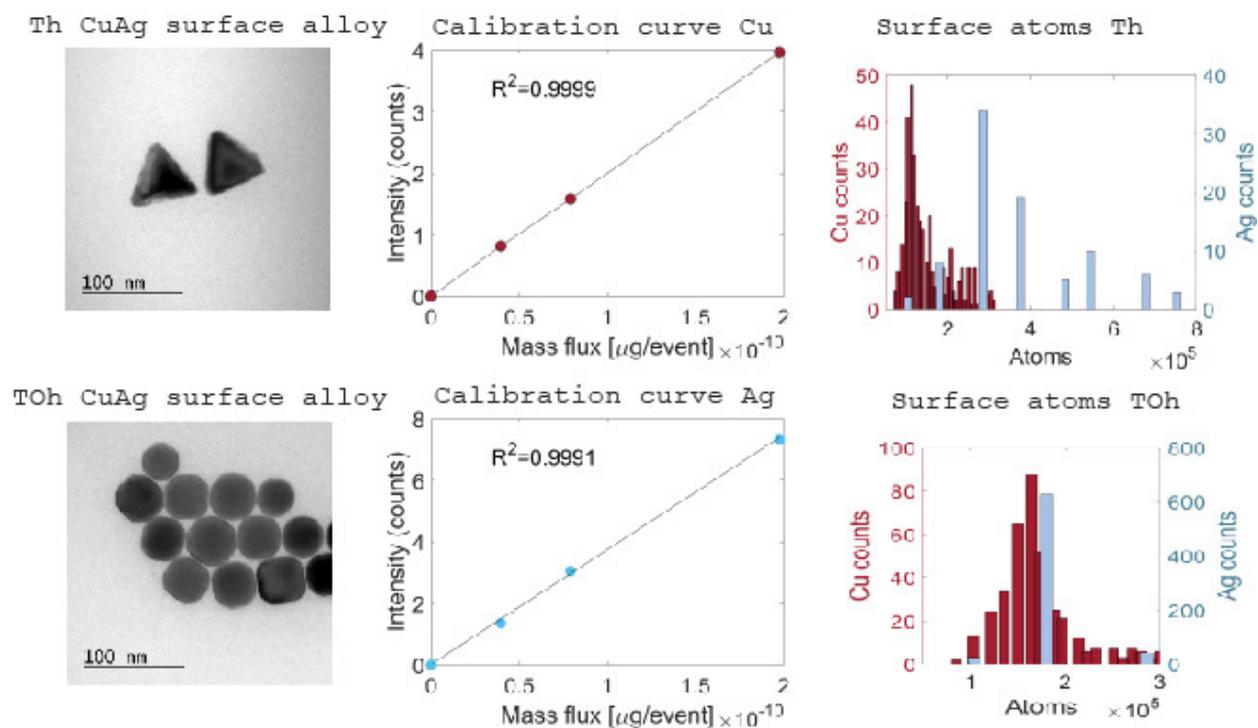


Figure S5. Surface atom compositions of Th- and TOh-CuAg NSA as determined by SP-ICP-MS.

Theoretical particle concentration [NPs mL ⁻¹]	Measured particle concentration [mL ⁻¹]	particle	Measured particle concentration [mL ⁻¹]	particle
		Calibrated micropipette		Uncalibrated micropipette
16,667	14,197 ± 562		15,027 ± 3964	
Nanoparticle concentration [mL⁻¹]				
	19889*		13170	14102
calibration 1				
	14771		14342	14603
calibration 2				

Table S2.1. Measured particle concentration based on calibrated pipettes. *Outlier.

Particle concentration [mL ⁻¹]	~10 ¹³	~10 ¹⁴	~10 ⁷	~10 ⁵
Volume pipetted (μL)	20	20	200	-
Manufacturer uncertainty	σ _a = 1%	σ _b = 1%	σ _c = 0.8%	σ _x = 2%

Table S2.2. Overall uncertainty determined through error propagation of each dilution step in 3-fold dilution series.

$$\sigma_x = \sqrt{(\sigma_a^2 + \sigma_b^2 + \sigma_c^2)}$$

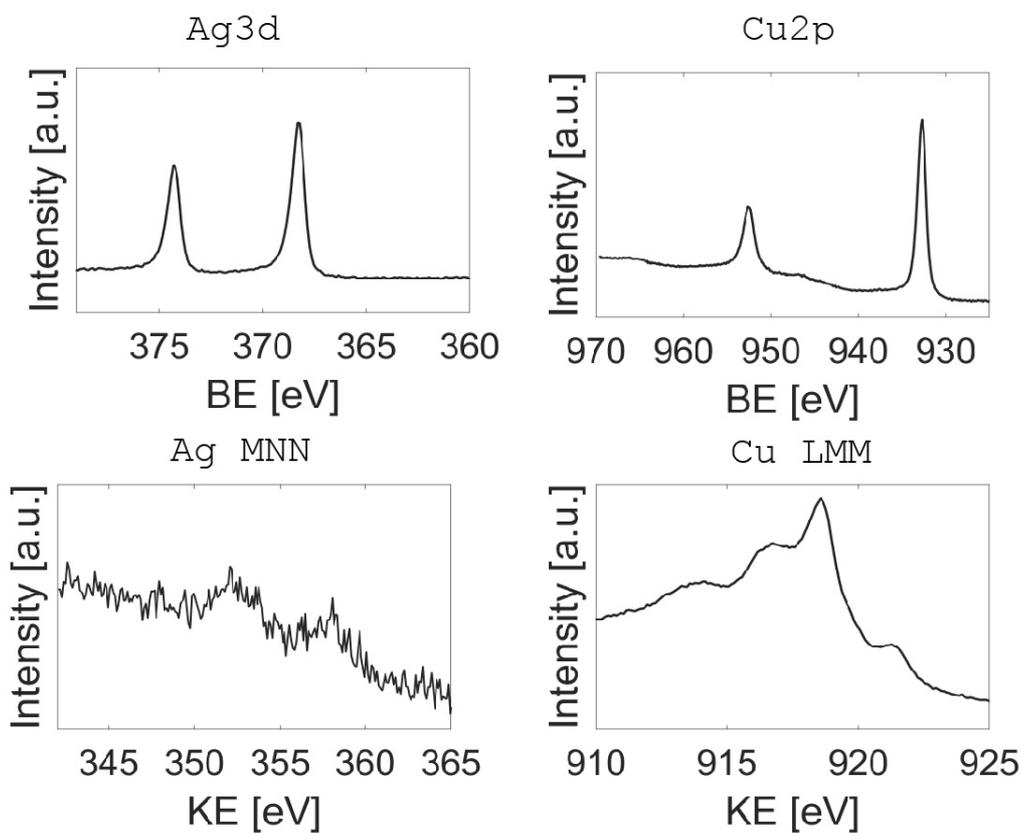


Figure S6. XPS and Auger spectra of C-CuAg NSA.

	KE [eV]	IMFP/Å	$\lambda/\text{Å}$
Ag 3d _{5/2}	1118.5	16.03	48.09
Cu 2p _{3/2}	554	10.09	30.27
Cu LMM	916.7	14.47	43.41
Subsurface model	-	-	31.36
(CuAg _{0.09})			

Table S3. Comparison penetration depths determined via IMPF method and modelled penetration depth based on normalized surface composition C-CuAg NSA as determined with XPS and SP-ICP-MS data.

Note S2. Penetration depth and overlay thickness calculation XPS

The inelastic mean free path (IMFP) of the photoelectrons is calculated using the QUASES-IMFP-TPP2M Ver. 3.0 software.¹ And the information depth is three times of the IMFP.

The thickness of the Ag overlayer is calculated using the method developed by Hill et al using Eq. 11.²

$$t = -\lambda \cos\theta \ln \left(1 + \frac{\left(\frac{I_o}{S_o}\right)}{\left(\frac{I_s}{S_s}\right)} \right) \quad (11)$$

where t is the overlayer thickness, λ is the attenuation length of the photoelectrons in the overlayer (obtained from the NIST electron effective-attenuation-length database³, ϑ is the emission angle (58.2° in this work), I_o and I_s are the peak intensities of the overlayer and the substrate, respectively, and S_o and S_s are their relative sensitivity factors. The thickness of the overlayer was determined at 0.25 ML of Ag assuming planar geometry, which is almost half of the thickness determined by SP-ICP-MS assuming cubic geometry.

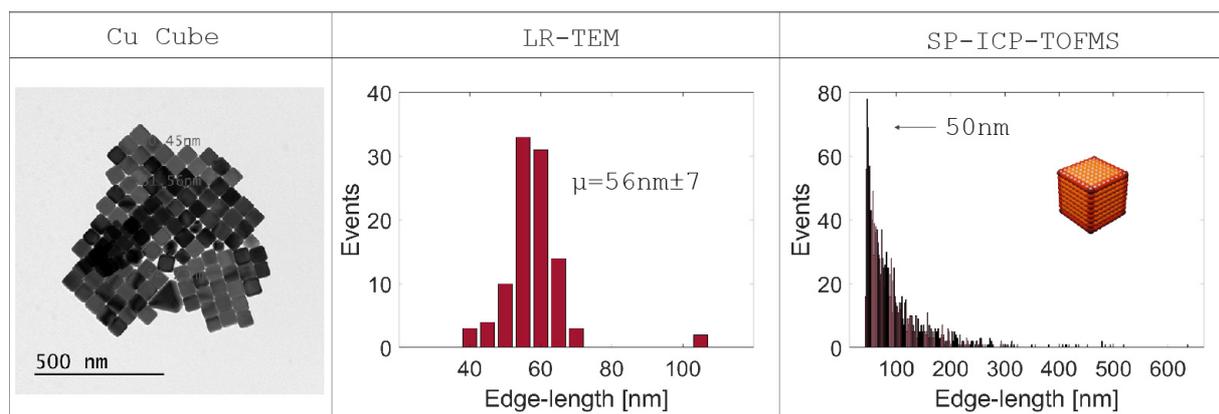


Figure S7. To ensure the reliability of the SP-ICP-TOFMS method, bare C-Cu NPs were introduced to the instrument and sized. An excellent match exists between the low resolution TEM particle counting and SP-ICP-TOFMS size distributions.

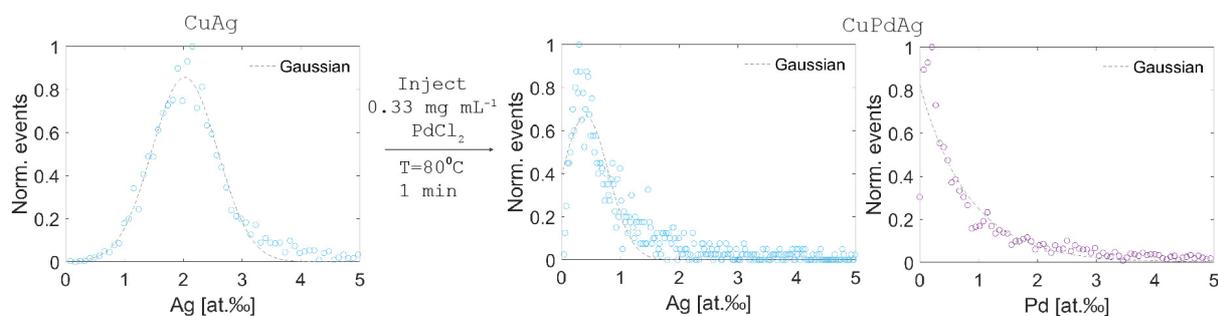


Figure S8. Conversion of C-CuAg NSA into C-CuPdAg NSA. Based on the Ag distribution upon introduction of the PdCl₂ precursor, and the subsequent shift of the maximum to lower Ag compositions, it can be deduced that Ag is being corroded more strongly than Cu. Based on the standard reduction potentials of the metals involved alone (Cu(II) + 2e⁻ → Cu: +0.337 V, Cu(I) + e⁻ → Cu: +0.52 V, Ag(I) + e⁻ → Ag: +0.7996 V, Pd(II) + 2e⁻ → Pd: +0.915V), the reverse would be expected. However, the presence of Cl⁻ ions greatly suppresses Ag's resistance towards oxidation (AgCl + e⁻ → Ag + Cl⁻: +0.22233 V vs PdCl₆⁴⁻ + 2e⁻ → Pd + 6 Cl⁻: +0.615 V).

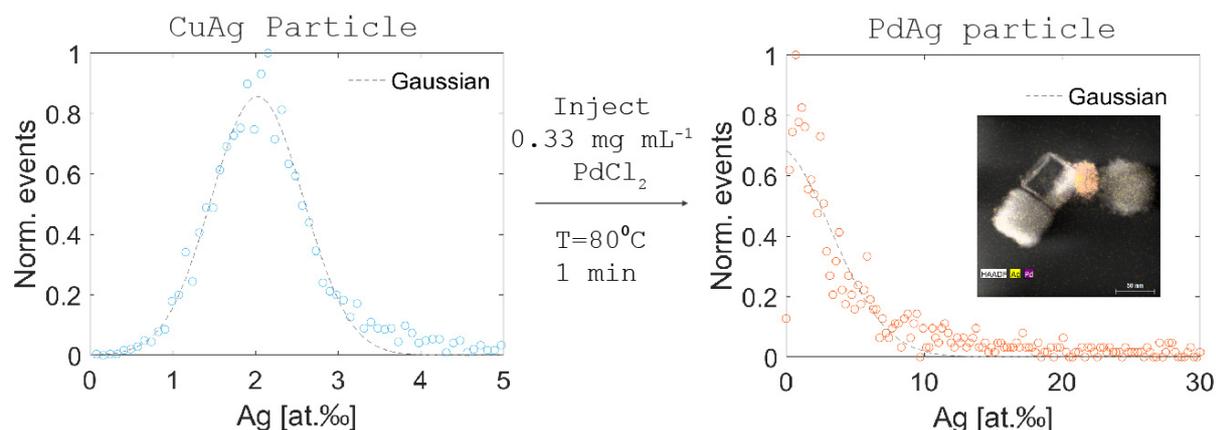


Figure S9. Other than the presence of C-CuPdAg NPs as determined with the SP-ICP-TOFMS, particles consisting solely of PdAg were detected as well. This could be confirmed with STEM-HAADF and STEM-EDX (see inset). This can be explained invoking a co-reduction mechanism in which the dissolving Ag is reduced together with unreacted Pd precursor. Alternatively, AgCl is poorly soluble and might precipitate out of solution possibly adhering to Pd NPs formed through homogeneous nucleation or unreacted PdCl₂ precursor.

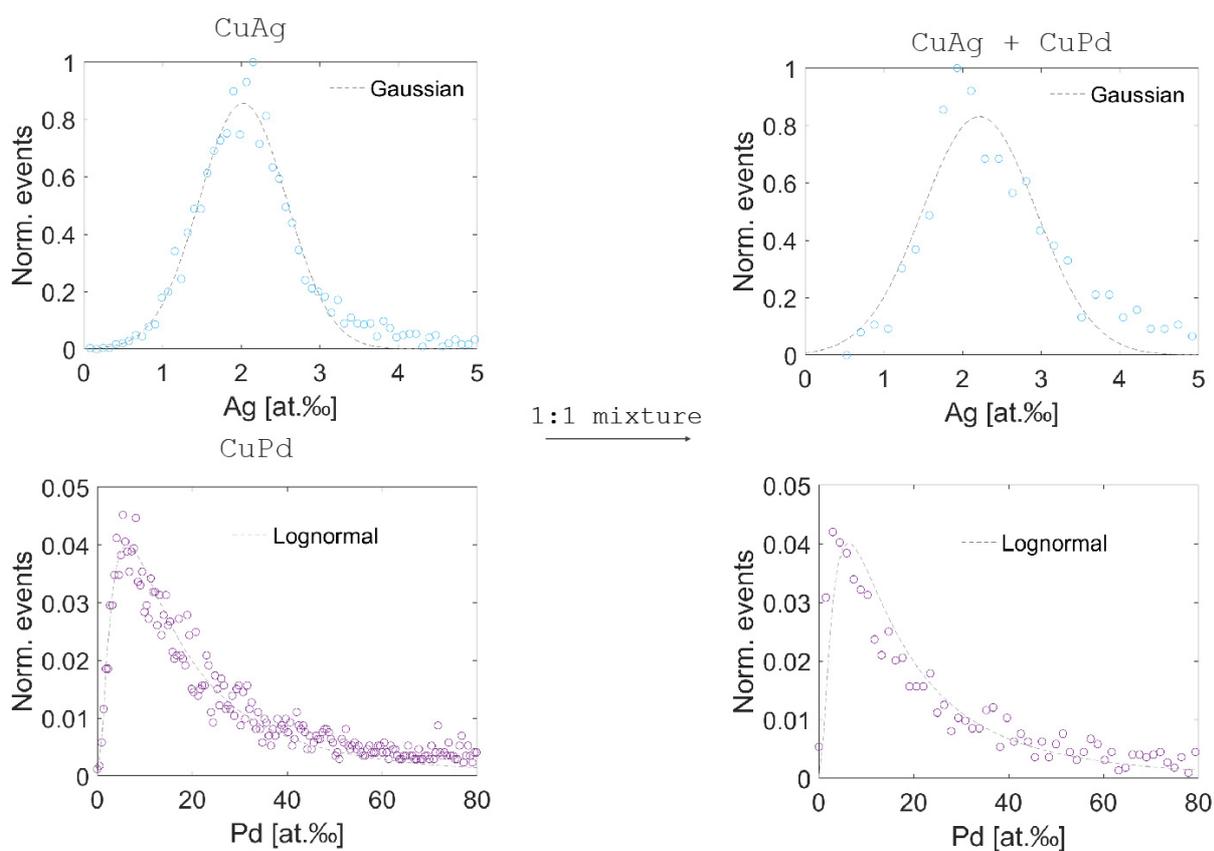


Figure S10. Normalized composition distributions of C-CuAg and C-CuPd NPs as compared to those obtained by analyzing a physical mixture of both. C-CuAg was normalized using the maximum value. C-CuPd was normalized such that the probability density function integral equaled to 1. The same distribution could be obtained by sequential as well as simultaneous measurements. <10 counts of PdAg NPs were observed in the physical mixture, which is most likely an artifact stemming from intensity spill-over effects. With well over 1000 particles counted, the significance of this result is minimal. This clearly shows the superiority of the TOF mass analyzer to study multimetallic NP systems over the quadrupole-based process as events containing either element from single elements cannot be distinguished.

	Quadrupole	Time-of-flight
Acronym	ICP-QMS	ICP-TOFMS
Separation mechanism	DC/RF stability	Ion velocity
Manufacturer	PerkinElmer	TOFWERK AG
Simultaneous acquisition range	None	14-275 m/z, 7-175 m/z
Concentration limit of detection	0.01 [pg g ⁻¹]	0.1-100 [pg g ⁻¹]
Sensitivity	10 ⁹ [cps ppm ⁻¹]	6x10 ⁷ [cps ppm ⁻¹]
Linear dynamic range (Au)	At least 30-100 [nm]	30-250 [nm]
Limit of detection (Au)	13-20 [nm] ^{4,a}	18 [nm] ^{5,b}
Cost	low	high
Isotope ratio precision	<0.1% ⁶	<0.023% ⁶

^aLimit of detection as determined using the $3\sigma+\mu$ method. ^b Limit of detection as determined using the Poisson ($3.27\sigma+\mu+2.72$) method.

Table S4. A comparison of the general specifications of the quadruple ICP-MS and ICP-TOFMS used in the present study.

The periodic table is color-coded as follows:

- Green:** Elements for which a limit of detection using SP-ICP-TOFMS has been reported. These include: Mg, Al, Si, P, S, Ga, Ge, As, Se, Br, Kr, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.
- Blue:** Elements for which the technique is sensitive and could be reported. These include: Li, Be, B, C, N, O, F, Ne, Na, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Cn, Nh, Fl, Mc, Lv, Ts, Og, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.
- Yellow:** Elements that cannot be detected with SP-ICP-TOFMS. These include: H, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Cn, Nh, Fl, Mc, Lv, Ts, Og, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.

Table S5. Periodic table of elements. In green elements of which a limit of detection using SP-ICP-TOFMS has been reported, in blue those elements for which the technique is sensitive and could be reported and in yellow those elements that cannot be detected with SP-ICP-TOFMS.^{6,7} Size detection limits extracted from Hendriks et al. are converted from the absolute mass LODs using the bulk density and assuming spherical geometry.⁶ LODs were determined using the Poisson equation. Montañó et al did not report the background extraction method used but also made use of a TOFWERK AG instrument. Only 30 out of 90 possible elements have been reported to our knowledge.

Note S3. Goodness of the fit of the SP-ICP-TOFMS composition distributions.

Fitting was achieved using the curve fitting application of MATLAB.

CuPd Pd At.% Lognormal distribution fit

General model:

$$f(x) = \frac{1}{(b*x*((2*\pi)^{(1/2)}))} * \exp(-((\log(x)-a)^2)/(2*b^2))$$

Coefficients (with 95% confidence bounds):

$$a = 3.126 (3.093, 3.158)$$

$$b = 1.28 (1.25, 1.31)$$

Goodness of fit:

SSE: 9.082e-05

R-square: 0.9816

Adjusted R-square: 0.9814

RMSE: 0.0008326

CuAg At.% Gaussian fit

val =

$$b1 = 2.132 (2.125, 2.14)$$

$$c1 = 0.7254 (0.715, 0.7358)$$

General model Gauss1:

$$\text{val}(x) = a1 * \exp(-((x-b1)/c1)^2)$$

Coefficients (with 95% confidence bounds):

$$a1 = 0.8563 (0.8474, 0.8652)$$

$$b1 = 2.024 (2.017, 2.031)$$

$$c1 = 0.7866 (0.7772, 0.796)$$

Goodness of fit:

R-square: 0.9986

Adjusted R-square: 0.9986

RMSE: 0.0034

CuAg Ag% Cu65Ag109

General model Gauss1:

$$f(x) = a1 * \exp(-((x-b1)/c1)^2)$$

Coefficients (with 95% confidence bounds):

$$a1 = 0.7647 (0.7553, 0.7742)$$

RMSE: 0.05944

CuAgPd Pd At.%

Goodness of fit:

SSE: 0.4776

R-square: 0.9723

Adjusted R-square: 0.9722

RMSE: 0.02189

CuAgPd Ag At.%

General model Gauss1:

$$f(x) = a1 * \exp(-((x-b1)/c1)^2)$$

Coefficients (with 95% confidence bounds):

$$a1 = 0.6685 (0.6421, 0.6949)$$

$$b1 = 0.407 (0.3819, 0.4322)$$

$$c1 = 0.5564 (0.5182, 0.5947)$$

$$b1 = 0.1308 (0.1273, 0.1344)$$

$$c1 = 0.323 (0.3187, 0.3272)$$

General model Gauss1:

$$f(x) = a1 * \exp(-((x-b1)/c1)^2)$$

Coefficients (with 95% confidence bounds):

$$a1 = 4.225e+293 (-Inf, Inf)$$

$$b1 = -1130 (-4.448e+04, 4.221e+04)$$

$$c1 = 43.47 (-789.3, 876.3)$$

Goodness of fit:

SSE: 0.5869

R-square: 0.8852

Adjusted R-square: 0.8852

RMSE: 0.007662

CuAgPd Ag/Pd At.%

Adjusted R-square: 0.8595

RMSE: 0.01819

CuAg+CuPd Ag at.%

Goodness of fit:

SSE: 1.756

R-square: 0.8627

Adjusted R-square: 0.8621

Goodness of fit:

SSE: 5384

R-square: 0.9467

Adjusted R-square: 0.9466

RMSE: 0.7341

CuAgPd AgPd At.%

General model Gauss1:

$$f(x) = a1 * \exp(-((x-b1)/c1)^2)$$

Coefficients (with 95% confidence bounds):

$$a1 = 0.6988 (0.6647, 0.7328)$$

$$b1 = -0.83 (-1.326, -0.3335)$$

$$c1 = 5.713 (5.339, 6.087)$$

General model Gauss1:

$$f(x) = a1 * \exp(-((x-b1)/c1)^2)$$

Coefficients (with 95% confidence bounds):

$$a1 = 39.27 (39.06, 39.48)$$

General model Gauss1:

$$f(x) = a1 * \exp(-((x-b1)/c1)^2)$$

Coefficients (with 95% confidence bounds):

$$a1 = 0.8312 (0.795, 0.8675)$$

$$b1 = 2.214 (2.178, 2.251)$$

$$c1 = 1.022 (0.9698, 1.074)$$

Goodness of fit:

SSE: 0.3166

R-square: 0.9346

Adjusted R-square: 0.9339

RMSE: 0.040

Goodness of fit:

SSE: 0.992

R-square: 0.8596

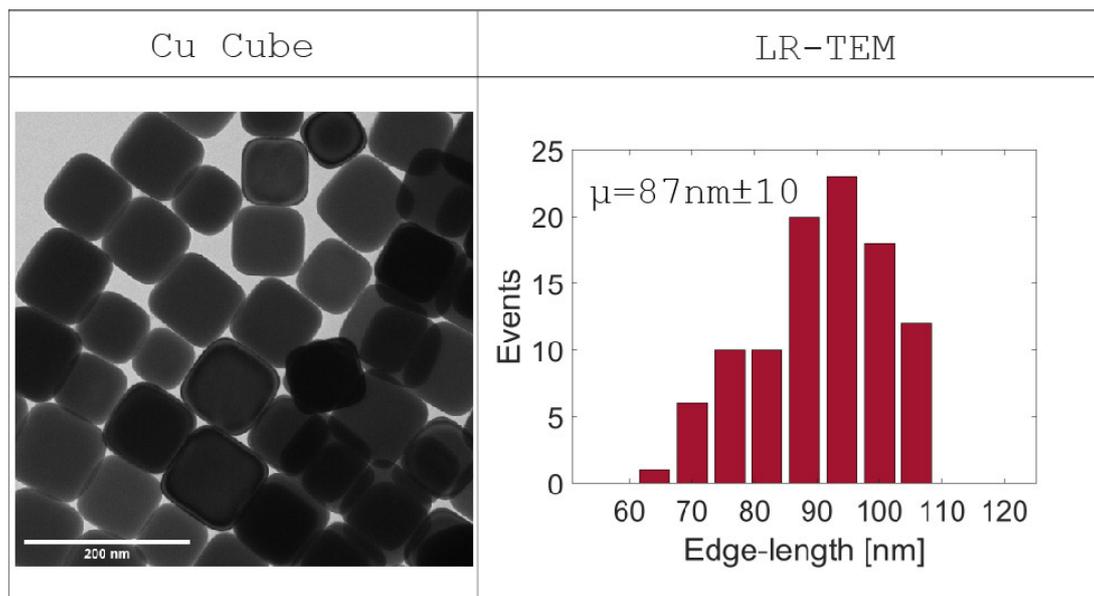


Figure S11. Particle size distribution of the C-Cu core used to synthesize the CuAg NSA quantified using the quadrupole. Larger average particle size (87 vs 56 nm) results in ~4-fold smaller particle number concentration at the same mass loading as for the C-Cu used to produce the C-CuAg, C-CuPd and C-CuPdAg NSAs analyzed with the TOF mass analyzer.

Poisson	[63Cu] ⁺ (cts)	[65Cu] ⁺ (cts)	[105Pd] ⁺ (cts)	[106Pd] ⁺ (cts)	[107Ag] ⁺ (cts)	[109Ag] ⁺ (cts)
SD BKG signal (cts)	4.9	3.2	0.17	0.18	0.18	0.18
LOD (Poisson) (cts)	20	13	3.3	3.3	3.3	3.3
Sensitivity (cts/fg)	38.8	19.7	37.8	47.2	107	105
LOD (fg)	0.488	0.663	0.0866	0.0701	0.0310	0.0317
LOD (g)	4.88E-16	6.64E-16	8.66E-17	7.01E-17	3.10E-17	3.17E-17
Density of a pure metal (g/cm ³)	8.96	8.96	12.023	12.023	10.49	10.49
LOD Metal particle volume (cm ³)	5.44E-17	7.41E-17	7.20E-18	5.83E-18	2.96E-18	3.02E-18
LOD Metal particle diameter (nm)	47.0	52.1	24.0	22.3	17.8	17.9
3*SD	[63Cu] ⁺	[65Cu] ⁺	[105Pd] ⁺	[106Pd] ⁺	[107Ag] ⁺	[109Ag] ⁺

Table S6. Optimized operational conditions used for the NexION 350D and icpTOF ICP-MS instruments used in the present study.

TOh	Particle concentration (NPs mL ⁻¹)	Most frequent size (nm)	Particle size mean (nm)	Dissolved. Concentration (µg L ⁻¹)	η _t (%)	R ²
Stock	100000	20.0	36.4	3.1	3.46	0.9997
3x	33333	15.1	28.5	0.94	3.46	0.9997
6x	16667	13.3	18.3	0.35	3.46	0.9997

TOh_2	Particle concentration (NPs mL ⁻¹)	Most frequent size (nm)	Particle size mean (nm)	Dissolved Concentration (µg L ⁻¹)	η _t (%)	R ²
Stock	100000	18.8	34.9	3.1	4.11	0.9997
3x	33333	15.8	25.7	0.90	4.11	0.9997
6x	16667	13.5	19.6	0.31	4.11	0.9997

Table S7. Results of the TOh-Cu NP suspension of 10⁵ NPs mL⁻¹ (15 nm) and its dilution series. Complete raw data processing achieved using our in-house developed MATLAB script.

Name	Manufacturer	Ligand	Diameter (TEM)
30 nm Spherical Nanoparticles	Gold Nanopartz	Carboxylic acid	30±2 nm
50 nm Spherical Nanoparticles	Gold Nanopartz	Carboxylic acid	50±2 nm
60 nm Gold Nanospheres	NanoComposix	Citrate	61±7 nm
80 nm Spherical Nanoparticles	Gold Nanopartz	Carboxylic acid	50±6 nm
80 nm Gold Nanospheres	NanoComposix	Citrate	78±9 nm
100 nm Gold Nanospheres	NanoComposix	Citrate	98±9 nm

Table S8. Detailed specifications of the Au NPs purchased from NanoComposix and PerkinElmer (Nanopartz) of **Figure S1** and **S2**, respectively.

	Truncated Octahedra [⁶³ Cu] ⁺ (cts)	Tetrahedra [⁶³ Cu] ⁺ (cts)
Threshold ($\mu+3\sigma$) [cts]	1.4	3.1
Sensitivity (cts/fg)	92.6	92.6
LOD (fg)	0.015	0.033
LOD (g)	1.49E-17	3.33E-17
Density of a pure metal (g/cm ³)	8.96	8.96
LOD Metal particle volume (cm ³)	1.67E-17	3.71E-18
LOD Metal particle Edge-length (nm)	10.6	15.2

Table S9. Limit of detections for the TOh- and Th-Cu NPs based on their edge-length as defined in **Figure 1** in the main text determined via the 3σ background subtraction method.

Poisson	[63Cu]+ (cts)	[65Cu]+ (cts)	[105Pd]+ (cts)	[106Pd]+ (cts)	[107Ag]+ (cts)	[109Ag]+ (cts)
SD BKG signal (cts)	4.9	3.2	0.17	0.18	0.18	0.18
LOD (Poisson) (cts)	20	13	3.3	3.3	3.3	3.3
Sensitivity (cts/fg)	38.8	19.7	37.8	47.2	107	105
LOD (fg)	0.488	0.663	0.0866	0.0701	0.0310	0.0317
LOD (g)	4.88E-16	6.64E-16	8.66E-17	7.01E-17	3.10E-17	3.17E-17
Density of a pure metal (g/cm ³)	8.96	8.96	12.023	12.023	10.49	10.49
LOD Metal particle volume (cm ³)	5.44E-17	7.41E-17	7.20E-18	5.83E-18	2.96E-18	3.02E-18
LOD Metal particle diameter (nm)	47.0	52.1	24.0	22.3	17.8	17.9
3*SD	[63Cu]+ (cts)	[65Cu]+ (cts)	[105Pd]+ (cts)	[106Pd]+ (cts)	[107Ag]+ (cts)	[109Ag]+ (cts)
SD BKG signal (cts)	4.9	3.2	0.17	0.18	0.18	0.18
LOD 3*SD (cts)	15	9.5	0.50	0.54	0.55	0.55
Sensitivity (cts/fg)	38.8	19.7	37.8	47.2	107	105
LOD (fg)	0.381	0.479	0.0133	0.0114	0.00517	0.00526
LOD (g)	3.81E-16	4.79E-16	1.33E-17	1.14E-17	5.17E-18	5.261E-18
Density of a pure metal (g/cm ³)	8.96	8.96	12.023	12.023	10.49	10.49
LOD Metal particle volume (cm ³)	4.25E-17	5.35E-17	1.10E-18	9.47E-19	4.93E-19	5.01E-19
LOD Metal particle diameter (nm)	43.3	46.8	12.8	12.2	9.80	9.86

Table S10. Limit of detections for the C-CuPdAg NPs assuming spherical geometry comparing the Poisson and 3 σ background subtraction methods.

Note S4. Background determination via Syngistix software/ MATLAB script.

Syngistix and our MATLAB script uses the $\mu+3\sigma$ method to determine the threshold iteratively ($Th(i)$). This means that all intensities \leq the $\mu+3\sigma$ ($Th(1)$) of the entire data set are collected and stored in a new data set. Then, the $\mu+3\sigma$ is determined again of the new data set ($Th(2)$) and the previous procedure repeated until the threshold converges ($Th(N-1)=Th(N)$). The final threshold is then used to do peak identification. The ionic background signal is then the average intensity of all intensity values \leq that threshold. Figure S13 shows the background determination process reported in the PerkinElmer US patent on which the Syngistix software is built.

Although we acknowledge the importance of reducing false positives, we would like to stress that reducing false positives by increasing the threshold not necessarily results in the desired outcome as it is highly dependent on particle size. Laborda et al showed that for Au NPs of 100 nm, the compromise between overestimation of the critical value (threshold) and the reduction of false positives is optimal for the $\mu+5\sigma$ case.⁸ However, this optimum is size dependent. For smaller particles, overestimation is obviously more problematic than for large

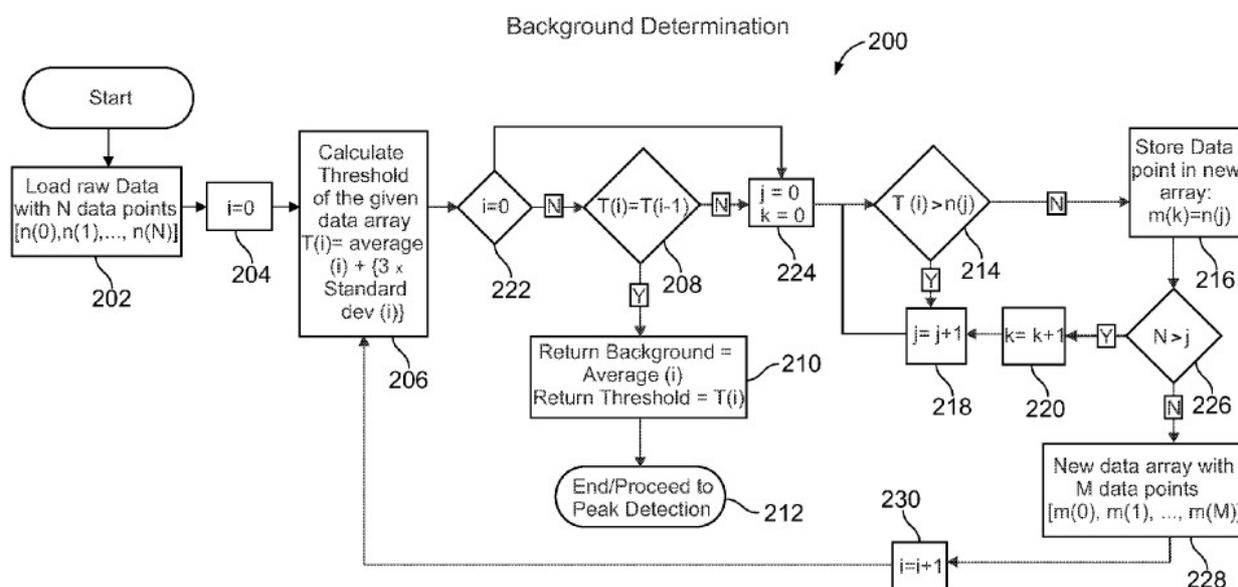


Figure S12. The background determination process. (US20150235833A1 Single Particle Data Treatment)

particles. This suggests that this optimum actually shifts with particle size. Indeed, when we change the threshold criteria to $\mu+5\sigma$ in our MATLAB script, the number concentration of the TOh (**Figure 4**) is $<2000 \text{ mL}^{-1}$ and the average size to 37 nm (from $\sim 18000 \text{ mL}^{-1}$ and $\sim 18 \text{ nm}$). We have effectively raised the threshold so much that the smallest particles are no longer visible (similar to the effect of having a high ionic background).

An alternative approach to reduce false positives is to add additional criteria to the peak determination process other than

having an intensity above a predetermined threshold. For instance, having the condition that a signal can only be considered a peak as it has a certain number of consecutive values higher than the threshold. Syngistix makes use of such an approach as well as do we in our MATLAB script (**Figure S14**). However, the details on this are subject to a later study. Be advised that for instruments with long minimum dwell times such false positives reduction methods cannot be used as each dwell in assumed to either contain a complete particle or not.

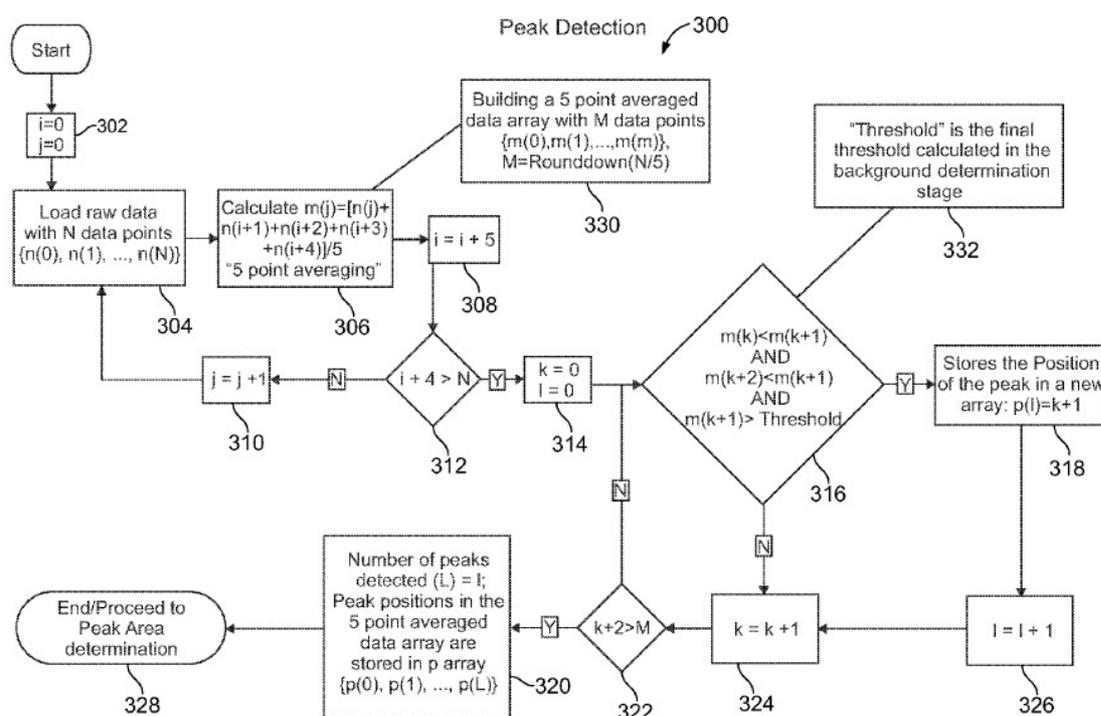


Figure S13. The peak detection process. (US20150235833A1 Single Particle Data Treatment).

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Chapter 5

Low-temperature non-equilibrium synthesis of anisotropic multimetallic nanosurface alloys for the electrochemical CO₂ reduction reaction

Preprint version: this section has been accepted as a full-length article in *Nature Synthesis*.

Edit: caption numbers of figures, tables, and equations were edited to match the thesis chapter number.

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Abstract

Multimetallic nanoparticles are of interest as functional materials for their highly tunable properties. However, synthesizing congruent mixtures of immiscible components is limited to high-temperature procedures followed by rapid quenching which lack size and shape control. Here, we report a low-temperature (≤ 80 °C) non-equilibrium synthesis of nanosurface alloys (NSAs) with tunable size, shape and composition regardless of miscibility. We show the generality of our method by producing both bulk miscible and immiscible monodisperse anisotropic Cu-based NSAs of up to three components. We demonstrate our synthesis as a screening platform to investigate the effects of crystal facet and elemental composition by testing tetrahedral, cubic and truncated-octahedral NSAs as catalysts in the electroreduction of CO₂. Finally, we resort to machine-learning to predict and synthesize both multicarbon-product selective and phase stable Cu-Ag-Pd compositions. This combination of non-equilibrium synthesis and theory-guided candidate selection is expected to accelerate test-learn-repeat cycles of structure-performance optimization schemes.

5.1. Introduction

Multimetallic nanoparticles are becoming increasingly important in fields such as heterogeneous-, electro- and photocatalysis.^{1,2,3,4,5,6,7} Multimetallic systems allow for advanced active site tunability beyond size, support and facet effects to include electronic and geometric effects likewise. In combination with advanced simulations to predict the most active and selective candidates,⁸ theory-guided catalyst selection may greatly speed up test-learn-repeat cycles in catalyst performance optimization. To harvest the potential of such approaches, a homogeneous mixture of relevant elements in the material is required. Generally, however, production of multimetallic nanomaterials has been limited to various forms of heterostructures due to the often-large miscibility gaps that exist for various metal systems whenever conventional routes are used yielding thermodynamic, phase-segregated products.⁹ This limits the added value of a multicomponent system in reaction optimization to concurrent catalysis, e.g. tandem schemes.¹⁰

Recently, various non-equilibrium methods

have been established that allow for the mixing of the elemental constituents at the nanoscale such as spark ablation, carbo-thermal shock synthesis and laser deposition and offer, thereby, electronic and geometric tuning of the active site.^{11,12,13,14,15} Unfortunately, these techniques require extremely harsh conditions ($\Delta T > 900$ °C) with subsequent quenching to yield the non-equilibrium states rendering the possibility to control the exposed crystal facet improbable. As it has been shown that crystal facets play an important role in controlling reaction pathways,¹⁶ allowing for mixing of various elements at the nanoscale congruent with shape control would offer tremendous insight in the fundamentals of various multimetallic catalyzed processes. One such example is the electrochemical reduction of CO₂ (CO₂RR) in which convoluted facet and electronic effects induced by elemental mixing have been shown. For instance, for single crystals and nanoparticles (NPs) of Cu, facet dependence has been determined, e.g., Cu(111) surfaces produce CH₄, Cu(110) shows selectivity for oxygenates and

Cu(100) produces C_2H_4 .^{17,18,19,20} Instead, upon the introduction of Ag adatoms in Cu(100) single crystals, the selectivity switches towards oxygenates instead.^{21,22} Further, three-component Cu based systems such as Ag-Ru-Cu have recently been reported as the state-of-the-art in the conversion of CO towards n-propanol.²³

With the opportunities of combined phase and facet control in mind, we revisited a well-known colloidal synthesis known as the galvanic replacement reaction generally yielding thermodynamic products,²⁴ but enforced kinetic trapping of non-equilibrium structures by introducing a kinetic barrier, thereby obtaining nanosurface alloys (NSAs) in which congruent mixing of multiple components is achieved in a shell surrounding a pure core (**Figure 29**). We used the Cu-Ag system as proof-of-concept to overcome immiscibility for its positive heat of mixing at nearly any composition.²⁵ Generally, syntheses of Cu-Ag yield phase-segregated materials such as core-shell, core-cluster, crescent and nanodimers,^{26,27,28,29} and with a few exceptions alloys, but lack size and shape control.^{21,30,31} We show that with our simple yet elegant low temperature seeded-

growth, thin film-based colloidal method, anisotropic {e.g. tetrahedral (Th), cubic (C) and truncated octahedral (TOh)} non-equilibrium multimetallic nanocrystals can be synthesized independent of size and shape, with tunable (surface) composition. We further extend our bimetallic library to include other components with a higher reduction potential than the seed, as evidenced in our Cu-M system with M = Pd, Au and Ag-Pd, to show the generalizability of our synthetic methodology towards other anisotropic NSAs.

We screen our Cu-Ag NSA library in CO_2RR , of which bulk and morphologically undefined alloyed materials have shown strong selectivity towards multicarbon products (C_{2+}).^{21,30} As such, we investigate the effect of the facet in this system. We find that both Cu-Ag(100) and Cu-Ag(111)/Cu-Ag(100) faceted C- and TOh-NSA show a high faradaic efficiency (FE) of ~58% towards C_{2+} products but that the interfacially truncated particles show strong selectivity towards liquid fuels (~62%), including acetate, acetaldehyde, ethanol and n-propanol. We confirm expected surface segregating tendencies of the Cu-Ag system³² by various ex-situ electron

microscopy techniques and correlate it to the observed dynamic changes in the product distributions. We then demonstrate that the phase stability can be improved by introducing a ternary miscible element (Pd) into the Cu-Ag system. Further, using a supervised machine-learning approach, $\text{Cu}_{79}\text{Ag}_{16}\text{Pd}_5$ was predicted to show high C_{2+} selectivity and phase stability, which was synthesized and its predicted performance

qualitatively met with experiment. With our seeded-growth synthesis platform, we offer unprecedented control over the facet of multimetallic non-equilibrium structures as catalysts for energy applications.

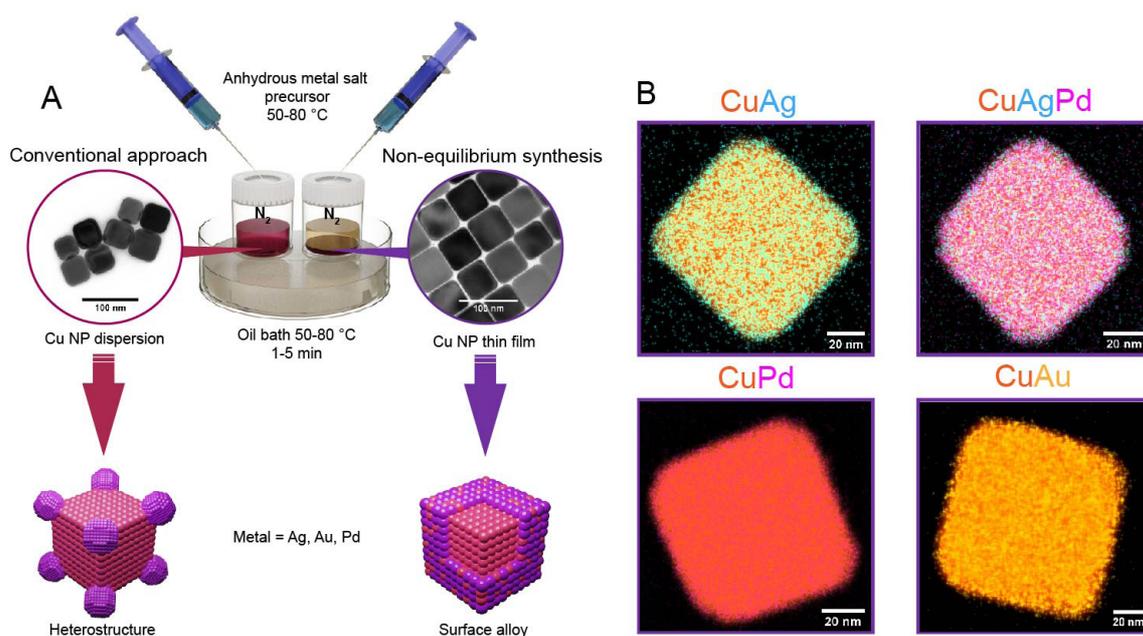


Figure 29. (A) Schematic illustration of the conventional and non-equilibrium galvanic replacement reaction, where phase-separated heterostructures and homogeneous surface alloys were formed, respectively. (B) STEM-EDXS elemental maps of cubic Cu-Ag, Cu-Ag-Pd, Cu-Pd and Cu-Au NSAs prepared by using the non-equilibrium method showing the random nature of the added component(s) and increased intensity at the particle edges.³³

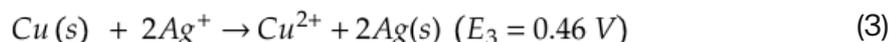
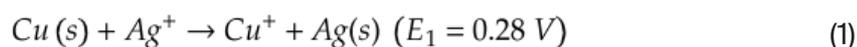
5.2. Results and Discussion

5.2.1. Low-temperature non-equilibrium synthesis of Cu-Ag anisotropic nanosurface alloys

A typical Cu-Ag galvanic replacement reaction comprised of two steps: (1) a colloidal wet-chemical synthesis to produce anisotropic Cu nanocrystals (NCs), and (2) a subsequent galvanic exchange of Cu with Ag salt. This two-step synthesis was specifically selected to have freedom of choice in seed shape. In the first step, Th-, C-, TOh-Cu NCs were synthesized as reported previously with a colloid synthesis method (**Figure S1**).³³ In the second step, we differentiate between a conventional galvanic replacement reaction and a non-equilibrium one. For the conventional galvanic exchange reaction, Cu crystals are well dispersed in the solution. Thus the reaction is thermodynamically controlled, where the rapid exchange rates and the positive heat of mixing of Cu seeds and Ag ions lead to the formation of individual Ag domains at the particle surfaces, preferentially at the corners and edges.^{26,27,28} For details on the thermodynamics and kinetics of the synthesis see **Figure S3** and **Note S1** of the Supporting Information. Instead, for the non-equilibrium synthesis,

anisotropic seeds are kept undisturbed at the bottom of the vial and homogeneously-distributed Ag atoms are incorporated in the Cu lattice as the kinetic product. **Figure 1A** gives an overview of the conventional and non-equilibrium synthesis. **Figure 1B** shows the randomly-distributed solute in the Cu-based NSAs. **Figure 2** shows the extended characterization of the non-equilibrium synthesis for anisotropic Cu-Ag NSAs. Further details on the non-equilibrium synthesis can be found in **Figure S4**, and **Note S1** of the Supporting Information. For a detailed description of the protocol see **Materials and Methods**, and for a scaled-up version of the non-equilibrium synthesis, see **Figure S5**.

The key to the successful synthesis of NSAs is to precisely control the reaction kinetics by limiting the mass transport of the reactants. Take the Cu-Ag system as an example, reaction (1)-(3) can take place spontaneously during the galvanic replacement reaction.



If the replacement process proceeds through reaction (1), each Cu atom is exchanged by exactly one Ag atom. However, if reaction (2) directly follows reaction (1), or Cu is twice oxidized in a single step via reaction (3), two Ag atoms are exchanged per Cu atom. Consequently, reaction (2) and (3) require two Ag⁺ ions for the reaction to occur, i.e., a high local concentration of Ag⁺, whereas reaction (1) can occur at any given concentration. Therefore, through confining the Cu seeds in a thin-film and restricting the diffusion of Ag⁺ ions to the depletion zone, the non-equilibrium synthesis ensures the predominant occurrence of reaction (1), and ultimately leads to the formation of kinetic phase Cu-Ag NSAs, rather than thermodynamically favorable phase-separated products. This mechanism is supported by the kinetic study shown in **Figure S6**, where the nonequilibrium synthesis shows a much lower reaction rate compared to the conventional synthesis at equal bulk electrolyte concentration. Further, we show that by accelerating reaction (2) (i.e., introducing additional Cu⁺ ions in the reaction mixture), the kinetic product can be converted into the thermodynamic heterostructure (**Figure**

S7), demonstrating again the importance in controlling the reaction kinetics.

The morphology of anisotropic Cu-Ag-NSAs with different shapes was studied with transmission electron microscopy in bright-field mode (BF-TEM, **Figure 30A-C**). The well-defined tetrahedral, cubic, and truncated octahedral structure indicate that the original Cu NCs structures are well preserved during Ag deposition. A homogeneous distribution of Ag at the surface of the Cu NCs was confirmed by energy dispersive X-ray spectroscopy (EDXS) in scanning transmission electron microscopy (STEM) (**Figure 30D-F**). Further, we probed the valence band spectra of the as-prepared NSAs by X-ray photoemission spectroscopy (XPS) to verify whether an alloy or separated phases have formed, as previous studies have shown that charge transfers from Cu to Ag occurs upon alloying.^{34,35} It

is shown that the point-of-gravity of the Cu-Ag NSA valence bands shift towards the Fermi level, indicating charge-transfer, corroborating the surface alloy nature (**Figure 30J**, see **Materials and Methods** for details).³⁶

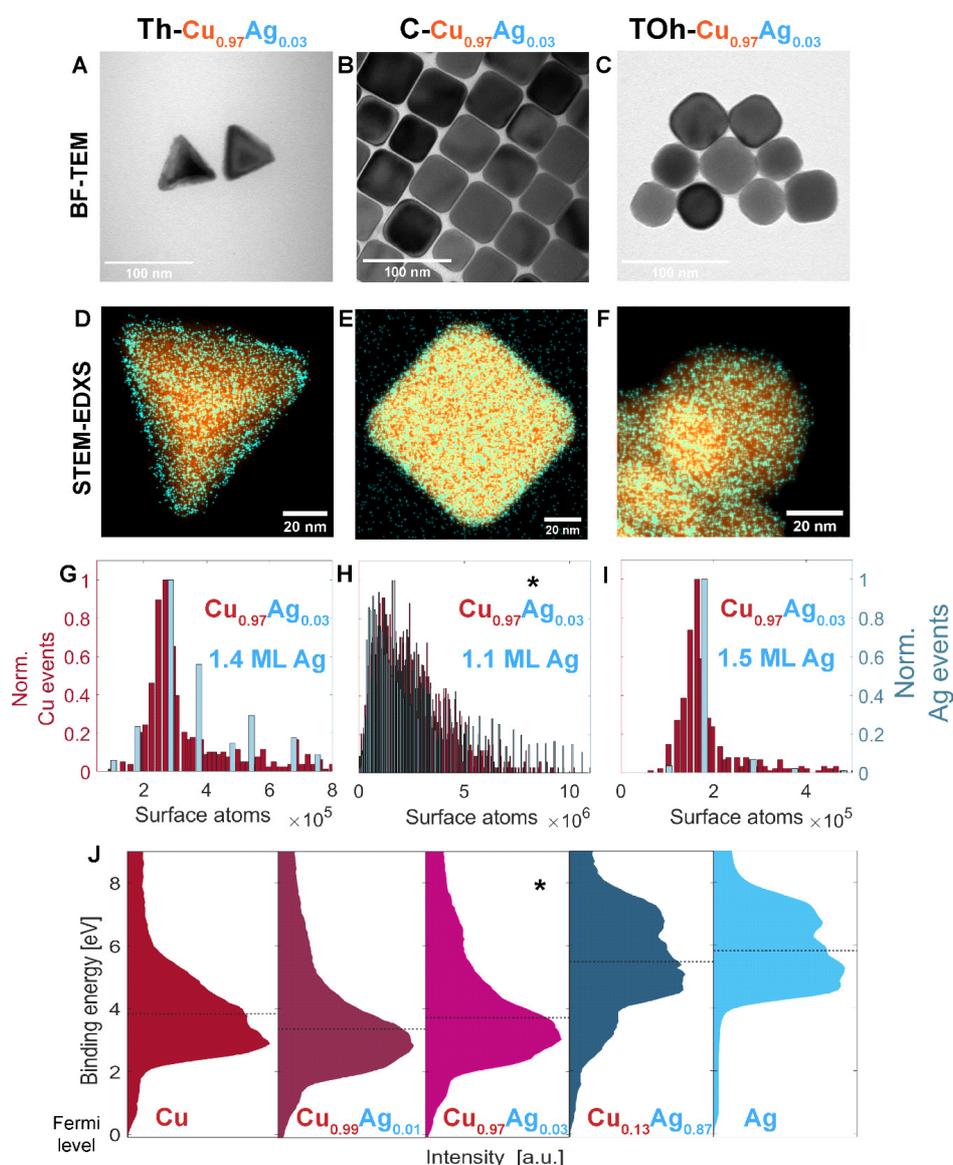


Figure 30. Characterization of the anisotropic Cu-Ag NSAs obtained via the non-equilibrium synthesis. Inductively coupled plasma optical emission spectroscopy (ICP-OES) determined particle bulk composition provided in the title. (A-C) BF-TEM images of C-, Th- and TOh-Cu-Ag NSAs. (D-F) STEM-EDXS elemental maps of C-, Th- and TOh-Cu-Ag NSAs with Cu in orange and Ag in turquoise showing normally distributed Ag and increased intensity at the particle edges. (G-I) Distribution of the number of atoms in the surface for N single particles of the C-, Th- and TOh-Cu-Ag NSAs as determined with single particle-inductively coupled plasma mass spectrometry (SP-ICP-MS) with $N > 500$, with an equivalent of 1.4, 1.1 and 1.5 ML of Ag deposited, respectively. (J) Valence band spectra of pure Cu and Ag references and three C-Cu-Ag particles synthesized at different reaction times using the non-equilibrium synthesis (1, 5 min and 2 hrs). The point-of-gravity of the valence band construed exactly half the area-under-the-curve of the spectra (denoted by the dotted line), which was determined by numerically integrating the spectra with fixed bounds at 0 and 9 eV, respectively. The shift of the valence band towards the Fermi level as compared to pure Cu confirms the random alloy nature of the C-Cu_{0.99}Ag_{0.01} and C-Cu_{0.97}Ag_{0.03} NSAs as charge-transfer occurs from Cu to Ag. Instead, for a phase-segregated material (C-Cu_{0.13}Ag_{0.87}), the valence band spectrum is a linear combination of the Cu and Ag reference spectra showing no charge-transfer. The asterisk (*) in (J) indicates the valence band spectra of the same ensemble of particles indicated in (H).

We further applied the previously developed single particle-inductively coupled plasma mass spectrometry (SP-ICP-MS) method to probe the ensemble representative composition distribution.³³ This method allows for the determination of the complete elemental makeup of individual NPs with ensemble representative statistics, and by further geometrical modelling, surface compositions can be extracted from the obtained elemental distributions. Independent of the facet, a nearly 1:1 ratio between the number of atoms of the outermost Cu monolayer (ML) and the total number of Ag atoms present in the particles was determined, further corroborating the limit of the presence of Ag to the outermost layers of the Th-, C- and TOh-Cu-Ag NSAs (**Figure 30G-I**). We determine that an equivalent of 1.1-1.5 MLs of Ag have been deposited (as based on the 1st Cu ML, see **Figure S8**, **Table S2** and **Note S2**). Further, by determining the surface composition with XPS ($\text{Cu}_{0.91}\text{Ag}_{0.09}$), we estimate a diffusion of Ag into the Cu lattice of up to 11 MLs in the C- $\text{Cu}_{0.97}\text{Ag}_{0.03}$ NSA (**Figure S9** and **Table S3**).

To determine the absolute penetration depth of the Ag atoms, we designed a microtomy based experiment³⁷ in which

the top and bottom face of C-Cu-Ag NSA was removed with a diamond knife (see **Figure S10**). This resulted in a 2D particle consisting of a Cu-Ag random alloy outer ring surrounding a pure Cu core (**Figure 31**). Atomic resolution imaging and EDXS performed on an aberration-corrected STEM³⁸ reveal that Ag is only present in the first 6 MLs of the NSA (**Figure 31B-D**). A refit of the SP-ICP-MS surface atom distribution using the revealed Ag penetration depth, puts the average surface composition at 21.3 at.% Ag (**Note S2**). Interestingly, the measured composition surpasses the bulk solid solubility of Ag in Cu at room temperature by at least two orders of magnitude, stressing the importance of this work.³⁹ We further show that by controlling the reaction time of the non-equilibrium synthesis, the surface composition of the Cu-Ag NSA can be tuned (**Figure 30J** and **Table S3**). Finally, we studied the thermal stability of our metastable NSA using in situ TEM at identical location of the specimen (**Figure S11**). The results show that C-Cu-Ag NSA remained stable until 200 °C, ~25 °C higher than that reported for $\text{Ag}_{0.60}\text{Cu}_{0.40}$ solid solution thin films.⁴⁰

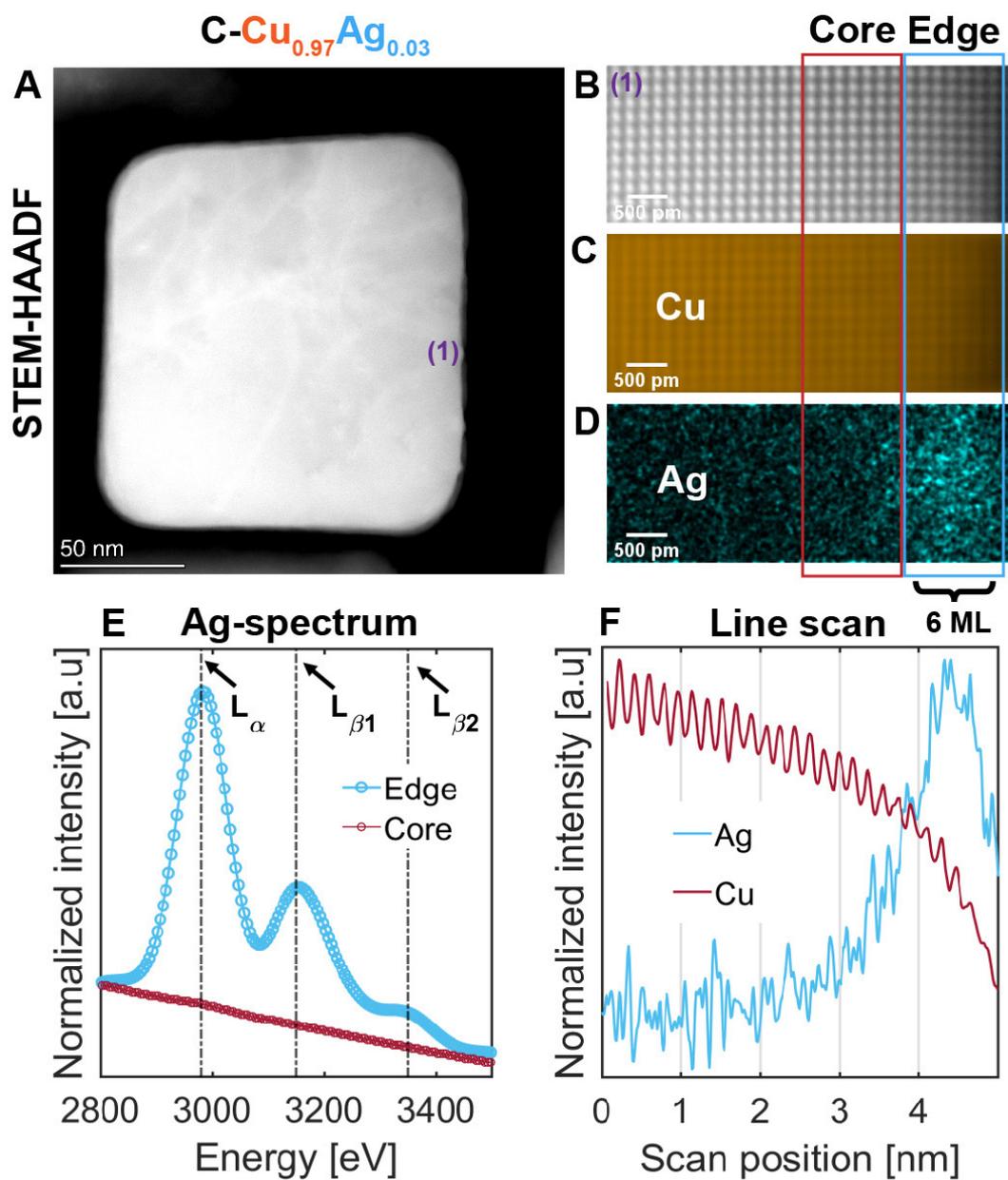


Figure 31. Determination of the penetration depth of Ag on the C-Cu_{0.97}Ag_{0.03} NSA. (A) High-resolution STEM-HAADF image of a 40 nm slice of a Cu-Ag NSA NP embedded in an epoxy resin. (B) Atomic resolution HAADF image of the Cu-Ag NSA edge. (C, D) Cu and Ag EDXS elemental maps of (B). (E) EDX spectra of the core and edge regions of the Cu-Ag NSA (indicated in B-D) showing the presence of the characteristic Ag L_α and L_β EDXS peaks at edge regions only, corresponding to the first 6 MLs of the particle. (F) Line scan of intensity over the image in (B).

As the low-temperature non-equilibrium synthesis is based on the galvanic replacement reaction, it should be applicable to different systems as long as there is an appropriate overall cell potential.²⁴ With this in mind, Cu-Au, Cu-Pd and Cu-Pd-Ag were successfully synthesized using the same reaction parameters as those for Cu-Ag (see **Materials and Methods, Figure 29, Figure S12, and Figure S13**). We would like to emphasize that for a seed with a lower standard reduction potential than Cu, a wider range of exchangeable metals should be possible. Nonetheless, larger potential differences could result in a substantial increase in the reaction

rate, potentially compromising the control over the structure. Therefore, the overall cell potentials investigated in this study (+280 mV to +410 mV for Cu-Ag and Cu-Au systems, respectively) represent a safe range for synthesizing NSAs.⁴¹ Finally, we propose that our synthesis methodology can be extended to produce multicomponent systems beyond three-elements such as high-entropy NSAs by sequentially pairing metals of progressively increasing overall cell potentials.

5.2.2. Facet dependent selectivity of Cu-Ag nanosurface alloys in CO₂RR

We further tested our anisotropic Cu-Ag system in the CO₂RR to demonstrate the low-temperature non-equilibrium synthesis as a screening platform for anisotropic alloyed multimetallic electrocatalysts (**Figure 32**). We first benchmarked our system by testing the C-, Th-, TOh-Cu single element NCs at a constant potential (-1.1 V vs RHE) in 0.1 M KHCO₃ in an H-cell (**Figure 32A**). Indeed, we could confirm that our faceted Cu seeds followed the same general trend as found in the literature: C-Cu(100) NCs are mostly ethylene selective (FE of 31%),^{18,42} Th-Cu(111) is mostly methane selective (29%),⁴³ and TOh-Cu(100)/Cu(111) shows a slightly higher selectivity towards liquid fuels such as acetate and ethanol etc. (14%).⁴⁴ Then, to test if any Ag introduced using the galvanic replacement reaction was catalytically active, we synthesized Ag-Cu NPs as control samples and tested their CO₂RR activity (**Figure S14**). By extending the reaction time and increasing the Ag⁺ concentration in the non-equilibrium synthesis, near-to-complete conversion of the anisotropic Cu NCs to isotropic Ag NPs was achieved (> 96 at.% Ag, see **Materials and Methods** for details, **Figure S14A-D**). It is shown that CO is the majority product (FE

> 59%) independently of the shape of the seed (**Figure S14D**), confirming the activity of the introduced Ag, which is a well-known CO evolving catalyst.⁴⁵

With the pure NCs benchmarked and the Ag activity confirmed, we turn to the investigation of the facet effect in bimetallic Cu-Ag alloys. To deconvolute facet from composition effects, we tested specifically those Cu-Ag NSA of equal composition in the CO₂RR (C-, Th, and TOh-Cu_{0.97}Ag_{0.03}, **Figure 32B**). Independent of the facet, a selectivity shift from C₁ products to C₂₊ could be noted upon the introduction of Ag with the starkest shift for the Th-Cu-Ag NSA (C₂₊ FE from 15% to 40%, **Figure 32C**). Further, a significant amount of acetaldehyde could be detected in the catholyte (FE >9%, **Figure 32C-D**, **Table S4**, **Figure S15**), which is absent for the pure Cu samples.⁴⁶ Further, the selectivity towards ethanol improved as well, whereas the FE towards ethylene increased only marginally (**Figure 32C-D**). Therefore, we conclude that Ag adatoms in Cu surfaces favor the C₂₊ (especially oxygenate products) over the C₁ products, which is in agreement with the results reported by Clark et al. for Cu-Ag(100) bulk single-crystal surface alloys.²¹

Notably, the TOh-Cu-Ag NSA showed the strongest gains in selectivity towards liquid fuels with acetaldehyde, ethanol and n-propanol approaching double digits (9%, 16% and 9%, respectively, **Table S4**). To our knowledge, no Cu-Ag-based NP system exists that surpasses, at comparably low overpotential in the H-cell, the 35% overall FE towards C_{2+} liquid fuels.

We attribute the remarkable general trend favoring C_{2+} liquid fuels (acetate, acetaldehyde, ethanol and n-propanol) over ethylene upon the introduction of Ag in both Cu(111) and Cu(100) faceted crystals to the electronic tuning of the active site, which is distinctly different from tandem-based catalysts.^{47,48,49} The electronic nature of the surface determines the binding strength of key intermediates and can thereby greatly influence the selectivity.⁵⁰ For transition metals, the binding strength is dictated by the interaction of their d-band with an adsorbate. The closer the d-band center lies to the Fermi level, the stronger the adsorbate binding.⁵¹ Stronger binding of $*CO$ as compared to pure Cu due to charge transfer-effects enhances the C-C coupling rate and thus the selectivity for C_{2+} products for Cu-Ag surface alloys (**Figure 30J** and

Figure S16). This also explains the larger enhancement factor of C_{2+}/C_1 for Cu-Ag(111) vs Cu-Ag(100) surfaces: the charge-transfer for Th-Cu_{0.97}Ag_{0.03} and C-Cu_{0.97}Ag_{0.03} is 100 and 90 meV, respectively. The reason for the more pronounced production of liquid fuels over ethylene is two-fold. First, the shift of the valence band originates from charge-transfer from Cu to Ag and charge-depleted Cu has been shown to favor C_{2+} products,^{29,35} and especially oxygenates.⁵² Second, the weak hydrogen adsorption strength of Ag results in lower $*H$ coverage.⁸ As a result, further hydrogenation is limited, steering the selectivity towards oxygen containing products. This is in agreement with observations for tandem Cu-Ag catalysts⁵³, and bulk surface alloys^{21,22}.

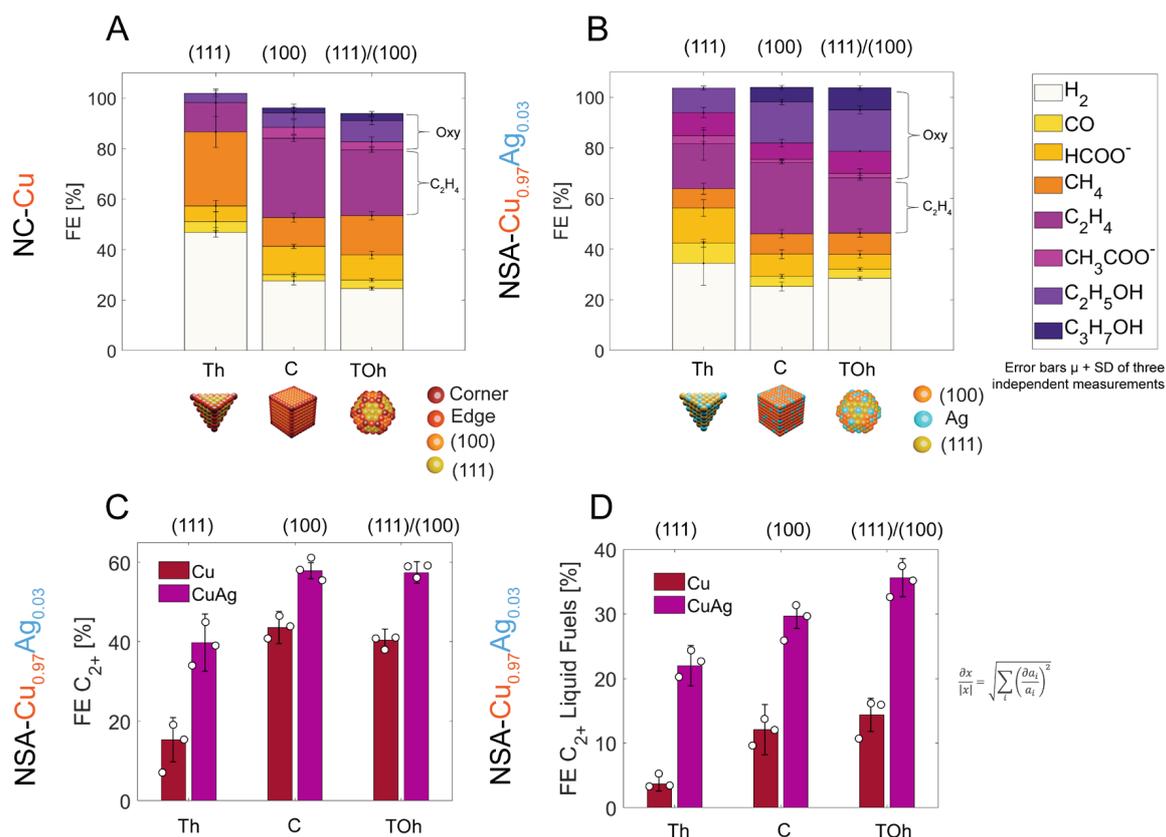


Figure 32. Electrocatalytic screening of the as-synthesized (an)isotropic Cu-Ag NPs, error bars represent the standard deviation of three independent measurements. Ball models in the title indicate the geometrical description of the anisotropic particles consisting of Cu(100) facets in orange, Cu(111) facets in yellow, edge sites in red and corner sites in red brown. Ag is indicated in turquoise. (A) Product distribution of the C- Th- and TOh-Cu NCs. (B) Product distribution of the anisotropic Th-Cu_{0.97}Ag_{0.03}, C-Cu_{0.97}Ag_{0.03} and TOh-Cu_{0.97}Ag_{0.03} NSA. (C) C₂₊ selectivity as a function of facet and composition. (D) C₂₊ liquid fuel selectivity as a function of facet and composition. The interface between Cu-Ag(111) and Cu-Ag(100) offers evidently the best C₂₊ liquid fuel producing active site(s).

5.2.3. Phase-segregation induced selectivity shift

The strong surface segregating tendencies of the Cu-Ag bimetallic system could significantly influence the selectivity,³² thus we deem this of utmost importance to evaluate the stability of our surface alloys. We subjected our best performing catalyst (TOh-Cu-Ag NSA) to a stability test at -1.1 V vs RHE and collected aliquots of the catholyte at 10 min intervals to determine the liquid product FEs during operation (**Figure S17**). As expected, the selectivity towards liquid fuels started to wane as soon as the reaction started. Therefore, we further investigated the product distribution in the initial stages of the reaction for all three NSAs (**Figure 5**). For each anisotropic Cu-Ag NSA (Th-, C-, and TOh-Cu_{0.97}Ag_{0.03}), a decreasing FE for liquid fuels could be observed with the fastest decay observed for the TOh-Cu_{0.97}Ag_{0.03} (from 35% to 25% in a matter of minutes). This was accompanied by an increase in FE of H₂. Also, the geometrical partial current densities pointed towards a decaying liquid fuel activity accompanied by an increase in the H₂ evolution reaction (HER, **Figure S18**).

To confirm phase-segregation as the culprit for the loss in selectivity, we analyzed the spent catalyst using TEM (**Figure 33C1-3**).

Strong contrasted extrusions at the particle surface could be discerned for the Th-, C- and TOh-Cu-Ag NSA after CO₂RR, which were absent in the pristine samples (**Figure 33B1-3**). The presence of extrusions at the particle surfaces of the spent catalysts could be confirmed with scanning electron microscopy (SEM), while the extrusion for the control C-Ag_{0.97}Cu_{0.03} NPs, which lacked the tendency of phase separation, can be excluded (**Figure S19** and **S20**). We assign these extrusions to the mobile Ag phase. Since phase-segregation results in Ag domain formation predominantly at the most undercoordinated sites, i.e., edges and corners (**Figure S10**), which are most selective for C-C coupling and especially the production of oxygenates,^{43,48} we argue that phase-segregation blocks those active sites explaining the progressive loss of liquid fuels selectivity over time. We, therefore, stress the importance of monitoring all products of the CO₂RR and the sample at least *ex situ* when testing metastable catalysts. Fast adsorbate-induced changes to the surface chemistry may otherwise cloud interpretations of the intrinsic activity.

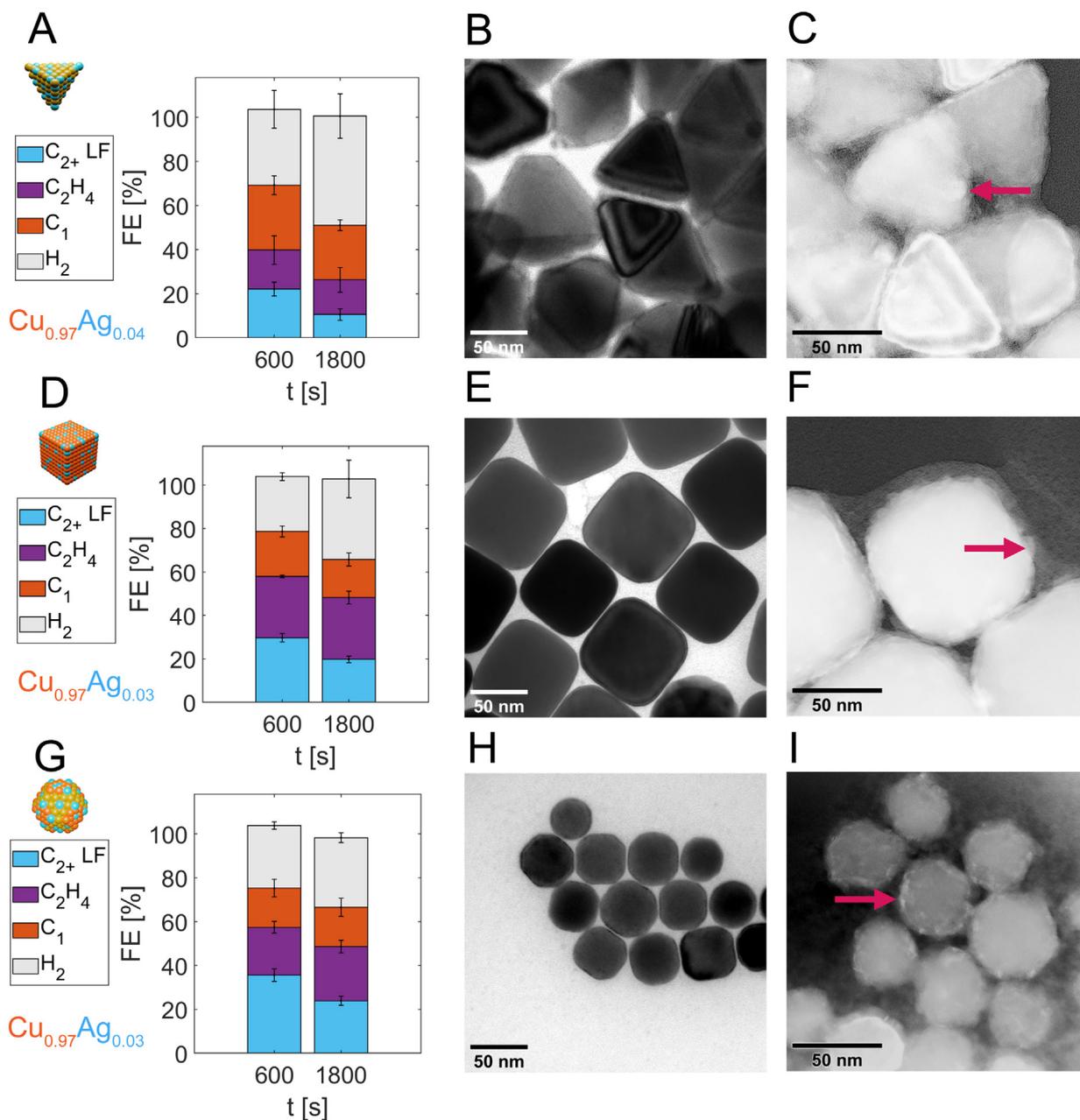


Figure 33. (A, D, G) Time evolution of the product distributions of the Th-,C- and TOh-Cu-Ag NSA at -1.1 V vs RHE in CO_2 saturated 0.1 M KHCO_3 . C_1 products including HCOO^- , CO and CH_4 are depicted in orange. C_{2+} liquid fuels products including CH_3COO^- , CH_3CHO , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{C}_3\text{H}_7\text{OH}$ are depicted in blue. C_2H_4 is depicted in purple and H_2 in grey. Error bars indicate the standard deviation of three-independent measurements (**Table S5**). Liquid products are collected under operation from a gas-tight H-cell using a clean syringe. (B, E, H) BF-TEM images of the pristine anisotropic Cu-Ag NSAs. (C, F, I) Negatives of BF-TEM images of the electrocatalysts after 30 min of CO_2RR offered as a visual-aid to observe the extrusions with higher contrast at the particle surfaces (indicated with arrows) assigned to the Ag phase. Note that the alternating bright/dark areas in the BF-TEM images are the result of thickness-fringes.

5.2.4. Theory-guided Cu-Ag-Pd catalyst selection for stable C₂₊ liquid fuel electrosynthesis

Based on the wide applicability of our low-temperature non-equilibrium synthesis, we set out to improve the stability of the metastable Cu-Ag NSA using metals that are miscible with Cu. Limited only by the difference in standard reduction potentials of the metals and the solubility of the salt in the reaction medium, a range of candidates (e.g., Rh, Pt, Pd, and Au) can be selected.⁵⁴ Interestingly, our previous investigations of the Cu-Ag-Pd system showed that Ag could be selectively exchanged for Pd whereas Cu remained untouched by choosing the right metal salt precursor.³³ This offered the opportunity to systematically tune the Ag:Pd ratio without changing the bulk Cu content and determine its effect on the performance and phase-stability. Notably, Pd has a strong tendency in reducing H₂O to H₂,⁵⁵ Therefore, a delicate balance exists between HER/CO₂RR upon the introduction of the ternary element.

Using a supervised machine-learning algorithm reported previously⁸ but trained with a ternary Cu-Ag-Pd data set of density functional theory (DFT) simulated *CO and *H adsorption energies, compositions with high CO reduction reaction (CORR) selectivity (i.e., selectivity towards CH₄ and C₂₊ products) and low H₂ selectivity could be predicted and selected (**Figure 34A**). CORR selectivity is here predicted as the proportion of surface sites on disordered face-centered cubic (111) surfaces with stronger *CO adsorption than on the reference Cu(111) surface. Selectivity for reducing CO₂ and subsequently CO (i.e., by suppressing H₂ formation) is predicted as the proportion of sites with weaker *H adsorption than on Cu(111). Prediction of adsorption energies was achieved on arbitrary surface sites using a linear regressor (**Figure S21, Table S6**). In **Figure 34A**, each data point represents a predicted CO₂RR/CORR selectivity for a specific

composition of the ternary alloy. With the low-temperature non-equilibrium synthesis, such NSAs could then be synthesized and tested in CO₂RR (**Figure 34B**). Computation predicted good C₂₊ selectivity for Ag:Pd of 1:3 whereas the inverse would suffer from H₂ production. Indeed, extended liquid fuel production could be observed for the Cu₇₉Ag₁₆Pd₅ system whereas the higher Pd content particle (16 at.%) switched dramatically to HER (**Figure 34C**). The

good agreement between the predicted and the experimentally determined CO₂RR and CORR selectivity observed confirms the validity of the machine-learning based approach in predicting selectivity relations in alloy systems.

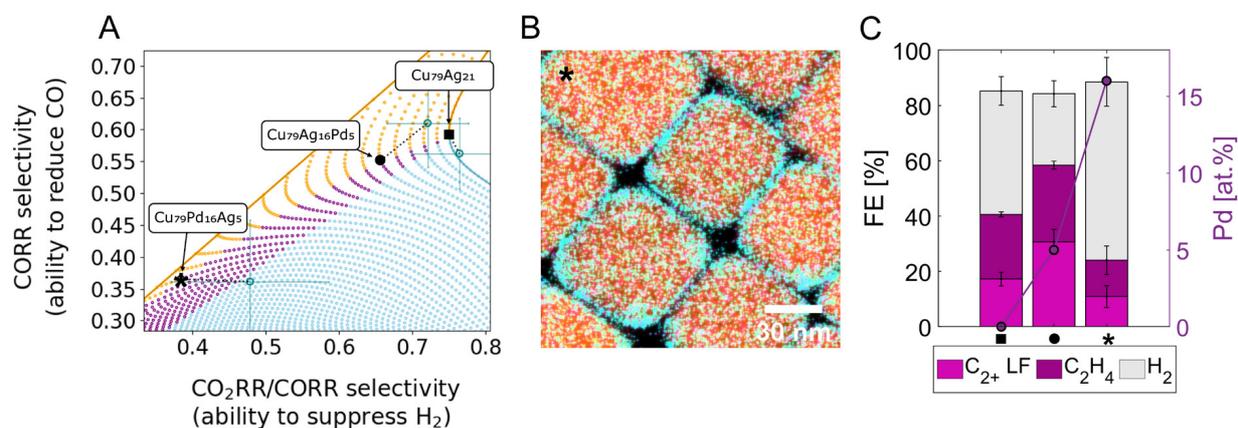


Figure 34. Theory-guided optimization of the ternary alloy for extended phase-stability. (A) Activity-selectivity plot of CO₂RR/CORR of the ternary alloy system. Orange colored dots indicate compositions with ≥ 74 at.% Cu, light blue and purple colored with < 74 at.% Cu and > 13 at.% Ag and Pd, respectively. Black symbols (circle, star and square) denote the predicted values from the machine learning-based algorithm. Blue symbols and error bars indicate molar yields as calculated from experimental data in (C) and **Table S7** and **S8**. (B) STEM-EDXS elemental map of as-synthesized C-Cu-Ag-Pd NSA with Ag:Pd equals 1:3. (C) Time averaged FEs of C₂₊, liquid fuels, C₂H₄ and H₂ of the C-Cu₇₉Ag₂₁, C-Cu₇₉Ag₁₆Pd₅ and C-Cu₇₉Pd₁₆Ag₅ NSAs, respectively. Electrochemical test was performed for 30 min at -1.1 V vs. RHE in 0.1 M KHCO₃. Square, circle and star insets reflect matching composition in (A)-(C). Error bars indicate the standard deviation of three independent measurements.

5.3. Conclusion

Multicomponent congruently mixed nanoparticles are well underway in playing a dominant role in the energy research field. To fully harvest the catalytic potential of such systems, not only do miscibility gaps need to be overcome with advanced syntheses, it must be achieved with shape control to deconvolute the effect of the facet from that of the composition. We show with our generalizable low-temperature non-equilibrium seeded-growth method that this is now possible as evidenced by the production of anisotropic (cubic, tetrahedral, and truncated octahedral, etc.) multimetallic nanosurface alloys (Cu, Ag, Pd, and Au, etc.) of up to three components.

Further, to show the applicability of our synthesis products in electrochemical screening, we tested our shape-controlled Cu-Ag nanoparticles in the CO₂RR and showed improved selectivity towards C₂₊ liquid fuels compared with their monoelemental counterparts. Finally, guided by machine learning, we synthesized Cu-Ag-Pd NSAs with high C₂₊ selectivity and phase stability. With a large number of multimetallic compositions and systems accessible as well as the added facet control, we expect our low-temperature non-equilibrium synthesis to be of great advantage for researchers seeking nanomaterials of specific spatial atomic arrangements.

5.4. Materials and Methods

5.4.1. Chemicals

The following chemicals and solvents were acquired from Sigma-Aldrich: copper bromide 99.99% (CuBr), palladium chloride 99% (PdCl₂), gold chloride (AuCl₃), nitric acid 70% (HNO₃), trioctylphosphine oxide 99% (TOPO), trioctylphosphine 99% (TOP) and oleyl amine 70% (OAm). Anhydrous ethanol

95% was purchased from ACROS organics (EtOH) and anhydrous toluene (99.8%) from Alfa Aesar. Lastly, silver nitrate (AgNO₃) 99.9995% was obtained from Puratrem. All chemicals were used as received without any further purification.

5.4.2. Non-equilibrium synthesis

The low-temperature non-equilibrium synthesis is inspired by the protocol from Lee et al.²⁷ Typically, 4 mg of anisotropic Cu NPs synthesized using a Schlenk-line (**Figure S1**) dispersed in a minimal amount of anhydrous toluene (19 mg/mL based on ICP-OES) were added to a 10 mL glass vial in the glove box creating a NP thin film, to which 3.5 mL of degassed OAm were added carefully without disturbing the film (non-equilibrium synthesis). Further, 0.5 mg of dry AgNO₃ were added to 1.5 mL of degassed OAm and dissolved at 50 °C using an oil bath to prevent homogeneous nucleation (Cu:Ag equals 21:1, **Figure S21**). Then, using a clean syringe, the Ag salt precursor solution were dropwise added to the reaction vial. For the C-Cu-Ag NSAs, the reaction mixture was then allowed to

react at 80 °C for 1 or 5 min. For the TOh-Cu-Ag for 5 min at 80 °C and for the Th-Cu-Ag 1 min at 50 °C. For the isotropic Ag-Cu NPs the Cu:Ag ratio was increased to 1:3 and the reaction time extended to 24 hrs to ensure near-to-complete exchange (**Figure S12**). In each case, the reaction was quenched with an excess of anhydrous toluene and washed with the same solvent. Substitution of the AgNO₃ with AuCl₃ or PdCl₂ and increasing the dissolution temperature to 80 °C but keeping all other conditions the same obtained the C-Cu-Au and C-Cu-Pd MMNPs. By reintroducing C-Cu-Ag NSAs and reacting with a Pd salt precursor solution, C-Cu-Pd-Ag MMNPs could be obtained as well. For details on the conventional synthesis, see SI **Note S1**.

5.4.3. Annealing experiments

A monolayer of C-Cu-Ag NSAs was deposited on thermally resistant Si_3N_4 grids purchased from Ted Pella Inc. and placed in a MILA-5000 rapid thermal annealer. After flushing the gas tight system with N_2 for 30 min. The temperature was increased to 100 °C with ramp of 50 °C·s⁻¹ and kept at that temperature for 30 min after which the reaction was quenched by flushing again with N_2 . After the reaction, the wetting

behavior of the NSA was investigated using TEM imaging performed on identical sample locations. The experiment was further repeated for 200 °C, 300 °C and 400 °C and the wetting behavior observed. After the final annealing experiment, STEM-EDXS (on identical locations) was performed to confirm the mobility of the Ag phase.

5.4.4. Cathode preparation

Belt-shaped pieces of Toray TGP-60r carbon paper were cut out with a geometrical surface area of 0.5 cm², to which 0.8 mg·cm⁻² worth of the anisotropic Cu NCs, Cu-Ag, Cu-Ag-Pd NSAs or isotropic Ag-Cu NPs dispersed in toluene were added using drop casting in the glovebox. Finally, 20 µL of 0.83 wt% Nafion dispersed in *iso*-propanol were added as binder.

5.4.5. Characterization

Electron microscopy (EM). SEM images were acquired using a Thermo Scientific Teneo. TEM images were acquired with a FEI Tecnai Basic Spirit operated at 120 kV in bright field mode. The microscope was equipped with a Gatan charge-coupled device (CCD) camera and Digital Micrograph for imaging. Samples were drop-casted on Au grids (400 mesh) from Ted Pella Inc. with ultrathin carbon film, which were washed with ethanol before and after drop-casting. Ni based grids were used for Au containing samples. Scanning transmission electron microscopy high-angle annular dark-field (STEM-HAADF) micrographs and EDXS elemental maps were obtained on a Thermo Scientific Tecnai-Osiris operated at 200 kV. This instrument is outfitted with a high brightness Schottky X-FEG. This microscope is equipped with a high brightness Schottky X-FEG gun, a Super-X EDX system comprising of four silicon drift detectors. Atomic resolution scanning transmission electron microscope images were acquired in the high-angle annular dark-field (HAADF-STEM) condition on an aberration-corrected (double Cs-corrected)

Thermo Scientific Titan-Themis 60-300 operated at 200 kV and using a beam current of 200 pA. The Super-X EDX system and Velox acquisition software were used to acquire and analyze the EDXS elemental maps. To study the penetration depth of the Ag inside the particle, some samples were embedded in the G2 resin and sliced to 40 nm thick slices by ultramicrotomy using a Leica EM FC7 machine (equipped with a Diatome cryo-knife 35° angle) at room temperature and with a cutting speed of 0.2 mm s⁻¹. Ultramicrotomed slices were deposited on an ultra-thin carbon support grid for imaging and EDXS.

X-ray photoelectron spectroscopy (XPS). XPS was performed on a Kratos Axis Supra system (analysis chamber base pressure 1 × 10⁻⁹ mbar), using a monochromated Al K_α (1486.61 eV) X-ray source at a nominal power of 225 W. A pass energy of 20 eV was used for acquiring all core-level and Auger electron spectra, as well as the X-ray excited valence band spectra. The binding energies (BEs) were referenced to Au 4f_{7/2} at 83.95 eV. The samples were drop-casted on a gold foil in a N₂ glovebox and transferred

for measurement without exposure to air. No charge compensation was required as the samples were conductive.

Inductively coupled plasma - optical emission spectroscopy (ICP-OES). The concentration of the digested NP solutions was determined with an Agilent 5110 ICP-OES with a VistaChip II CCD camera. The NPs were digested overnight in 2% HNO₃ and filtered with 400 μm pore size Ultrapore nylon filters. The calibration curves were obtained through the preparation of a dilution series of elemental standards obtained from Sigma Aldrich.

Inductively-coupled plasma mass spectrometry (ICP-MS). Elemental analysis of the Th-, C- and TOh-Cu-Ag NSAs

was achieved with a NexION 350D ICP-MS instrument from PerkinElmer operated in continuous data acquisition mode. Calibration of the transport efficiency (η_t) was achieved with Au NPs standards 30, 50 and 80 nm purchased from PerkinElmer at a NP number concentration of ~50,000 NPs mL⁻¹.

5.4.6. Density Functional Theory Simulations

126 atop *CO and 160 face-centered cubic (fcc) threefold hollow *H adsorption energies were simulated on fcc (111) surfaces of randomly generated, periodically repeated surface slabs sized 3x3x5 atoms with 10 Å of vacuum above and below the slab. The lattice constants were set to the average of the constituent elements in the top layer.⁵⁵ Simulations were performed in the GPAW code^{56,57} version 22.1.0 and the atomic simulation environment (ASE)⁵⁸ version 3.22.1 for atomic manipulations. Energies were computed using the RPBE exchange-correlation functional⁵⁹ using a plane wave basis set with an energy cutoff of 400 eV. The Brillouin zone was sampled on a 4x4x1 uniform Monkhorst-Pack grid of k-points, and atoms were relaxed to a force below 0.075 eV/Å. Atomic structures have been made freely available at nano.ku.dk/english/research/theoretical-electrocatalysis/katlabdb/co2-reduction-on-ag-cu-pd/.

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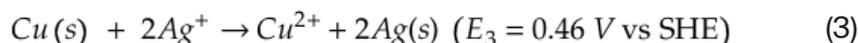
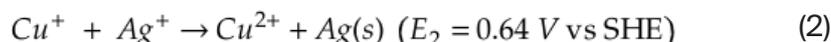
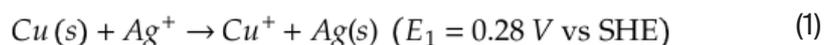
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5.6. Supporting Information

Note S1. Thermodynamic and kinetic considerations of the conventional and non-equilibrium synthesis.

In order to understand the reaction kinetics of the Cu-Ag non-equilibrium system, we will begin to describe the thermodynamics of the conventional approach in which the seeds (in our case anisotropic Cu NPs,

Figure S1) are fully dispersed in the reaction medium. In its simplest form, three redox reaction can take place in the Cu-Ag system:



For all three reactions the overall cell potential is positive and, following the Nernst equation, the change in Gibbs free energy negative. Therefore, each reaction can take place spontaneously. The thermodynamic driving force follows the series (3)>(2)>(1). Since reaction (2) is dependent on reaction (1), only reaction (1) and (3) can take place in the initial stages of the reaction. From a thermodynamic standpoint, reaction (3) should dominate the overall galvanic replacement. However, since this reaction requires the participation of two Ag⁺ ions, a significant kinetic barrier

exists and, therefore, the oxidation of Cu to Cu⁺ dominates for low relative Ag salt concentrations. Interestingly, the further oxidation of Cu⁺ to Cu²⁺ and simultaneous reduction of Ag⁺ to Ag(s) is strongly energetically favorable (~62 kJ/mol). Therefore, upon the formation of Cu⁺ ions and given that enough Ag⁺ ions are present for the reaction to proceed, the exchange should actually accelerate upon the occurrence of reaction (1). Further, with increasing Ag salt concentration, direct oxidation of Cu to Cu²⁺ becomes more and more likely resulting in simultaneous

deposition of two Ag atoms per exchange reaction. Both effects, the acceleration of the reaction upon Cu^+ formation as well as the 2:1 Ag:Cu stoichiometry in the two-electron oxidation, suggest a strong galvanic tendency towards the progressive

local deposition of Ag over its homogeneous distribution throughout the particle surface.

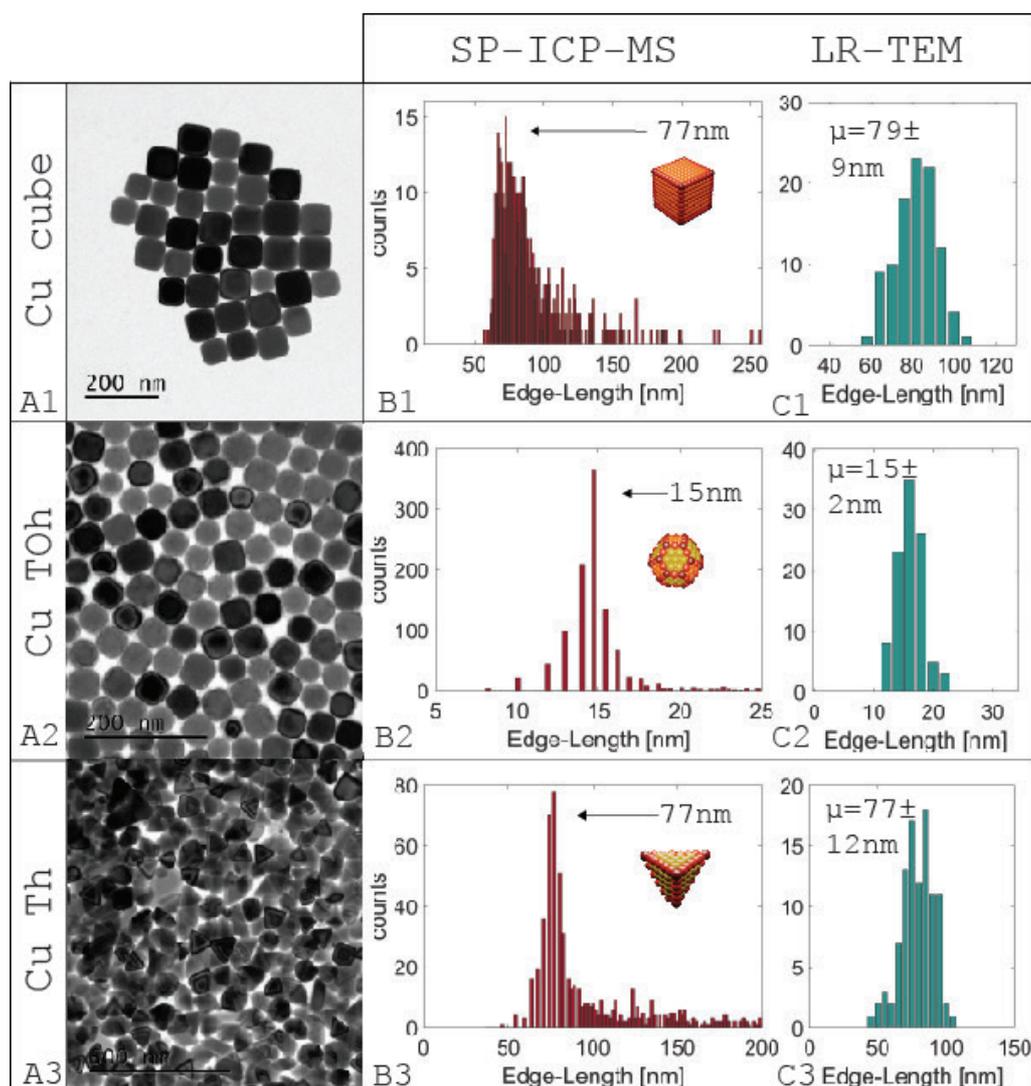


Figure S1. Synthesis of the anisotropic Cu seeds according to the protocol published in Ref. ¹. SP-ICP-MS measurements with up to 1100 particles counted show matching edge-lengths, i.e., the corner-to-corner distance, determined using the geometrical fitting in **Note 8** (and as indicated by the deep-red colored atoms in the ball models), with bright-field TEM micrograph particle counting ensuring ensemble size and shape homogeneity. Figure reprinted with permission from Ref. ¹

Let us now consider a cubic Cu NP (fcc) consisting of six faces, 12 edges and eight vertices (**Figure S2**). The coordination number for atoms of given spatial configuration is respectively eight, five and three. Therefore, the oxidizability (the ease at which a Cu atom oxidizes) becomes more energetically favorable for corners, followed by edges and finally facets due to the increased surface energy of undercoordinated surface species. Therefore, a preferentiality should exist for the galvanic exchange to take place at the particle edges and corners over the

faces. Beyond the coordination number, the higher degree of freedom by which an Ag^+ ion may approach the Cu lattice at the edges and corners further suggest exchange to preferentially take place at the low coordination number atoms. Following the previous thermodynamic and kinetic considerations, and considering the positive interfacial energy of Cu-Ag surfaces², we conclude that the formation of phase-segregated domains at the particle edges and or corners construes the thermodynamic product.

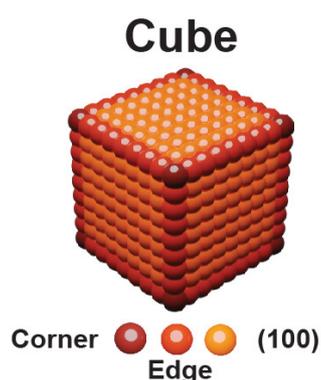


Figure S2. Ball model of the Cu cube with in brown red the corner atoms, red the edge atoms and orange the (100) facets.

Indeed, when the AgNO_3 is fixed at ~ 0.6 mM, and the Cu NPs are fully dispersed in the reaction mixture, heterostructures can be observed independently of the reaction time with strong preferential growth for edges/corners (**Figure S3A-C**). Further, the average domain size increases with the reaction time indicating that growth of individual domains is favored over the nucleation of a new domain, which agrees with Gibbs free energy consideration. The

phase-segregated nature of the bimetallic anisotropic Cu-Ag NPs and the preferential domain growth at particle edges and corners is further confirmed by STEM-EDX spectroscopy (**Figure S3D**). It is interesting to note that already after 5 min of reaction, a green color in the reaction mixture could be observed indicating the presence of Cu^{2+} ions.

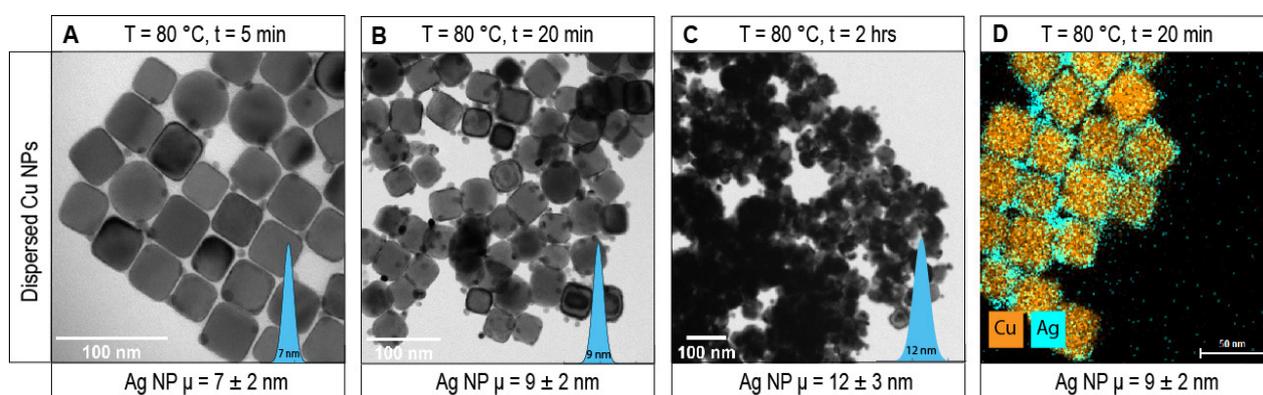


Figure S3. Conventional galvanic exchange reaction of C-Cu NPs (4 mg) using a 0.333 mg/mL AgNO_3 in OAm precursor solution (final AgNO_3 concentration ~ 0.6 mM, Cu:Ag 21:1) prepared by dissolving the Ag salt at 50 °C. (**A-C**) Phase-segregated Ag domains grow with increased reaction time (blue inset shows the gaussian fit of the size distribution of 100 unique particles counted with the mean shifting to the right with increasing reaction time). (**D**) STEM-EDXS elemental map shows Ag domains (turquoise) preferentially situated at particle edges and corners.

As we can explain the reaction behavior of the thermodynamic product, we now know that in order to obtain kinetic control, it is required to suppress reaction (2) and (3). In this way, exchange may only occur in equimolar ratios. Other than the undercoordinated sites, no facet atom shows any preferentiality towards exchange, and as such, replacement becomes a random event. While it might be possible to achieve this by reducing the bulk Ag salt concentration further, a much more elegant approach would be to reduce the local Ag salt concentration as in that way, the complete composition range of the Cu-Ag system could still be probed. As mentioned in the main text, this was achieved by means of a thin film reaction and independently of the reaction time and at equally high Ag:Cu ratios, the formation of heterostructures could be excluded (**Figure S4**). After 20 min at 80 °C and high relative Ag loading, a distinct contrast difference can be noticed at the particle edges associated with the stronger diffracting Ag phase absent for the random NSA in the main text produced at low relative Ag loading (**Figure S4B, Figure S4A** and **Figure 2**). This is likewise reflected in the three-fold higher bulk Ag composition (9 at.% Ag). When looking at the STEM-EDXS elemental map of this system, it is clear that while some particles have

retained a homogeneous Ag distribution, others are partially overgrown by Ag (**Figure S4E**). This is in excellent agreement with observation for Ag sputtered bulk Cu(100) surfaces.³ Upon extension of the Ag surface composition, beyond a certain coverage, strain built up in the lattice cannot sustain additional Ag adatoms, and island formation ensues. This is practically the highest Ag loading we could achieve in which the cubic shape was retained. If we extend the reaction further (two hours), deformation ensured matching the observation in the conventional synthesis (**Figure S4C, Figure S3C**). Finally, by enlarging the Ag to Cu ratio and further extension of the reaction time (24 hrs) a near-complete-exchange (Ag content >97%) could be achieved as well where spherical hollow structures ensured typical of the galvanic replacement reaction (**Figure S4D**).⁴ Deposition of inert Ag at the particle edges in combination with a continuous stream of Cu ions originating from the center of the particles can explain its morphology. Modulation of the Ag⁺ flux provides exquisite control over the Cu-Ag system.

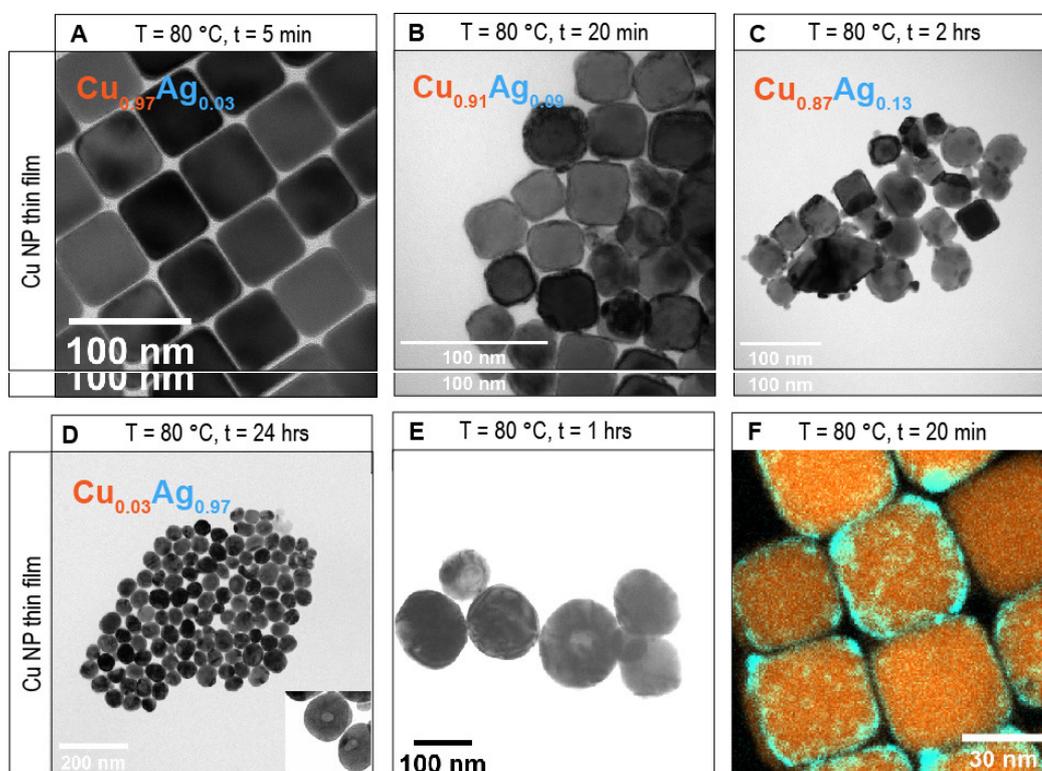


Figure 4. Non-equilibrium synthesis with C-Cu NP seeds. (A-C) Time evolution of the non-equilibrium synthesis where a C-Cu NPs thin film (4 mg) was exposed to a ~ 0.6 mM AgNO_3 in OAm precursor solution (Cu:Ag 21:1) and reacted for 5, 20 min and 2 hrs at 80 °C. (D) The non-equilibrium synthesis at high Ag:Cu ratio (3:1) for 24 hrs. The inset of the near-to-complete exchanged particle shows a hollow structure typical of the galvanic replacement reaction.⁴ (E) The accelerated non-equilibrium synthesis at further increased Ag:Cu ratio (8:1) shows the same morphology as in (D) already after 1 hrs. TEM image depicted at high contrast and high brightness show the hollow nature. (F) STEM-EDXS elemental map of the 20 min reacted C-Cu-Ag NSA shows a homogeneous distribution of the Ag elements with patches of Ag observable for some particles. Limiting the Ag:Cu ratio and reaction time is adamant to ensure the formation of a random alloy for all particles.

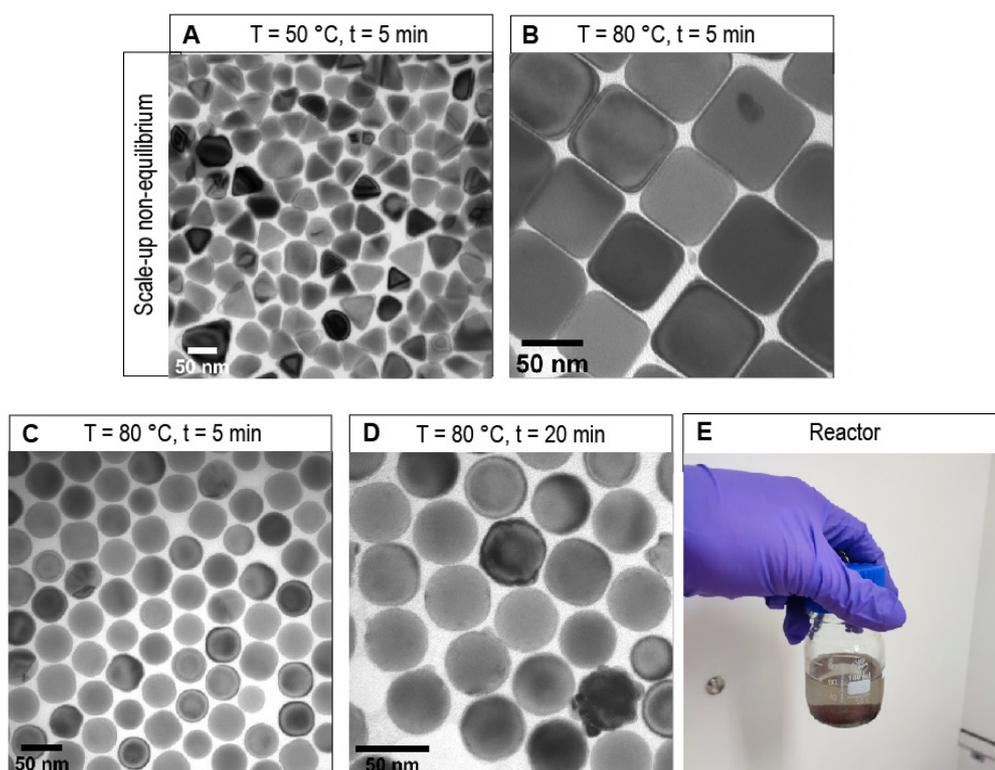


Figure S5. Overview of the 12.5-fold scaled-up non-equilibrium synthesis reaction. (A-D) TEM images of the synthesis products. (A) Tetrahedral Cu-Ag NSAs, (B) Cubic Cu-Ag NSAs, (C) Spherical Cu-Ag NSAs, (D) Spherical Cu-Ag NSAs with 4-fold higher Ag content, (E) Up-scaled reaction.

Reaction	E [V]	ΔG [kJ mol ⁻¹]	K_{eq}
1	0.28	-26.98	9.82E+03
2	0.64	-61.81	1.40E+09
3	0.46	-89.27	1.62E+13

Table S1. Thermodynamics of the redox reactions of Cu and Ag indicated in the above and in the main text. $\Delta G = -nFE$, with n the number of electrons transferred, E the cell voltage, and F Faraday's constant. $\Delta G = RT \ln K$ with R the gas constant, T the temperature and K the equilibrium constant.

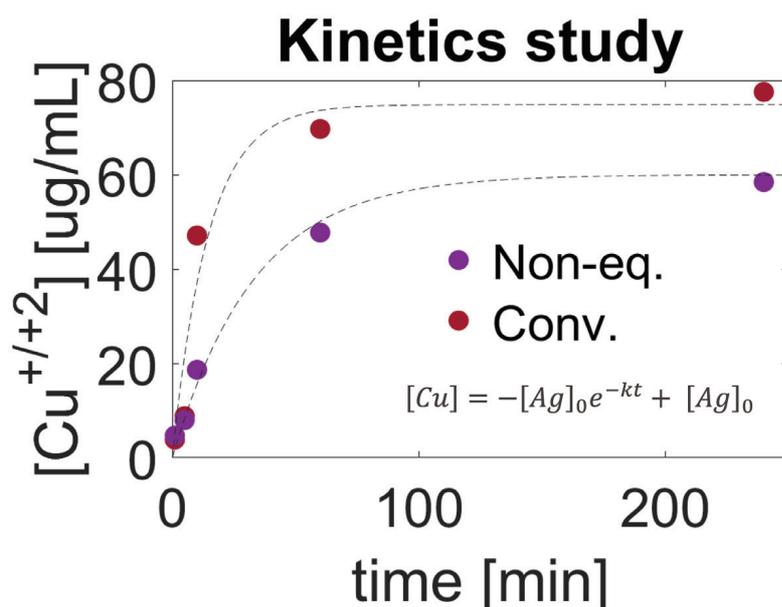


Figure S6. Kinetic study of the galvanic exchange rate of the conventional and the non-equilibrium synthesis in red and purple, respectively. The Cu concentration in the electrolyte was monitored using ICP-OES. Dashed-curves indicate the fitted curves according to the equation in the inset, conveying the first order rate law in which $[Ag]_0$ denotes the Ag^+ concentration at $t=0$, t the time in minutes, and k the rate constant. The Cu concentration is first order dependent on the concentration of the reactant $AgNO_3$ for both the conventional and the non-equilibrium synthesis, with $R^2 = 0.916$ and 0.989 and $k = 0.068$ and 0.030 [min^{-1}], respectively. The goodness of the fit excludes reaction 3 (which is second order to the concentration of Ag) from the non-equilibrium reaction. The factor 2.3 larger rate for the conventional reaction stems from a minor contribution of reaction 2 and 3 to the overall rate. Even though reaction 2 is second order dependent on both Cu^+ and Ag^+ , the much lower thermodynamic equilibrium constant of reaction 1 vs reaction 2 ($9.8 \cdot 10^3$ vs $1.4 \cdot 10^9$, respectively, see **Table S1**) suggests reaction 1 is rate limiting and the overall rate should therefore be dominated by reaction 1 and be first order as well.

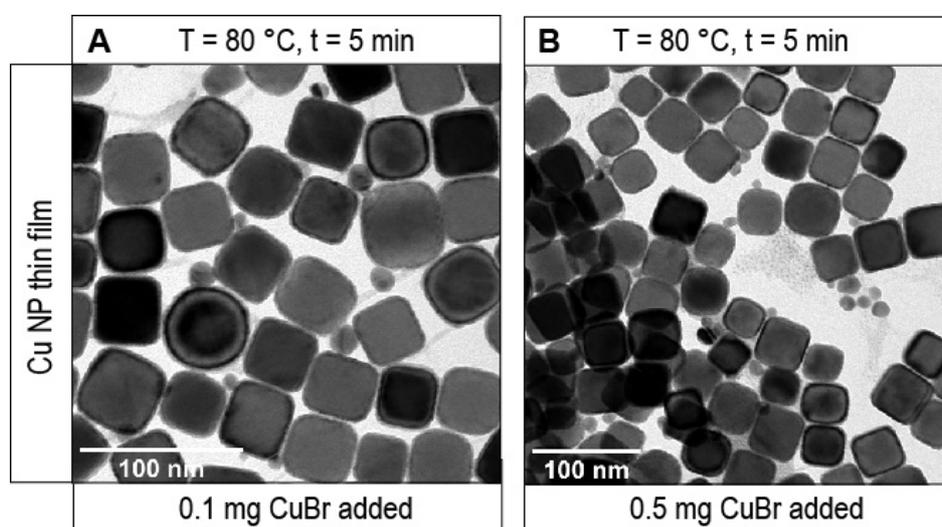


Figure S7. (A) BF-TEM image of the non-equilibrium synthesis of C-Cu NP in the presence of 0.14 mM Cu^+ ions yielding a phase-segregated material with individual Ag domains. (B) BF-TEM image of the on-equilibrium synthesis of C-Cu NP in the presence of 0.7 mM Cu^+ ions resulting in homogeneous nucleation of Ag NPs.

Note S2. Determination of the surface composition of anisotropic CuAg NSAs.

In order to determine the Ag overlayer and surface composition of the NSAs, fitting of the Cu-Ag elemental distributions is required. First, the Cu atom distribution was converted in a surface atom distribution by using a geometrical model (**Appendix S5**). For this, an outermost shell of Cu atoms was defined of the anisotropic particles consisting of the 1st and up to the 6th monolayer (ML). Both Cu (1st and 6th ML) and Ag distributions for C-, Th- and TOh-CuAg

NSA were fitted with a lognormal distribution (**Figure S5**). Further, the probability density functions were normalized to account for the difference in events. Finally, the area under the curve was determined by numerical integration of the probability density function and evaluation at a relevant interval. The surface composition is then defined as the ratio of Ag area: Cu area.

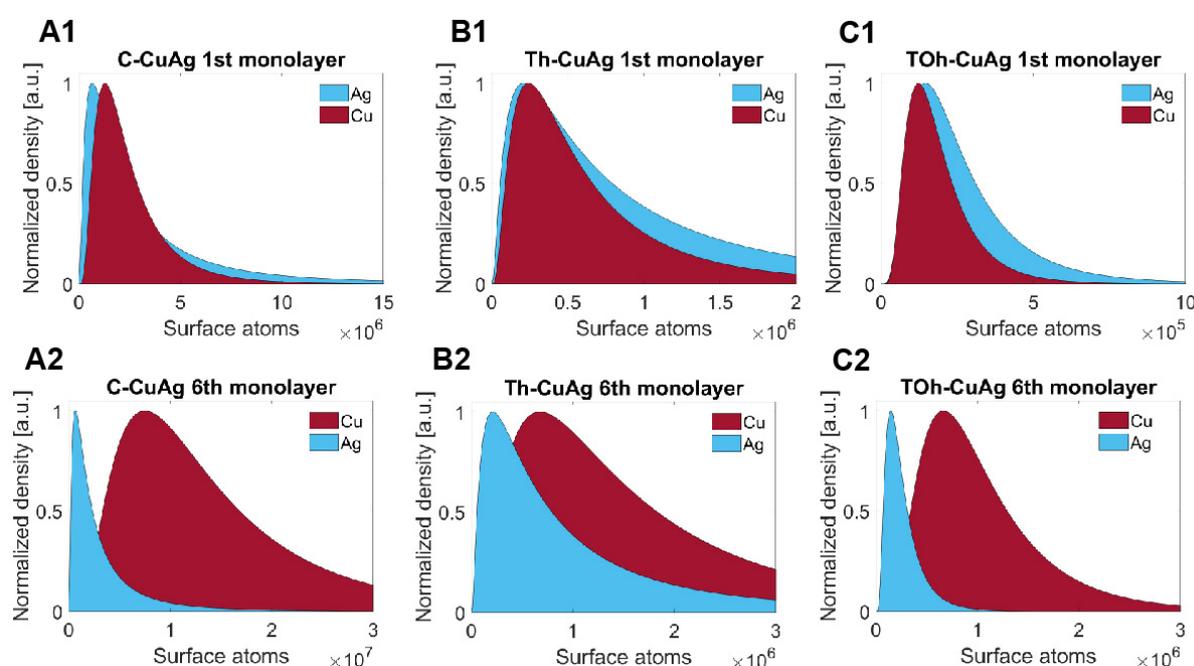


Figure S8. Determination of the Ag overlayer and surface composition of anisotropic Cu-Ag NSA. (A1, A2) C-Cu-Ag NSA fitted elemental distributions based on the 1st and 6th ML of Cu. (B1,B2) Th-CuAg NSA fitted elemental distributions based on the 1st and 6th ML of Cu. (C1,C2) TOh-Cu-Ag NSA fitted elemental distributions based on the 1st and 6th ML of Cu.

	Ag overlayer (1 st ML)	Surface composition (6 th ML)
C-Cu _{0.97} Ag _{0.03} NSA	1.15 ML	Cu _{78.7} Ag _{21.3}
Th-Cu _{0.97} Ag _{0.03} NSA	1.43 ML	Cu _{44.3} Ag _{55.7}
TOh-Cu _{0.97} Ag _{0.03} NSA	1.46 ML	Cu _{64.0} Ag _{26.0}

Table S2. Ag overlayer and surface composition of the Cu-Ag NSAs extracted from the fitting.

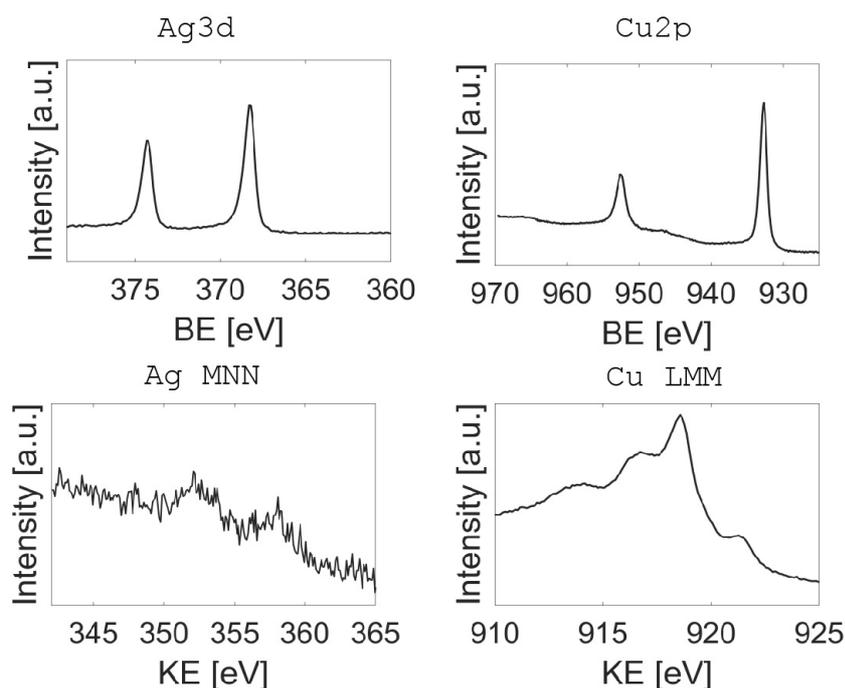


Figure S9. Example of XPS and Auger spectra of the C-Cu-Ag NSAs ($\text{C-Cu}_{0.97}\text{Ag}_{0.03}$) used to determine the surface composition and depth of information in **Table S1**.

	Reaction time	Surface composition	Number of Ag atoms	Number of Cu atoms at Xth ML	Ag/Cu
C-Cu _{0.97} Ag _{0.03} NSA	5 min	Cu _{0.91} Ag _{0.09}	677,441	(11 th) 7,644,848	0.09
C-Cu _{0.99} Ag _{0.01} NSA	1 min	Cu _{0.95} Ag _{0.05}	752,647	(22 nd) 14,356,096	0.05

Table S3. Calculation of the penetration depth of Ag adatoms in the C-Cu-Ag NSA as based on XPS surface composition extracted from, e.g., **Figure S7** and the absolute number of Ag atoms of the most frequent peak in the Ag distribution of the C-Cu-Ag NSA obtained via SP-ICP-MS. A C-Cu NP of 100 nm was chosen as reference.

To determine the surface composition of the NSAs. It is mandatory to know the penetration depth of the Ag atoms into the Cu lattice, as through SP-ICP-MS only the absolute number of Ag atoms in the particle is known, not its internal distribution. For this we devised a microtomy based experiment in which C-Cu-Ag NSA were embedded in an epoxy resin, vacuum degassed, cured at 80 °C and sliced using a microtome at

40 nm thickness. Micron sized slices of 40 nm thick were then deposited on a Cu TEM grid with ultrathin carbon support. STEM imaging and EDXS were performed on Thermo Scientific Tecnai-Osiris and Titan-Themis microscopes, with the latter (aberration-corrected STEM) being used to determine the penetration depth of Ag (see **Figure 3** in the main text).

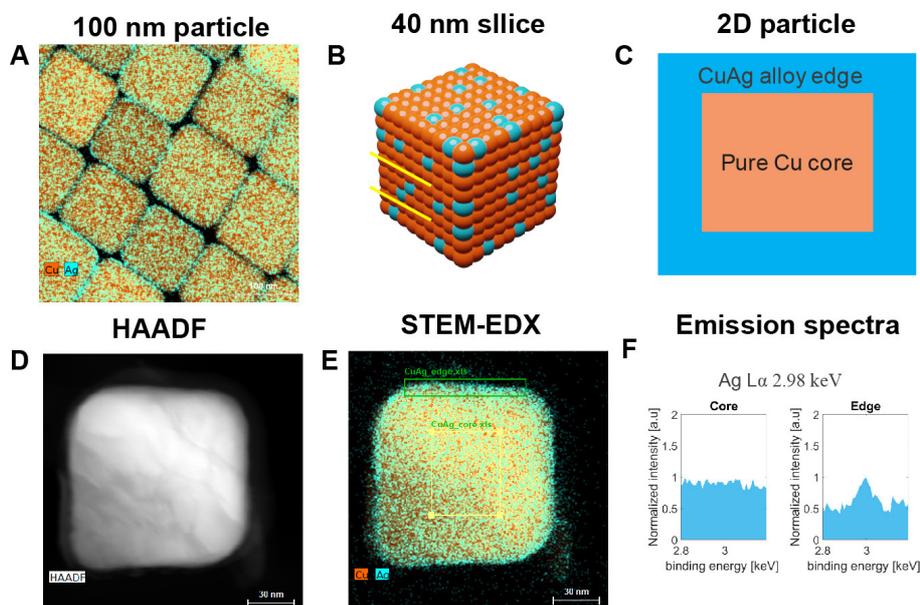


Figure S10. (A) EDXS elemental map of the C-Cu_{0.97}Ag_{0.03} NSA. Proposed microtome slice of the embedded particle cutting of the top and bottom face of the NP. The particle was embedded in a resin and sliced to a thickness of 40 nm using ultramicrotomy. (C) Schematic representation of the sliced composite NP. (D) STEM-HAADF image of a 40 nm microtomed slice and (E) corresponding EDXS elemental map of Cu and Ag. (F) Absence and presence of the characteristic Ag L_α peak in the EDX spectra from core and edge.

Note S3. Identical location TEM imaging of dewetting behavior of C-CuAg NSA.

Since we argue our surface alloys are a kinetic product, a small perturbation of the system may result in phase-segregation. To test this, we submitted the 20 min reacted C-Cu-Ag NSA (**Figure S9A**) to a step-wise temperature increase from room temperature to 400 °C under inert conditions (excluding contributions from oxidation) and observed the wetting behavior using identical location TEM (see **Materials and Methods** for details). TEM images acquired on identical locations showed that

already after 30 min at 300 °C, de-wetting of a stronger contrasting phase presented (most likely Ag, **Figure S9B**). Upon further raising of the temperature (400 °C), various particles fused (**Figure S9C**). By means of STEM-HAADF coupled with EDXS, we could confirm the segregating phase to consist of Ag (**Figure S9E-F**). The lower surface energy of Ag in comparison to Cu further corroborates Ag as the mobile phase.⁵

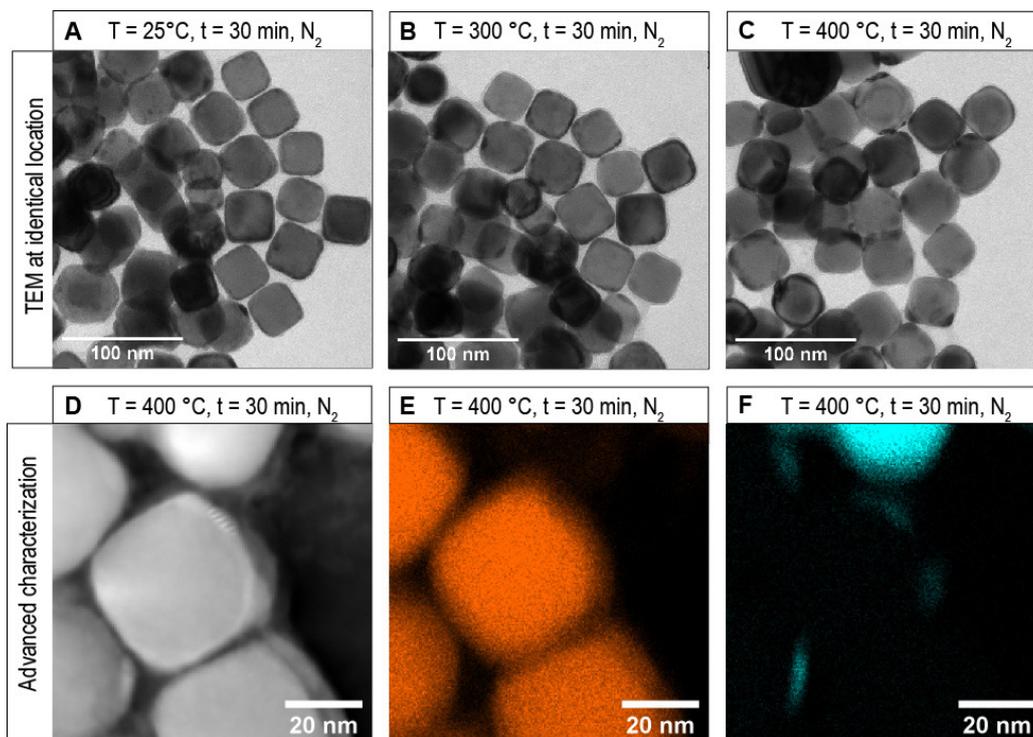


Figure S11. (A-C) TEM images of the C-Cu_{0.91}Ag_{0.09} NSA synthesized using a non-equilibrium synthesis as a function of temperature in an annealing experiment under inter conditions. (D) STEM-HAADF image showing the de-wetted nature of the particles with an Ag-rich region at the particle edge. (E-F) STEM-EDXS elemental map of Cu (in orange) and Ag (in turquoise) corroborating the phase-segregated nature of the thermally treated particles.

Finally, we devised a control experiment to corroborate our hypothesis that a low local Ag⁺ concentration could explain the formation of our surface alloy. By artificially introducing Cu⁺ ions in the non-equilibrium synthesis, offering a second route other than the galvanic replacement of the seed for the reduction of Ag⁺, we could convert the NSA into a phase-segregated material with individual Ag domains similar to the

thermodynamic product formed using the conventional synthesis (**Figure S10A**). Further, by enhancing the Cu⁺ concentration five-fold, complete phase-separation could be induced as homogeneous nucleation of Ag particles followed corroborating the strong thermodynamic driving force of reaction (2) provided earlier (**Figure S10B**).

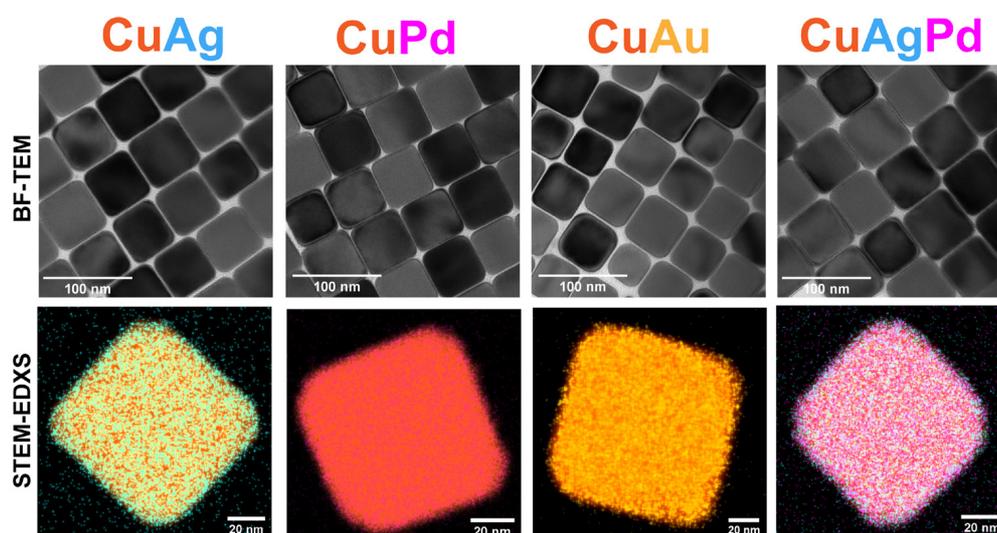


Figure S12. Cu-Ag, Cu-Pd, Cu-Au and Cu-Ag-Pd anisotropic multimetallic NSAs synthesized using the non-equilibrium synthesis.

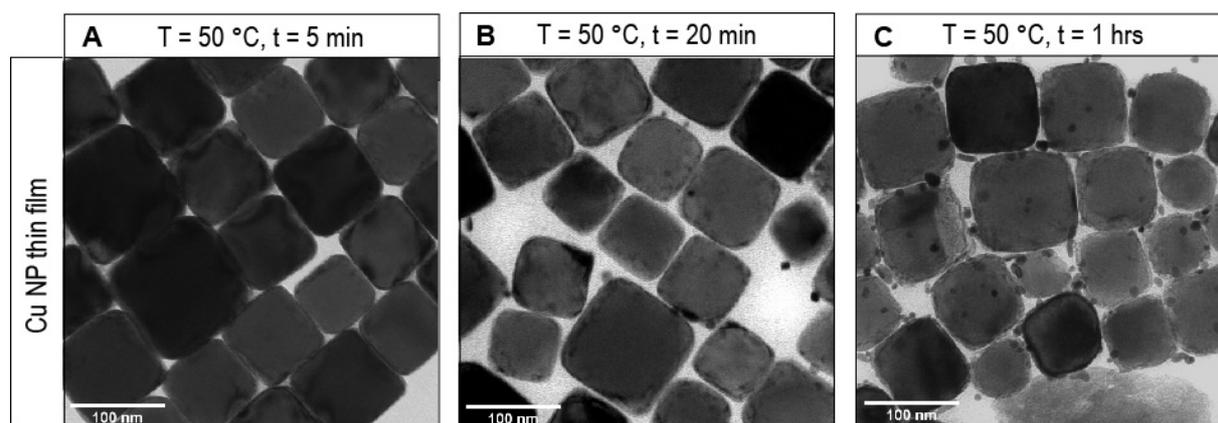


Figure S13. BF-TEM images of a morphology study as a function of reaction time of the Cu-Au system synthesized using the non-equilibrium synthesis.

Note S4. Evaluation of the electrochemical performance in the CO₂RR

S4.1. Electrochemical measurements

The CO₂RR performance of Cu-Ag NSAs were evaluated in a commercial gas-tight H-cell from Gaoss Union using constant potential mode controlled by a potentiostat (Autolab PGSTAT302N). All measurements were carried out in 0.1 M KHCO₃, which fungated as both catholyte and electrolyte (25 mL per chamber). Chambers were kept separate by means of a cation exchange (i.e., Nafion) membrane. Prior to electrochemical testing, the electrolyte was saturated with CO₂ by bubbling at 25 mL·min⁻¹ for at least 15 min. Also, during any measurement, CO₂ was bubbled through the catholyte continuously to ensure sufficient CO₂ supply during the measurement. A Pt wire was used as counter electrode for the oxygen reduction

reaction. An Ag/AgCl electrode was used as reference. All measurements were carried out at -1.1 V vs RHE. The value of the potential versus Ag/AgCl was converted to the scale of the reversible hydrogen electrode (RHE) using the equation: $E \text{ (versus RHE)} = E \text{ (versus Ag/AgCl (3 M KCl))} + 0.21 \text{ V} + 0.059 \cdot \text{pH}$. The potential was mathematically compensated for the ohmic resistance that was determined by the electrochemical impedance spectroscopy (EIS). The FEs and currents were repeatedly measured on three individual electrodes for each material evaluated.

S4.2. Collection of the liquid products

Collection of the liquid products was done at specific time intervals (i.e., 10 min) by means of a clean syringe operated through a septum as to minimize the introduction of

O₂ into the catholyte chamber and disturb the CO₂ to HCO₃⁻ equilibrium. Aliquots of 800 μL were collected in all cases.

S4.3. Quantification of the gas products

Gas products were analysed online (10 min interval) using a gas chromatography (GC, SRI Instrument 8610C) with the auto-sampling loop (1 mL) connected to CO₂ off-gas of the H-cell catholyte chamber. H₂ was

analysed using thermal conductive detector (TCD) and CO, CH₄, and C₂H₄ were analysed using flame ionization detector (FID) with a methanizer.

S4.4 Quantification of the liquid products using NMR

Quantification of the liquid products was achieved according to a previously reported method.⁶ In brief, the liquid products of all electrodes were quantified using nuclear magnetic resonance (NMR, Bruker 400 MHz AVIII HD). **Figure S15** shows a typical 1D ¹H NMR spectrum obtained for a standard solution containing typical liquid products from the CO₂RR and the internal standards (phenol and DMSO) as indicated by the arrows. The peak area ratio of a given product to that of the internal standard, as

obtained by peak fitting using MestReNova software, was used to determine the concentration of the products. Identical NMR acquisition parameters were used for all measurements. In addition, the water peak was suppressed using the solvent suppression function. The acquisition time of d1 was 5 s and the number of scans was 260. Products with peaks with chemical shifts than larger water (> 5 ppm) were quantified using phenol, all others with DMSO.

S4.5 Calculation of the faradaic efficiency

The faradaic efficiency (FE) was calculated for gas and liquid products, using $FE = \frac{nFC_iV}{jRT}$ and $FE = \frac{nFC_iV}{Q}$, respectively, where n is the number of transferred electrons to produce one molecule of product i , F is the faradaic constant, C_i is the concentration of the product as determined by GC or NMR, v is the flow rate of CO₂, P and T are the pressure (101325 Pa) and temperature (22

°C) of the gas sampled by the GC sample loop, respectively, j is the total current when sampling, R is the gas constant, V is the volume of the electrolyte, and Q is the total charge transferred to produce the target product. FEs of the liquid products were quantified taking the change in volume of the electrolyte upon aliquot collection into account.

Note S5. Supporting figures, tables and miscellaneous for the performance testing in the CO₂RR

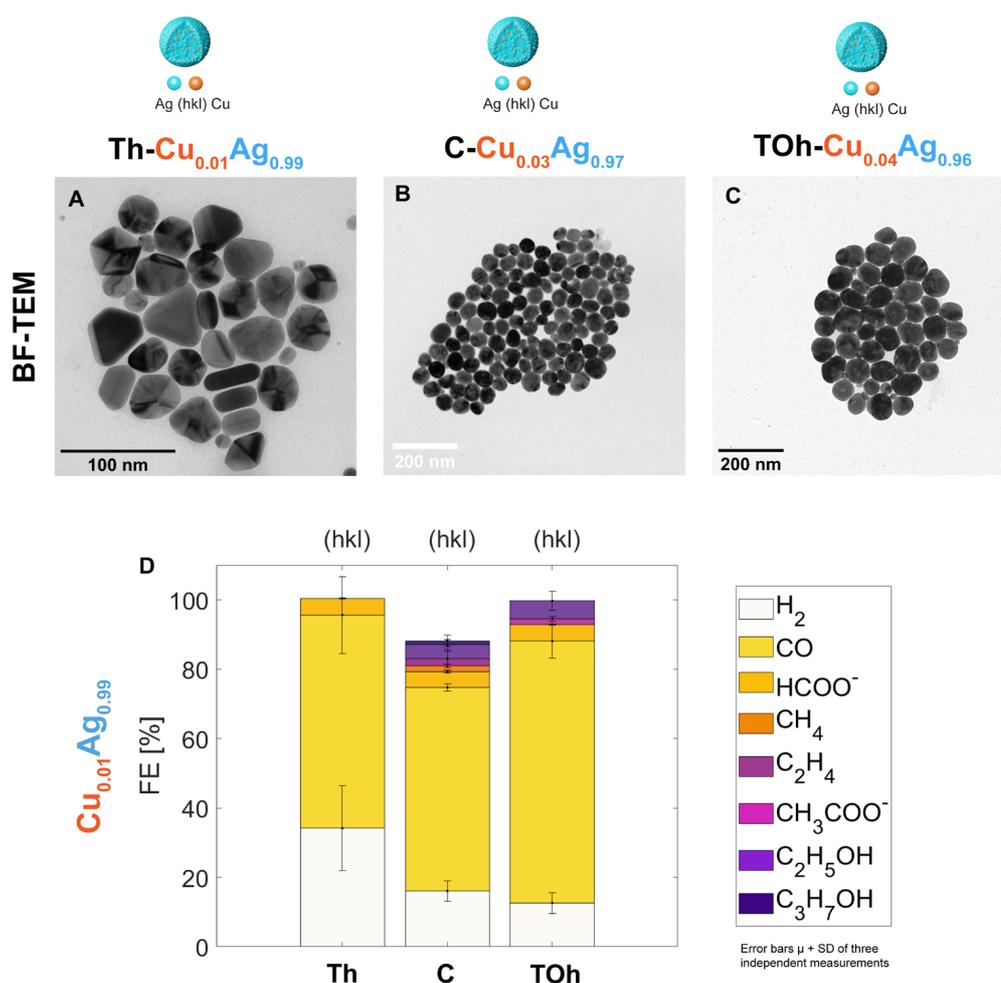


Figure S14. Near-to-complete-conversion of anisotropic Cu NCs in isotropic Ag NPs using the galvanic replacement reaction used as control experiment to confirm the catalytically active nature of galvanically deposited Ag. (A-C) Brightfield TEM images in which Th-, C- and TOh-Cu NCs thin films (4 mg) were exposed to a ~38 mM AgNO₃ in OAm precursor solution (Cu:Ag 1:3) and reacted for 24 hrs at 50, 80 and 80 °C, respectively. Ball model denotes the isotropic/undefined shape of the Ag NPs produced with the extended non-equilibrium synthesis. Bulk composition provided in the title as determined by ICP-OES. (D) Electrocatalytic screening of the as-synthesized isotropic Cu-Ag NPs, error bars represent the standard deviation of three independent measurements Control experiment showing the CO evolving nature of >95 at.% Ag NPs produced with the non-equilibrium synthesis confirming the activity of galvanically deposited Ag.

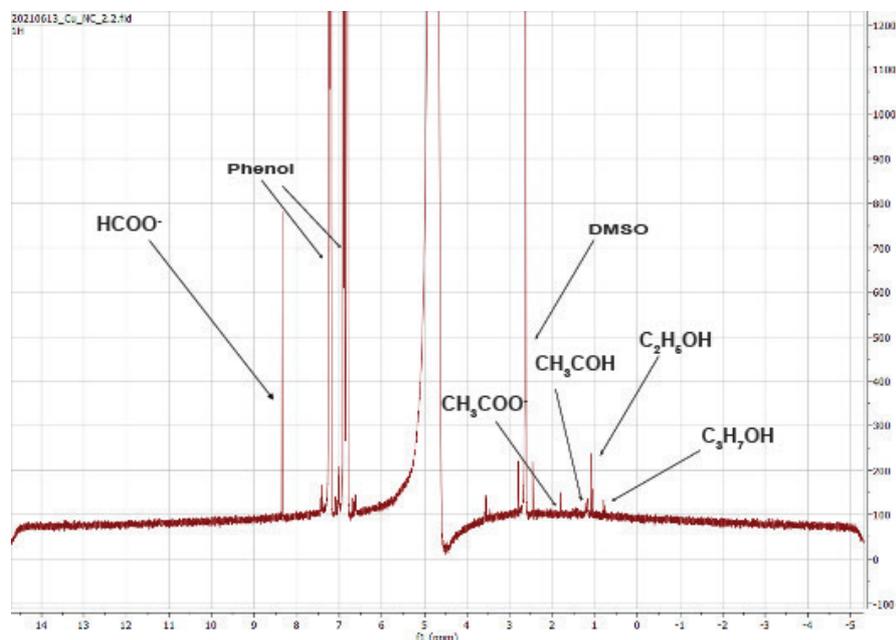


Figure S15. Representative NMR spectra obtained for a given electrolyte aliquot. Spectra obtained by averaging over at least 260 individual scans for signal-to-noise enhancement.

	H ₂	CO	HCOO ⁻	CH ₄	C ₂ H ₄	CH ₃ COO ⁻	CH ₃ CHO	C ₂ H ₅ OH	C ₃ H ₇ OH
Th-Cu NCs	46.87	4.31	6.10	29.35	11.59	0.00	0.00	3.72	0.00
σ	1.95	3.73	2.19	6.12	5.45	0.00	0.00	1.13	0.00
C-Cu NCs	27.61	2.50	11.19	11.36	31.44	4.40	0.00	5.65	2.05
σ	1.66	0.72	0.86	1.75	1.24	2.83	0.00	2.24	1.46
TOh-Cu NCs	24.57	3.40	9.88	15.62	26.11	3.15	0.00	8.32	2.89
σ	0.65	0.67	1.45	1.65	0.95	1.87	0.00	1.57	0.82
Th-Cu-Ag NSA	34.34	8.05	13.85	7.59	17.78	3.18	9.12	9.71	0.00
σ	8.60	1.57	3.25	2.26	6.48	2.28	1.97	0.78	0.00
C-Cu-Ag NSA	25.26	3.98	8.73	8.03	28.22	1.21	6.52	16.13	5.81
σ	1.81	0.80	1.81	1.55	0.60	0.19	1.45	0.93	0.84
TOh-Cu-Ag NSA	28.53	3.52	5.82	8.46	21.80	1.74	8.81	16.29	8.76
σ	0.65	0.67	1.45	1.65	0.95	1.87	1.44	1.57	0.82
Th-Ag-Cu NP	34.17	61.48	4.77	0.00	0.00	0.00	0.00	0.00	0.00
σ	12.25	11.08	0.10	0.00	0.00	0.00	0.00	0.00	0.00
C-Ag-Cu NP	16.05	58.72	4.56	1.69	2.04	0.00	0.00	4.00	1.15
σ	2.97	1.03	0.41	0.51	2.11	0.00	0.00	1.46	1.63
TOh-Ag-Cu NP	12.62	75.49	4.77	0.00	0.00	1.70	0.00	5.19	0.00
σ	3.00	4.90	0.10	0.00	0.00	0.68	0.00	2.76	0.00

Table S4. FEs of the gaseous and liquid products of the CO₂RR measured based on GC and NMR (see **Note S4**)⁶ after 10 min at -1.1 V vs RHE in 0.1 M KHCO₃. The electrolyte was saturated with CO₂ by bubbling at 25 ml·min⁻¹ for at least 15 min before starting the reaction and was continued during the reaction. Reported FEs are the average of three independent measurements reported with their associated standard deviations (σ) corresponding to the error bars in **Figure 4** in the main text.

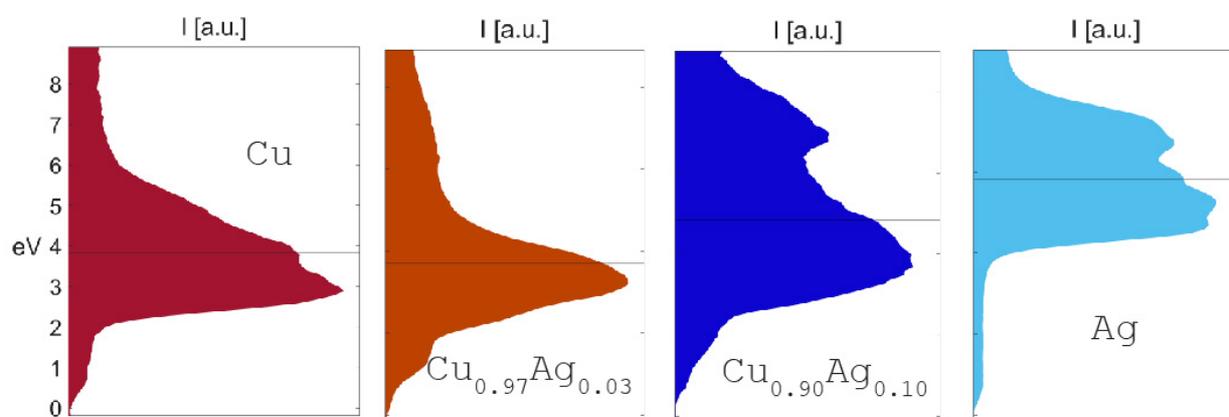


Figure S16. XPS valence band spectra of the as synthesized Th-Cu-Ag NSAs and pure Cu and Ag references. A Th-Cu NP thin film (4 mg) was exposed to a ~ 0.6 mM AgNO_3 in OAm precursor solution (Cu:Ag 21:1) and reacted for 1 and 5 min at 50°C , respectively. Solid black line indicates the point-of-gravity of the valence band as determined by numerical integration with the upper bound fixed at 9 eV indicating a shift towards the Fermi level for the 1 min reacted NSA corroborating its random alloy nature.

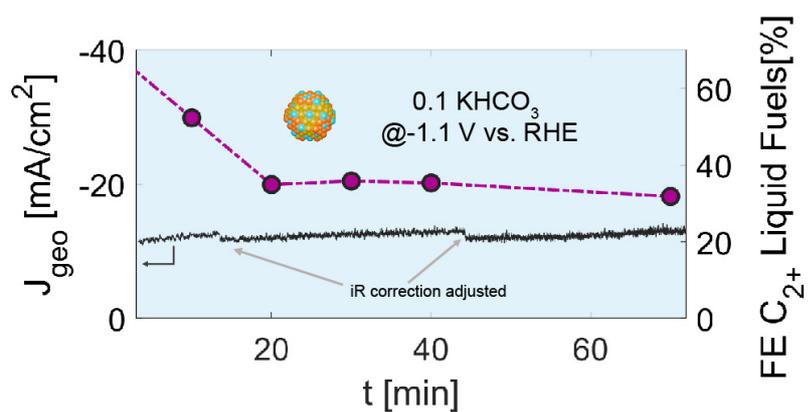


Figure S17. Stability test of the TOh-Cu_{0.97}Ag_{0.03} in CO₂ saturated 0.1 M KHCO₃ with respect to the C₂₊ liquid fuels. Increasing current density can be assigned to the enhancement in HER.

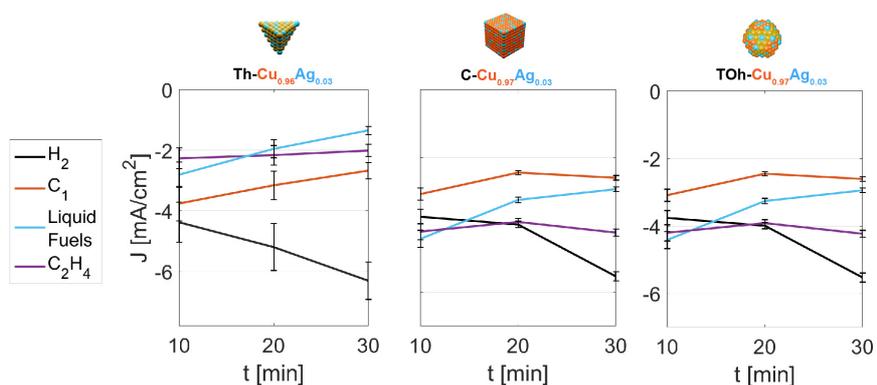


Figure S18. Evolution of the geometrical partial current densities of the anisotropic Cu-Ag NSAs upon applied potential (-1.1 V vs RHE) in CO₂ saturated 0.1 M KHCO₃.

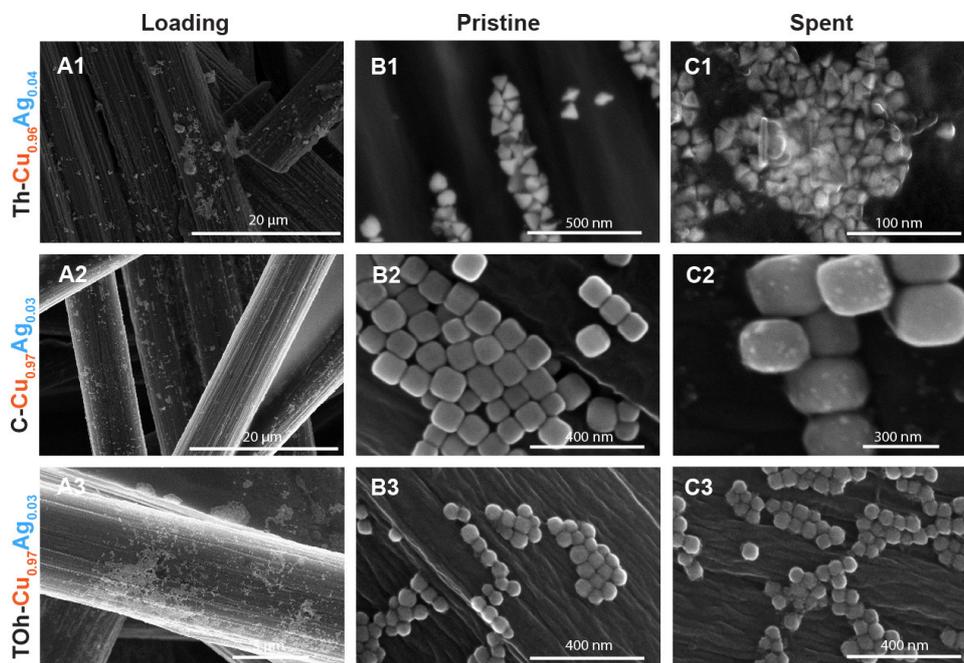


Figure S19. (A1-A3) SEM images showing the as synthesized Th-, C- and TOh-Cu-Ag NSAs on carbon paper support ($1.0 \text{ mg}\cdot\text{cm}^{-2}$) indicating good coverage of the NCs. (B1-B3) SEM images of the as-deposited Th-, C- and TOh-Cu-Ag NSAs on carbon paper support showing the pristine, smooth nature of the NC surfaces. (C1-C3) SEM images of the Th-, C- and TOh-Cu-Ag NSAs after 30 min of CO_2RR showing a roughened surface and extrusions at the particle surface indicating phase segregation.

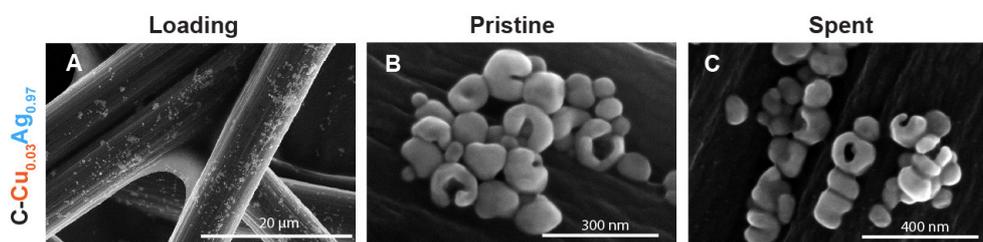


Figure S20. (A) SEM images of the loading studies of the drop-casted near-to-complete converted C-Cu-Ag on carbon paper support ($1.0 \text{ mg}\cdot\text{cm}^{-2}$) showing a good coverage of the NCs. (B) SEM image of the as-deposited near-to-complete exchanged Cu-Ag NPs. (C) SEM image of the near-to-complete exchanged Cu-Ag NPs after 30 min of CO_2RR not showing any extrusions.

	H ₂	CO	HCOO ⁻	CH ₄	C ₂ H ₄	CH ₃ CO O ⁻	CH ₃ CH O	C ₂ H ₅ OH	C ₃ H ₇ OH
Th-Cu- Ag NSA 10 min	34.34	8.05	13.85	7.59	17.78	3.18	9.12	9.71	0.00
σ	8.60	1.57	3.25	2.26	6.48	2.28	1.97	0.78	0.00
Th-Cu- Ag NSA 20 min	40.79	7.08	11.56	6.12	16.94	1.79	5.78	7.74	0.00
σ	9.12	1.30	2.34	1.85	4.17	1.16	0.80	1.29	0.00
Th-Cu- Ag NSA 30 min	49.50	6.72	9.26	4.97	15.77	0.39	2.44	5.77	1.93
σ	10.09	0.98	1.43	1.73	5.64	0.17	1.05	1.81	1.61
C - C u - Ag NSA 10 min	25.26	3.98	8.73	8.03	28.22	1.21	6.52	16.13	5.81
σ	1.81	0.80	1.81	1.55	0.60	0.19	1.45	0.93	0.84
C - C u - Ag NSA 20 min	26.82	3.57	7.40	5.49	26.30	0.98	3.74	12.90	4.29
σ	4.23	0.47	1.64	1.47	4.04	0.21	0.77	0.37	0.75
C - C u - Ag NSA 30 min	37.14	3.37	9.05	5.09	28.42	1.02	3.78	10.93	4.04
σ	8.65	0.18	0.48	1.52	2.98	0.18	0.68	1.11	0.85
TOh- Cu - Ag NSA 10 min	28.53	3.52	5.82	8.46	21.80	1.74	8.81	16.29	8.76
σ	1.75	0.23	0.76	3.93	2.66	0.47	1.44	1.90	1.41
TOh- Cu - Ag NSA 20 min	29.12	3.49	7.24	7.91	25.43	1.42	5.10	12.20	6.01
σ	0.85	0.28	1.89	3.96	2.83	0.15	1.07	1.38	0.08
TOh- Cu - Ag NSA 30 min	31.70	3.20	7.43	7.25	24.74	1.17	4.82	12.37	5.53
σ	2.17	0.32	1.49	3.84	2.83	0.19	1.79	0.44	1.04

Table S5. FEs of the gaseous and liquid products of the CO₂RR measured with GC and NMR (see section S2)⁶ after 10, 20 and 30 min at -1.1 V vs RHE in 0.1 M KHCO₃. The electrolyte was saturated with CO₂ by bubbling at 25 ml·min⁻¹ for at least 15 min before starting the reaction and was continued during the reaction. Reported FEs are the average of three independent measurements reported with their associated standard deviations (σ) corresponding to the error bars in **Figure 5** in the main text.

Note S6. Supporting tables theory-guided experiment

Atomic structures from the density functional theory simulations as well as scripts necessary for reproducing the analysis have been made freely available at <https://nano.ku.dk/english/research/theoretical-electrocatalysis/katlabdb/co2-reduction-on-ag-cu-pd/>.

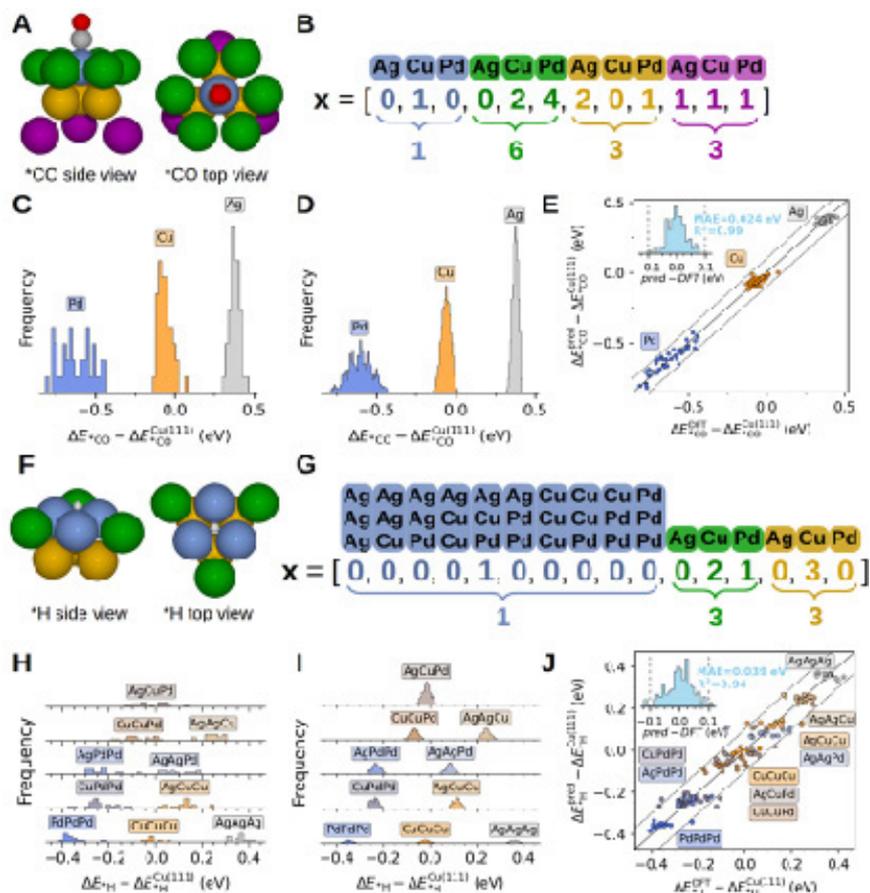


Figure S21. Overview of the machine learning model used to simulate *CO and *H adsorption energies on fcc(111) surface sites with arbitrary neighbors. (A) Structure used to account for neighboring atoms for atop *CO adsorption including adsorption ensemble atoms (blue), surface atoms (green), subsurface atoms (orange), and 3rd layer atoms (magenta). (B) Example of features used as input for learning the adsorption energy where the constituent elements are counted in groups corresponding to the colors in (A). The numbers in each group must sum to the number of atoms of that group. (C) Distribution of the 126 DFT simulated *CO adsorption energies used for training the linear model. The colors correspond to the adsorbing element. (D) Predicted distribution of *CO adsorption energies using the linear model. (E) Parity plot illustrating the performance of the *CO linear model on the training set. (F) Structure used to account for neighboring atoms for fcc hollow *H adsorption with color coding as in (A). (G) Example of features used for *H adsorption. Same as for (B), except that the adsorption ensemble atoms are one-hot encoded. (H) Distribution of the 160 DFT simulated *H adsorption energies used for training. The colors correspond to the adsorbing fcc hollow site ensembles. (I) Predicted distribution of *H adsorption energies using the model. (J) Parity plot illustrating the performance of the *H linear model on the training set.

*CO adsorption				
Adsorption ensemble		Ag	Cu	Pd
Intercept		0.405785	-0.042545	-0.819863
Surface element	Ag	0	0.010471	0.013992
	Cu	-0.002754	0	0.011118
	Pd	0.002621	0.010323	0
Subsurface element	Ag	0	-0.013674	0.057961
	Cu	-0.001988	0	0.102745
	Pd	-0.007844	-0.034921	0
3rd layer element	Ag	0	-0.008940	0.003461
	Cu	-0.002469	0	0.001129
	Pd	-0.019618	-0.004030	0
*H adsorption				
Adsorption ensemble	AgAgAg	0.360826		
	AgAgCu	0.241141		
	AgAgPd	0.085678		
	AgCuCu	0.113763		
	AgCuPd	-0.015389		
	AgPdPd	-0.230785		
	CuCuCu	-0.020279		
	CuCuPd	-0.067306		
	CuPdPd	-0.238576		
	PdPdPd	-0.349699		
Surface element	Ag	-0.001216		
	Cu	-0.002959		
	Pd	0.004175		
Subsurface element	Ag	0.000729		
	Cu	0.011141		
	Pd	-0.011870		

Table S6. Linear parameters for predicting adsorption energy distributions relative to Cu(111). All values have units of eV.

	H_2 , Liquid Fuels	C_2H_4	
	2		
C-Cu₇₉Ag₂₁ NSA 10 min	44.7	23.3	17.2
σ	5.18	0.93	2.50
C-Cu₇₉Ag₁₆Pd₅ NSA 10 min	25.8	27.7	30.7
σ	4.71	1.42	4.51
C-Cu₇₉Pd₁₆Ag₅ NSA 30 min	64.4	13.1	10.9
σ	13.1	5.18	3.96

Table S7. FEs of CORR and HER products obtained with GC and NMR (see **Note S2**)⁶ averaged over 30 min at -1.1 V vs RHE in 0.1 M KHCO₃. The electrolyte was saturated with CO₂ by bubbling at 25 ml·min⁻¹ for at least 15 min before starting the reaction and was continued during the reaction. Reported FEs are the average of three independent measurements reported with their associated standard deviations (σ) corresponding to the error bars in **Figure 6C** in the main text.

	CO ₂ RR products	CORR products
C-Cu₇₉Ag₂₁ NSA molar yield	0.76	0.56
Yield error	0.064	0.052
C-Cu₇₉Ag₁₆Pd₅ NSA molar yield	0.72	0.61
Yield error	0.055	0.069
C-Cu₇₉Pd₁₆Ag₅ NSA molar yield	0.48	0.36
Yield error	0.11	0.097

Table S8. Molar yields of CO₂RR and CORR products, which correspond to the molar rate of a product divided by the sum of the molar rates of all products as based on the FEs reported in **Table S7** and total current densities of C-Cu₇₉Ag₂₁, C-Cu₇₉Ag₁₆Pd₅ and C-Cu₇₉Pd₁₆Ag₅ (14.9, 15.0 and 28 mA cm⁻², respectively). Error propagation of the standard deviations in **Table S7** and the molar yields offer the data points and error bars in **Figure 6A** in the main text.

Note S7. Supporting figures, tables and miscellaneous for Materials and Methods

The galvanic exchange reaction was performed in OAm for its ability to act both as solvent and surfactant and particularly for its ability to form complexes with metal ions to facilitate the exchange.^{8,9} However, OAm can also fungate as reducing agent and due to the positive interfacial energy between

Cu and Ag, it is important to exclude the latter's homogenous nucleation. Therefore, we fixed the dissolution temperature of the precursor at 50 °C as above it, homogenous nucleation could not be excluded (**Figure S22**).

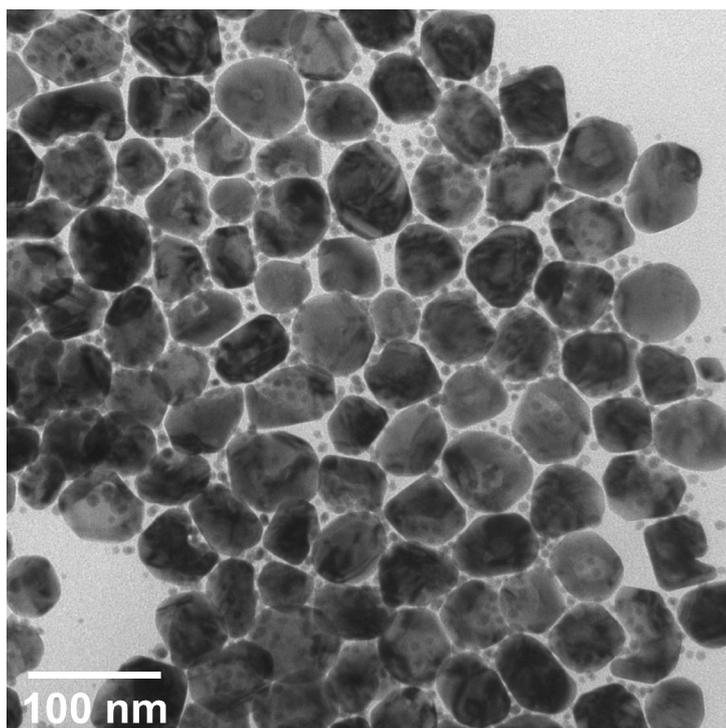


Figure S22. TEM image depicting the conventional galvanic exchange reaction (2 hrs 80 °C) of C-Cu NPs (500 μ g) using a 0.667 mg/mL AgNO_3 in OAm precursor solution prepared by dissolving the Ag salt at 80 °C instead of 50 °C. Homogenous nucleation of Ag NPs can be observed in combination with galvanic exchange reaction.

S8. References.

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Chapter 6

Scalable synthesis of Cu(Ag) oxide clusters for the highly selective electrochemical conversion of CO₂ to acetaldehyde

Preprint version: submission of this section has been delayed to enable incorporation of in situ data XAS studies to be collected at the SuperXAS beamline of the Swiss Light Source of the Paul Scherrer Institute in March 2023.

Edit: caption numbers of figures, tables, and equations were edited to match the thesis chapter number.

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Abstract

The electrochemical conversion of CO₂ to the base chemical acetaldehyde offers a sustainable and green alternative to the Wacker process. However, current electrocatalyst cannot compete due to their limited selectivity for acetaldehyde resulting in low energy efficiencies. Here, we report a series of Cu(-Ag) oxide cluster catalysts (~ 1 nm) immobilized on various hetero-atom doped carbonaceous supports produced via spark ablation of Cu (and Ag) electrodes, that achieve an acetaldehyde selectivity as high as 92% a mere 560 meV from the equilibrium potential. Further, the catalyst demonstrated reusability as it retained performance over 30 hrs during a stress test which included repeated start-stop cycles (3x). EXAFS and XANES post catalysis showed that the initial oxide clusters had completely reduced under cathodic potential and had retained its metallic nature even after air exposure explaining its recyclability.

6.1. Main

The electrification of the chemical industry is needed for a complete and unambiguous energy transition.¹ Many processes depend heavily on the petrochemical industry, which are neither green nor energy efficient. One such process is the well-known homogeneously catalyzed production of the base chemical acetaldehyde, used in the production of drugs, dyes, and fragrances.² Commercialized under the name of the Wacker process, the PdII catalyzed oxidation of ethylene to acetaldehyde supplies the vast majority of the global acetaldehyde market worth well over 1.2B USD.^{3,4,5} This process not only uses a cracking product, ethylene, it requires large amounts of hydrochloric acid to achieve required conversions.^{4,5} Although reliable, overcoming the limitations of this resource and energy intensive process is needed for a sustainable supply in the long term. Attempts have been made to heterogeneously convert ethylene to acetaldehyde using Pd-Cu zeolite catalysts fixing the acid sites on the support significantly reducing the environmental toll of the process.⁶ However, such methods

still rely on the petrochemically sourced ethylene and selectivity's are not yet at par. Here we propose a fully green, carbon neutral process instead to selectively produce acetaldehyde electrochemically using CO₂ as a resource.

The electrochemical CO₂ reduction reaction (CO₂RR) is a promising technology of industrial relevance that kills two birds with one stone: 1) it has the ability to significantly reduce our CO₂ footprint by fixating it in useful products and 2) it tackles the intermittence problem associated with renewable energy as it offers to store energy long-term in chemical bonds.⁷ However, it comes with significant challenges.⁸ In particular, the more valuable products that require carbon-carbon coupling such as ethanol, ethylene and acetaldehyde can only be produced on Cu.⁹ Moreover, polycrystalline Cu catalyzes the reaction of no less than 16 individual products resulting in low selectivity's for specific products and thus large energy losses.¹⁰ Previous works have shown that on bulk Cu specific active sites have activities for specific products, i.e. Cu(111) surfaces

produce majority CH₄, Cu(100) majority ethylene and Cu(110) majority oxygenates including ethanol.^{11,12,13,14} Further, defects, steps, kinks- and edge-sites have also shown preferentiality towards specific pathways.^{15,16,17} Therefore, tremendous efforts have gone out to engineer Cu electrodes to expose those facets, defects and or sites to produce specific products with unitary selectivity's.^{18,19,20,21,22} Also, attempts have been made to mix in other elements in the form of homogeneous Cu alloys and change the catalyst electronic nature.^{23,24,25,26} Unfortunately, for any of these attempts, selectivity's >50% have seldomly been reported.^{20,26}

Recently, Cu clusters <2 nm have been proposed as an opportunity to improve the

definition of the catalyst active site²⁷ and has successfully enhanced the selectivity towards ethanol to industrial relevance (>90%).^{28,29,30} Here, we report a scalable synthesis of Cu(Ag) oxide clusters <2 nm with 92% selectivity for the acetaldehyde and only 560 meV from the equilibrium potential. Further, by excluding the effect of support,^{28,29,30} we show that cluster atomicity is key in differentiating between pathways. This offers a new catalyst design strategy for the selective electrosynthesis of base chemicals.

6.2. Catalyst synthesis and characterization

The catalyst synthesis is depicted in **Figure 35**. In brief, a power source is applied to two hollow metal electrodes (Cu-Cu or Cu-Ag) in between a gap through which a carrier gas (Ar) is flowed (**Figure 35A**). Upon the breakdown of the potential, the gas is briefly ionized ($\sim\mu\text{s}$) and becomes conductive creating a plasma pulse producing temperatures $>20,000\text{ K}$ (similar to the workings of a spark plug).³¹ By controlling the gas flow rate, repetition frequency, and energy per spark, the electrode ablation rate can be controlled producing an aerosol of clusters of well-defined size and composition.^{32,33} However, the high degree of undercoordination of the cluster produced makes them extremely susceptible to agglomeration. Therefore, a selection of heteroatom doped carbonaceous supports with strong cluster-support interaction, i.e.,

graphene oxide and N-doped carbon black nanoparticles (GO-, NCB-NPs) synthesized in-house at $>1\text{ g}$ scale,^{34,35} were used for successful immobilization. Finally, cathodes were fashioned from a commercial gas diffusion layer (GDL) air brushed with an optimized loading of carbonaceous support, and used as filters to collect the clusters from the aerosol stream (**Figure 35B**). For information regarding the synthesis of the catalyst supports, see **Note S1** and **Figure S1** of the Supporting Information. For details on the cluster production see **Note S2** and **Figure S2-S4**. For details on the cluster immobilization see **Note S3-S4** and **Figure S5-S11**. For details on the cathode production process see **Note S4** and **Figure S12-S15**.

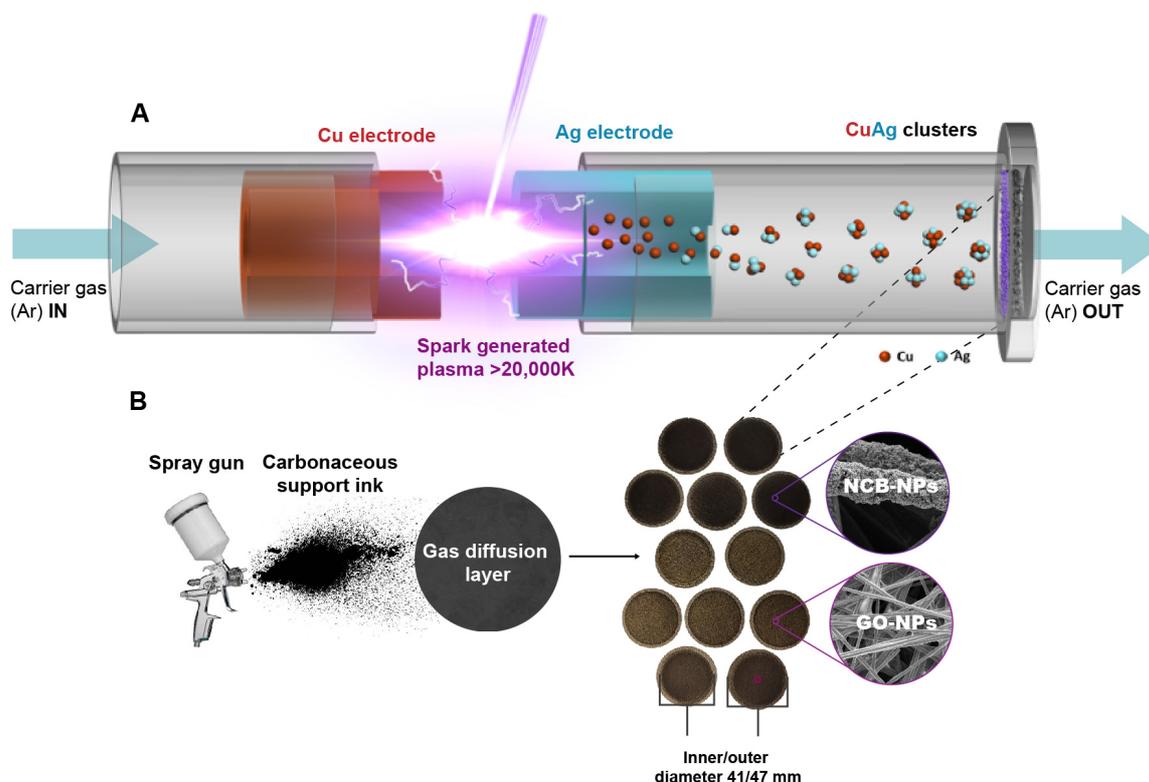


Figure 35. Schematic of the spark ablation (A) and immobilization (B) of Cu(-Ag) oxide clusters on heteroatom doped carbonaceous support GDL composites.

Four ~0.1wt% metal catalysts were produced and denoted Cu(-Ag)-GO (graphene oxide) and Cu(-Ag)-NCB (N-doped carbon black). We investigated the size of the clusters produced in the aerosol with a differential mobility analyzer (DMA) and the state of the immobilized clusters using scanning transmission electron microscopy high-angle annular darkfield (STEM-HAADF) imaging (**Figure 36**, **Figure S5-S9**). The average Cu and Cu-Ag cluster size of 1.6 and 1.5 nm measured with the DMA (**Figure S3-S4**) was confirmed with STEM-

HAADF with the FWHM of Cu, respectively, Cu-Ag clusters of 1.5 ± 0.5 and 1.4 ± 0.3 nm (**Figure 36A-B**, **S6** and **S8**). Interestingly, when N-edge functionalized graphene and multiwalled carbon nanotubes were used as supports, cluster agglomeration was observed (**Figure S7** and **S9**). The strength of the cluster-support interaction was not a measure of the support work function (**Figure S10**). Instead, both the crystallinity and absence of specific ligation sites explained the difference (**Figure S11-S12**). STEM-energy dispersive X-ray

spectroscopy (EDXS) was used to confirm the Cu, respective, Cu-Ag nature of the STEM-HAADF identified clusters (**Figure 36C-D**) and to determine the average composition of the bimetallic clusters at $\text{Cu}_{84}\text{Ag}_{16}$ (at. %), which was later confirmed with X-ray photoemission spectroscopy (XPS, **Figure S16**). XPS further pointed towards the complete oxidation of the clusters to CuI and AgI after 7 days (directly after deposition some CuI species could still be observed, which is an effect of purity of the Ar used as carrier gas, **Figure S16**). The coordination structure and oxidation state of the Cu atom in the as-synthesized catalysts was further investigated with X-ray absorption spectroscopy (XAS, **Figure 36E-H**). The pseudo radial distribution function extracted from the extended X-ray absorption fine structure (EXAFS) spectra excluded the presence of Cu_2O , $\text{Cu}(\text{OH})_2$ and or metallic Cu species corroborating the XPS results. Further, a Cu-Cu scattering event in the second coordination shell of CuO could be discerned to a higher and lesser degree for the NCB-, respectively GO-based catalysts (**Figure 36E-F**). The Cu coordination numbers of 3 ± 0.6 , respectively $\text{Cu } 2 \pm 0.4$ (vs 4 in the bulk) agrees with the small particle size and further indicates a slightly stronger support interaction with

GO than with NCB. This is most likely due to the higher density of ligation sites on the GO-support (heteroatom content $\sim 50\%$ vs $\sim 30\%$ for NCB). Further, by considering Cu phthalocyanine (CuPc) and Cu acetylacetonate ($\text{Cu}(\text{acac})_2$) as a reference, the ligation site of the clusters could be probed showing a strong contribution from Cu-N and Cu-O bonds in the first coordination sphere. In the case of Cu-NCB, these are most likely pyrrolic and pyridinic N and NO_x . For the Cu-GO, this is either from NO_x or C=O or COO^- species. Linear combination analysis of the near edge structure (XANES) spectra puts their relative contribution $>28\%$ (**Figure 36G-H**). We note that XANES analysis is limited by the lack of suitable references as all references available are of bulk materials, which are known to differ strongly by reduction of particle size.⁴⁵ Therefore, ongoing research is going towards the simulations of XANES spectra of CuO, Cu₂O and Cu clusters in the relevant size ranges to substitute the bulk reference spectra and improve our understanding of the cluster-support interaction.

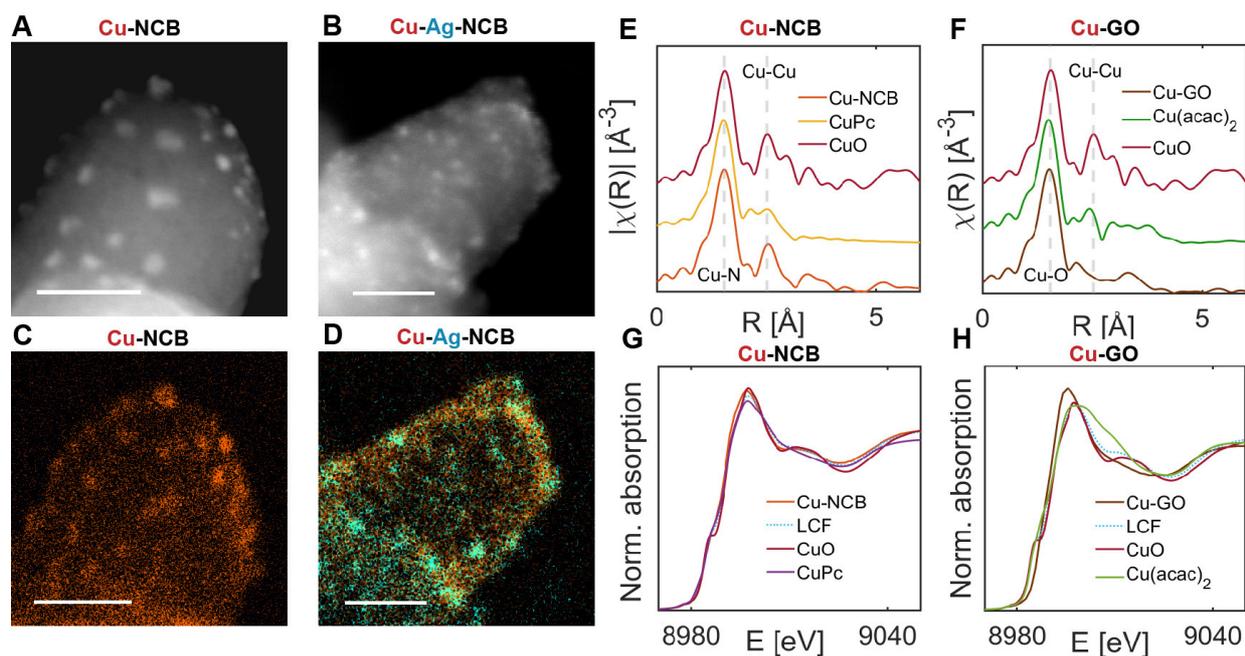


Figure 36. Advanced characterization of the as-synthesized Cu(-Ag) oxide clusters immobilized on heteroatom doped carbonaceous support. (A-B) STEM-HAADF images of the Cu and Cu-Ag-NCB catalyst. (C-D) STEM-EDXS elemental maps of the images in A and B showing Cu in orange and Ag in turquoise. Scale bars indicate 10 nm. (E-F) Pseudo radial distribution functions extracted from the EXAFS spectra of the Cu-NCB and -GO catalyst, respectively. CuO, CuPc and Cu(acac)₂ were used as a reference. (G-H) XANES spectra of the Cu-NCB and -GO catalyst, respectively. A linear combination fit (LCF) of the CuO and CuPc and Cu(acac)₂ reference spectra puts the contribution of the ligation sites to catalyst structure at 48% (Cu-GO) and 28% (Cu-NCB), respectively.

6.3. Electrochemical screening of the Cu(-Ag) oxide cluster carbonaceous support composite electrodes.

We subjected our Cu(-Ag)-NCB/GO GDL composites to a series of electrochemical screening tests to determine their activity in CO₂RR. Electrochemically speaking, the cluster support composites differ in two major ways: 1) NCB and GO are respectively a good and poor CO₂RR electrocatalyst for the production of CO,^{36,37} which could explain differences in performance by means of tandem-effects upon the introduction of the clusters³⁸ and 2) have different support-cluster interactions of varying strength, i.e. via N- and NO_x-ligation sites in the case of NCB and C=O,OH and COOH groups for GO, respectively, which may affect the performance, i.e. similarly to what has been observed for atomically precise ligand capped Au clusters.³⁹ Further, since support effect have been invoked to explain performance differences in Cu₃₋₄-cluster-NCB/GO based composites in the past,^{28,29} we deemed it of utmost importance to carefully deconvolute the contribution of the support from the cluster based composites. Therefore, before we investigated the effect of the introduction of clusters, we first determined the activity of the supports themselves.

As expected, the NCB catalyst showed

good selectivity (>90%) for CO, even at modest overpotential of 600 meV (**Figure S20A**) whereas the GO support was poorly selective for CO₂RR and produced H₂ as a majority product at all potentials tested (**Figure S20B**). Some HCOO⁻ could be detected in the catholyte but never more than 20% of the current was directed towards this product. Further, even though several acid washing steps had been performed, trace amounts of Mn leftover from the graphite oxidation step could not be fully excluded, which may explain the observed CO as a minority product.⁴⁰ Nevertheless, the strongly differentiating CO activities (2 mA cm⁻² vs 40 μA cm⁻² for NCB and GO, respectively) ensures the exclusion of CO-coverage effects in case of the cluster-GO composites. Finally, material degradation for potentials more cathodic than -1.1 V vs RHE could be observed for either support offering the upper limit for the potential screening of the clusters-based composites (**Figure S21**).

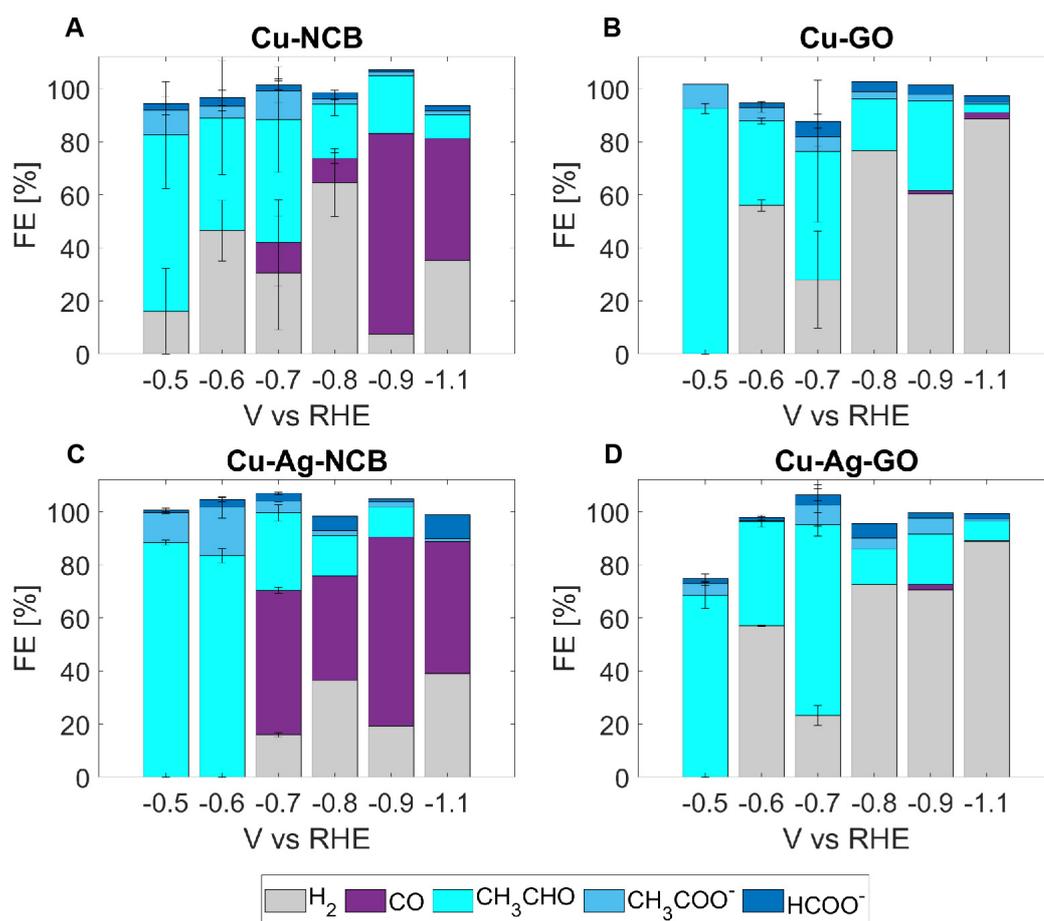


Figure 37. (A-B) Selectivity screening of Cu-NCB and Cu-GO GDL composites, respectively. (C-D) Selectivity screening of Cu-Ag-NCB and Cu-Ag-GO GDL composites, respectively. All electrochemical reactions were carried out in CO_2 saturated 0.1M KHCO_3 electrolyte in Nafion® membrane separated H-cell. Chronoamperometry was carried out in a cathodic potential window of -0.5 to -1.1 V vs RHE (half-cell potential) with 100 and lastly 200 meV increment (iR-drop corrected) using an Ag/AgCl reference electrode. A Pt foil (1 cm^2) was used as counter electrode. Gaseous products were quantified via gas chromatography. Liquid products were detected using $^1\text{H-NMR}$ and quantified using the Kuhl et al. protocol.¹⁰ For the lower overpotential experiments (<800 meV), liquid products were collected for at least 3 hrs for reasonable statistics. For all other potentials, FEs were averaged for a minimum of 30 min. Error bars represent standard deviations of at least two independent measurements. The less than 100% FE observed for the Cu-Ag-GO-GDL at -0.5 V vs RHE stems from unquantifiable gaseous products due to dilution of the CO_2 stream (H_2 most likely).

With the activity of the supports quantified, the effect of the introduction of Cu(-Ag) clusters could be investigated. **Figure 37** shows the chronoamperometry experiments performed to determine the selectivity as function of potential, support and type of cluster. Independently of the support (**Figure 37A-B**), acetaldehyde could be observed at any potential between -0.5 and -1.1 V vs RHE upon the introduction of Cu oxide clusters. As well as acetate, two electron transfers less reduced than acetaldehyde, as a minor product (<10%) and formate (<10%) at higher overpotential. Only for the NCB based samples was CO a notable product and especially at high overpotential which stems clearly from the support activity. Further, especially at lower overpotentials (more cathodic than -0.8 V vs RHE), significant acetaldehyde selectivity's could be reported. For Cu-NCB-GDL at -0.5 V vs RHE, an acetaldehyde selectivity of $66\pm 20\%$ was determined. At the same potential, for Cu-GO, the FEs was as high as $92\pm 2\%$. For the NCB based catalyst enhancement of the overpotential by 100-200 meV, put the acetaldehyde FEs in the 40-50% range. Interestingly, for Cu-GO, the

selectivity decreased to around 30% at -0.6 V vs RHE to then increase to nearly 50% at -0.7 V vs RHE. We assign this to a phase-transition of the GO support at -0.6 V vs RHE (i.e. -1.2 V vs Ag/AgCl) absent for NBC.⁴¹ Further enhancement of the overpotential reduced the acetaldehyde selectivity independent of the support but remained >10% upto -0.9 V vs RHE. Interestingly, upon the introduction of 8 at.% Ag into the clusters, a similar trend could be observed as for pure Cu oxide clusters (**Figure 37C-D**). However, for the Cu-Ag-NCB catalyst, at -0.5 V vs RHE the selectivity towards acetaldehyde was as high as $88\pm 1\%$ and $83\pm 3\%$ a 100 meV more cathodic. The C_{2+} selectivity was approximately 100% for either potentials. For the Cu-Ag-GO catalyst, again the selectivity dropped at -0.6 V vs RHE but more importantly, a ~70% selectivity could be maintained at -0.7 V vs RHE.

6.4. Resistance against potential cycling

An optimal catalyst is not only selective, it remains stable for long hours of operation and is indifferent to start-stop cycles.⁴² Therefore, we subjected one of our catalysts, the Cu-NCB GDL catalyst, to a stress test (**Figure 38**). First, we took a previously screened catalyst sample, exposed it to air for several hours, and then ran the operation again (**Figure 38A**, cycle 2). Notably, neither the current density ($200 \mu\text{A cm}^{-2}$) nor the acetaldehyde selectivity (40-50%) changed. We then repeated this process for a second time but extended the reaction time 10-fold and let it run for nearly 30 hrs (**Figure 38A**, cycle 3). After an initial stage of equilibration (first 3 hrs), a stable performance was obtained equivalent to the first and second cycle. To determine the reason of this remarkable resistance against start-stop cycles, we investigated the nature of our catalysts post-catalysis using EXAFS and XANES (**Figure 38B-E**). Interestingly, the EXAFS spectra showed that the clusters had not only reduced fully upon applied potential,⁴³ they had retained their metallic state even after exposure to air and independently of the support, i.e.

NCB or GO (**Figure 38B-C**). Similar to the pre-catalysis samples, Cu-N and Cu-O contributed significantly to the overall signal, which was confirmed by XANES linear combination analysis, and is suggested to originate from the cluster-support interaction (**Figure 38D-E**). However, post catalysis, the majority of the EXFAS intensity originated from a Cu-Cu single scattering event of metallic Cu for either catalyst. Fitting of the Cu coordination shell estimates a Cu-NCB, -GO catalyst Cu coordination number of 5.6 ± 0.9 and 4.8 ± 0.8 (versus 12 in the bulk), respectively.⁴⁴ We translate that into an average particle size of 1.0 and 0.9 nm,^{45,46} respectively, which is excellent agreement with a reduced CuO particle size of 1.6 nm (**Figure 36**). We, therefore, conclude that the recyclability of the Cu(-Ag) cluster-supported catalysts, is a direct result of their in situ transformation towards a metallic species, and their subsequent resistance towards oxidation.⁴⁷

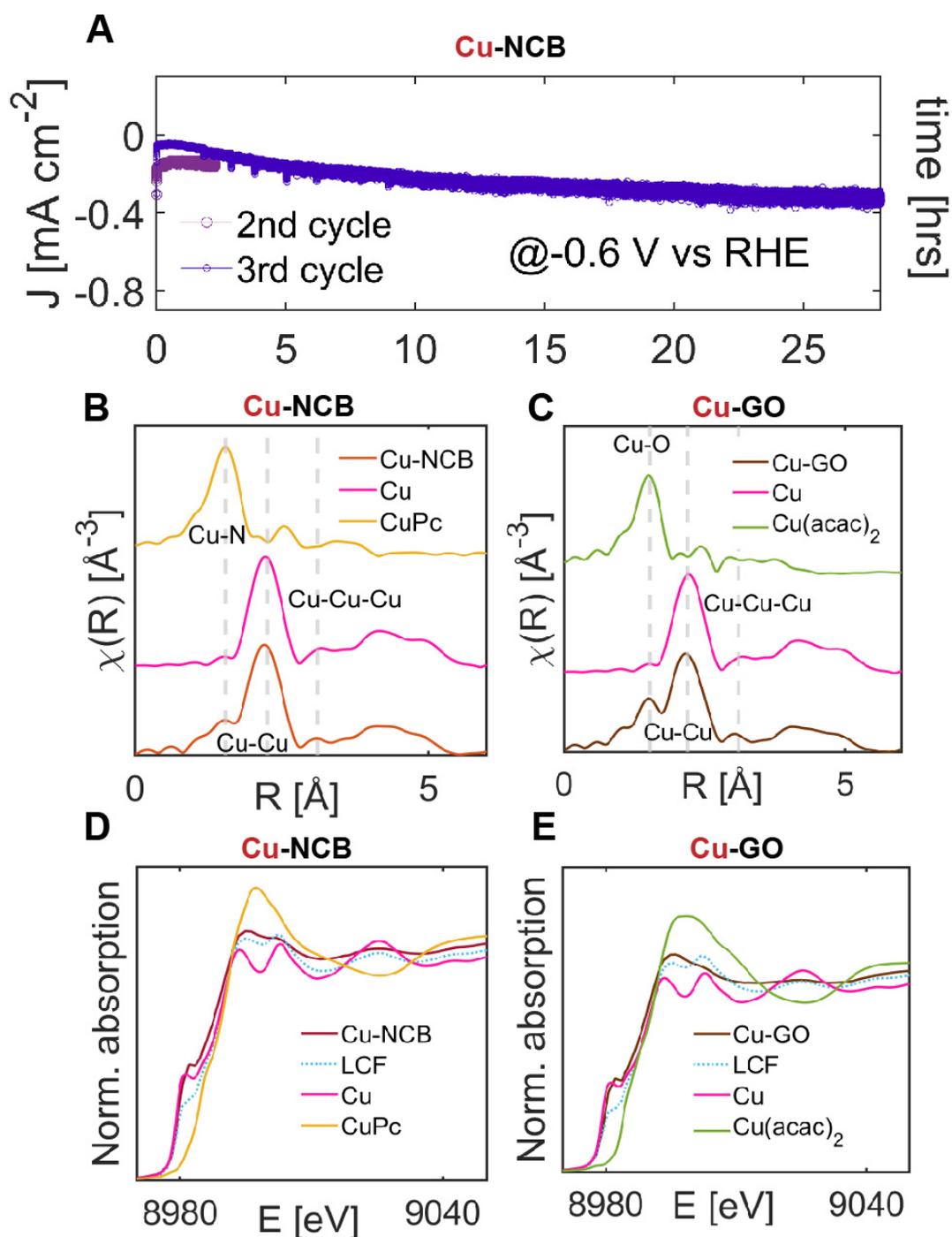


Figure 38. (A) Stress test of the Cu-NCB GDL at -0.6 V vs RHE in 0.1 M KHCO_3 . (B-C) Pseudo radial distribution functions extracted from the EXAFS spectra of the Cu-NCB and -GO catalyst, respectively, after catalysis and exposure to air. Cu, CuPc and Cu(acac)₂ were used as a reference. (D-E) XANES spectra of the Cu-NCB and -GO catalyst, respectively, after catalysis and exposure to air. A linear combination fit (LCF) of the Cu and CuPc and Cu(acac)₂ reference spectra puts the contribution of the ligation sites to catalyst structure at 40% and 30%, respectively.

6.5. Conclusions

We have developed a scalable production and immobilization method of bimetallic Cu-based clusters of sizes ~ 1 nm. We show that such composite materials have unique catalytic properties and show high selectivity towards acetaldehyde ($>90\%$) in the electrochemical conversion of CO_2 . We show that our catalysts retain their in situ formed metallic nature post catalysis, and demonstrate that this feature offers resistance against potential cycling. We

propose our catalyst production method as a platform technology that may offer researchers an entirely new class of catalyst to screen for activity in various electrochemical reaction such as water splitting, oxygen evolution, nitrogen reduction etc.

6.6. References

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6.7. Supporting Information

Note S1. Experimental part related to support synthesis

As catalyst support, a selection of materials was chosen based on their activity in the CO_2RR , overall conductivity, wettability, high-surface area, diverse heteroatom functionalities, scalability and overall economics from inhouse developed¹ as well as the literature inspired syntheses (**Figure S1**).^{2,3, 4,5,6} In brief, the materials produced which were N-edge functionalized (**Figure S1A,B**) were synthesized by mixing graphene nanoplatelets (Graphene Supermarket AO-4, 1 g) or multiwalled carbon nanotubes (PlasmaChem GmbH, 1g) with urea (Sigma Aldrich >99%, 3 g) and ball milled at 500 rpm for 48 hr at 20:1 ball (ZrO_2) to reactant mass ratio under nitrogen atmosphere.^{5,6} The products were washed and collected in i-PrOH reaching a concentration of 30 mg mL⁻¹. The N-doped carbon black based material was synthesized via a protocol adapted from Yang et al. (**Figure S1C**).⁴ In brief, Vulcan carbon black (FuelCellStore, 900 mg) was oxidized by means of mixing with an aqueous HNO_3 solution (Sigma Aldrich $\geq 65\%$, 30 mL) and heated to 80 °C whilst stirring under reflux for 3 hrs. The oxidized carbon black was collected with

50 mL of water and washed until neutral pH ~ 6.8 was reached. The washed product was dried overnight under vacuum of which 150 mg was mixed with urea in a mortar (Sigma Aldrich >99%, 1.5 g). The mixture was placed in a ceramic boat and heated to 800 °C in 80 min, kept for 60 min at 800 °C and then cooled naturally to r.t. all under Ar atmosphere. The 500 mg of NCB-NP were washed and collected with i-PrOH reaching a concentration of 30 mg mL⁻¹. Graphene oxide nanoparticles were produced according to a previously reported synthesis (**Figure S1D**).¹

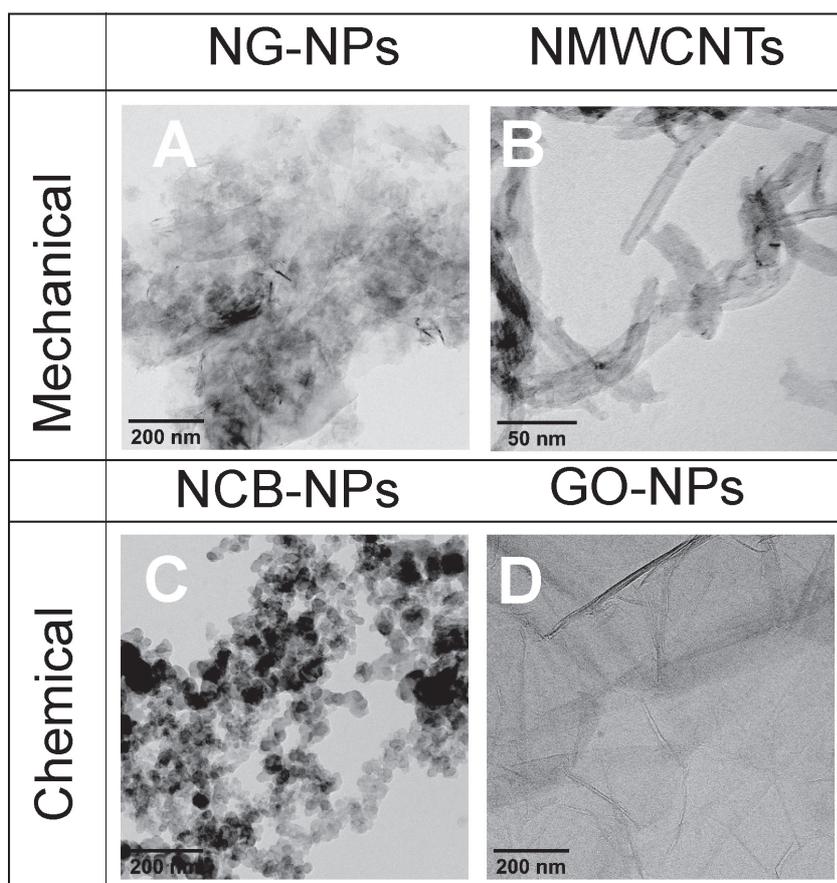


Figure S1. BF-TEM images of the carbonaceous support materials synthesized for cluster immobilization. A-B) Produced via the mechanical route i.e. ball milling that are nitrogen rich: NG-NPs⁵, NMWCNTs.^{5,6} C-D) Produced via chemical routes i.e. pyrolysis and oxidation: NCB-NPs⁴ and GO-NPs¹, respectively. A) N-edge functionalized graphene nanoparticles. B) N-edge functionalized multiwalled carbon nanotubes. C) N-doped carbon black nanoparticles. D) Graphene oxide nanoparticles.

Note S2. Experimental part related to cluster production

In order to achieve a scalable synthesis of metal oxide clusters of controllable size, composition and (surface) loading, we investigated the production of metal oxide clusters via spark ablation, in which two metal electrodes of arbitrary composition are ablated via a spark generated plasma (>5000 K, Ar) to produce particles in the aerosol.^{7,8,9,10,11} Traditionally, spark ablation has been used to produce nanoparticles of a single element in the size range 5-20 nm (i.e. C, Ag, Pd, Zr, and Nb).^{7,8} More recently, multicomponent materials have been produced as well including immiscible mixtures and high-entropy alloys on various substrates but all of sizes > 5 nm.^{12,9,10} On

the other hand, spark ablation has also been used to produce atomically precise metal (oxide) clusters (<2 nm) but only of single element (Ag, and Au) and purely in the aerosol and more importantly, not at practically relevant production levels (~pg/hrs).^{13,11} In here, we have achieved a scalable synthesis of Cu(Ag) metal oxide clusters <2 nm with a 6-orders higher mass production rate (μg/hrs). To produce such clusters of well-defined size and composition, and especially at high production rates, a highly specific spark generator configuration was chosen that optimized a set of parameters to control 1) the size, 2) the production rate and finally 3) the composition (**Figure S2**).

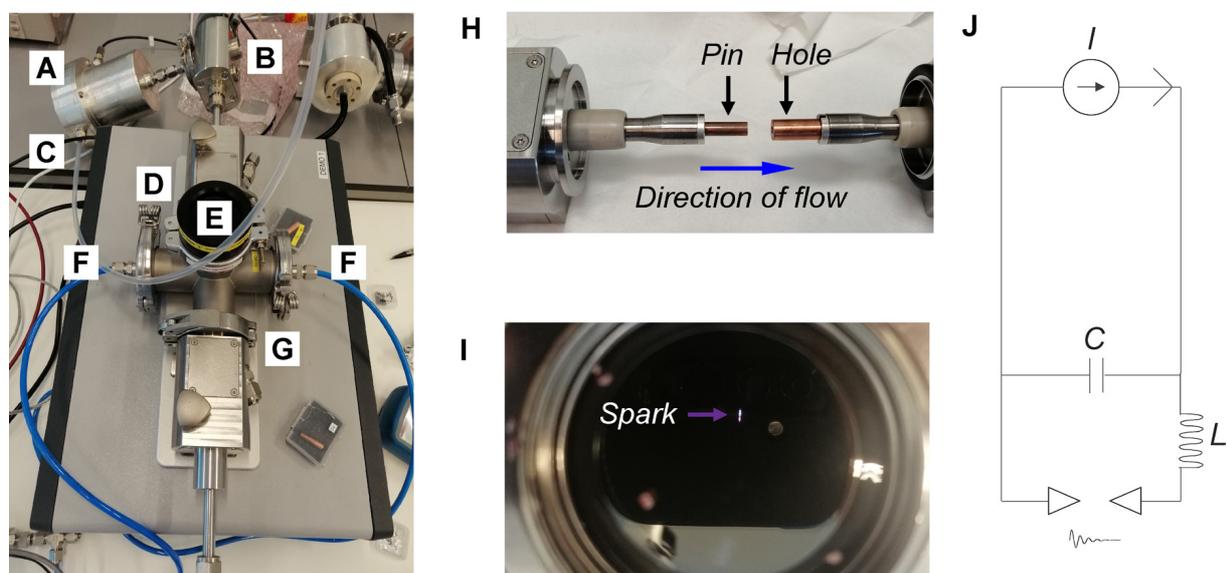


Figure S2. Description of the spark ablation and electrostatic deposition experimental set-up, operation, and electrical components. (A) Faraday cup used to collect either negatively or positively charged particles from the aerosol. The measured current (via an electrometer) allows to determine the number of ions hitting the cup per unit of time giving a measure of the ablation rate (cluster production rate). (B) Deposition chamber allowing for a filter deposition in which the entire aerosol flow is passed through a substrate as well as an electrostatic deposition method¹⁴ in which a bias is applied to a substrate and as such only particles of opposite polarity are adhered to it. (C) Aerosol exhaust. (D) Positive electrode (grounded). (E) Spark chamber. (F) Carrier gas (Ar) flow inlet. Direction of flow is from (E) to (B). (G) Negative electrode. (H) Pin-to-hole configuration of the electrode set-up of the spark ablator showing two Cu electrodes. Exchanging the pin or negative electrode for Ag allows for the production of bimetallic clusters. (I) Picture of the spark in operation. (J) Resistance-inductance-capacitance (RLC) electrical circuit, in which I denote the power supply. C denote(s) the capacitor, L denotes the inductor needed to store potential energy via the magnetic field needed for the oscillatory nature of the spark. The spark is indicated by the damped exponential with a ~ 100 ns time constant of the oscillation of the spark between the grounded and negative electrode.

Note S2.1. Controlling the particle size

The first objective, was to reduce the particle size, which can be estimated based on Eq. 1:

$$D \approx \left(\frac{3\beta V_{eff} \dot{m}}{\rho \pi Q^2} \right)^{1/3} \quad (1)$$

in which Q carrier gas flow rate in this case Ar [$\text{m}^3 \text{s}^{-1}$], V_{eff} the effective volume in the spark chamber [m^3], β the coalescence kernel [$\text{m}^3 \text{s}^{-1}$], which is rate at which two particles coalesce, the mass production rate [kg s^{-1}] and ρ the density of the material ablated [kg m^{-3}].^{15,16,9} Therefore, three parameters needed to be optimized: 1) the V_{eff} should be kept at a minimum, 2) the flow rate should be maximized and, finally, 3) the mass production rate should be minimized. To keep the effective volume as small as possible, we opted for a dual-mixed flow geometry using two inlets (**Figure S2A-G**) and a pin-to-hole configuration (**Figure S2H**).¹⁷ Further, we chose a gas flow rate of a factor of 2.5 higher with respect to a conventional nanoparticle spark generated synthesis ($\sim 6 \text{ nm Au}$)¹⁵, effectively reducing the particle size by a factor ~ 2 . And lastly,

we reduced the ablation rate, which is given by Eq. 2:

in which $\Delta m = \Delta m f \approx E_s c f$ (2) the electrode mass or ablated mass [kg] and f the repetition frequency of the spark [s^{-1}], which roughly equates to the product of the energy per spark (E_s) and c , a material dependent constant [kg J^{-1}], by reducing the energy per spark (**Figure S2I**). The E_s can be determined via Eq. 3:

$$E_s = \frac{1}{2} C U^2 \quad (3)$$

in which U denoted down-voltage [V] and C the capacitance [F] (**Figure S2J**). By bringing the energy per spark down by an order of magnitude (1 nF), the particle size should be reduced further by an estimated factor of ~ 2.2 , effectively pushing the particle size in to the cluster regime ($\sim 1 \text{ nm}$).

Note S2.2. Optimizing the ablation rate

The second objective, was to enhance the production rate. Therefore, we maximized the spark repetition frequency to ~ 10 MHz by enhancing the charging current of the capacitor banks whilst maintaining a stable spark and preventing continuous plasma formation, which would destroy the size distribution as the well-defined nature of the particles is a direct consequence of the pulsating nature of the spark (1 mA, **Figure S2K**).¹⁸ Further, as the ratio between

positively and negatively charged particles differs in the cluster regime as well as their most frequently observed size¹¹, we investigated the effect of charge as well. **Figure S3** shows the effect of capacitance and cluster charge on both the particle size and production rate for a Cu-Cu electrode configuration (i.e. **Figure S2H**).

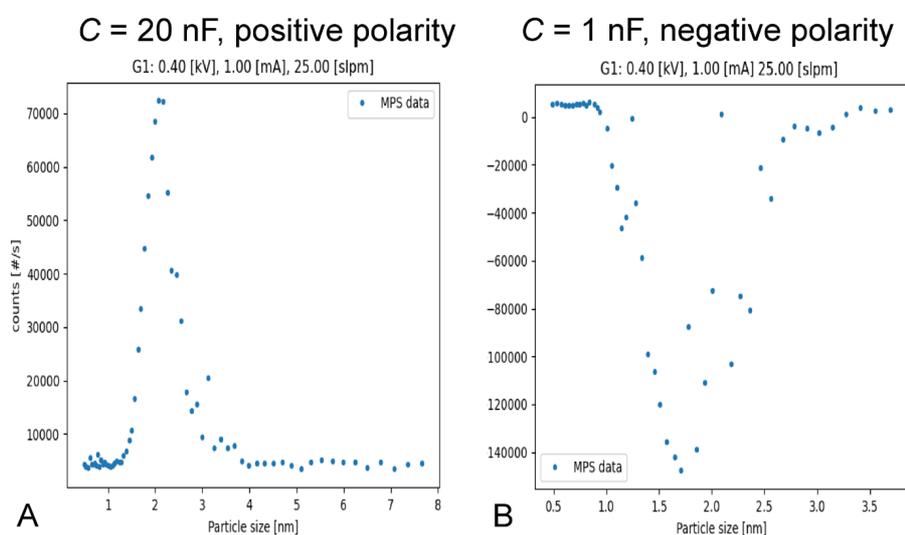


Figure S3. Size distributions of charged clusters produced in the aerosol as measured by a differential mobility analyzer (DMA) to determine the particle mobility (and thus size) and the production rate measured via the Faraday cup depicted in **Figure S2A** and an electrometer. The voltage scan of the DMA is converted to a particle size. The current measured by the electrometer is converted to a number concentration and thus the production rate (min losses). (A) The Cu oxide positively charged particle size distribution with an average size of ~ 2.1 nm, a $7 \times 10^5 \text{ s}^{-1}$ production rate, at 0.4 kV spark discharge voltage, 1 mA charging current, 25 lpm aerosol gas flow and 20 nF capacitance. (B) The Cu oxide size distribution of negatively charged particles with the average size of 1.6 nm and double the production rate at 1 nF capacitance but all other parameters kept the same ($1.4 \times 10^6 \text{ s}^{-1}$).

Note S2.3. Controlling the particle composition

The third and final objective was to control the particle composition by mixing in a second element. This can be achieved simply by switching out either the pin or the hole electrode for one of a different element (in this case Ag).¹⁰ Since the negatively charged electrode will have the highest relative ablation rate due to its attraction

of the Ar^+ ions existing in the plasma resulting in rapid ion bombardment¹⁹, and we need a majority Cu for a good electrochemical performance, we opted to swop this electrode. **Figure S4** shows the size distribution with a Cu-pin, Ag-hole configuration.

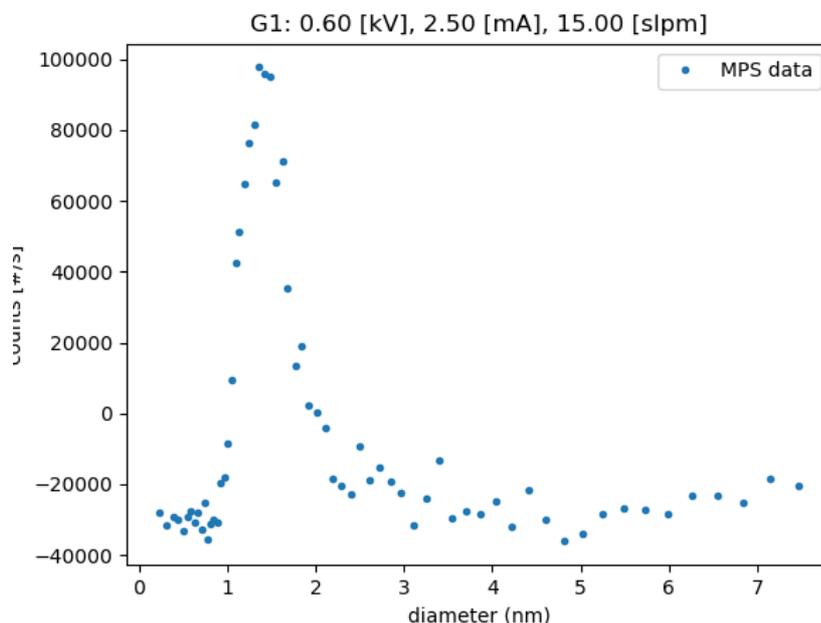


Figure S4. Size distribution and production rate of the positively charged Cu-Ag oxide clusters with an average size of 1.5 nm, which showed the smallest size and highest production rate whilst maintaining a stable spark.

Note S3. Experimental part related to electrostatic precipitation deposition.

In order to accurately deposit the metal oxide clusters on a substrate with a well-defined spot size to control the loading/dispersion on various substrates, we opted for the use of electrostatic precipitation.¹⁴ Since metal oxide clusters carry for the large part a charge, they are well suited to be extracted from the aerosol using an applied bias. Therefore, we placed a TEM grid coated with support material orthogonal to the particle beam (to minimize diffusion deposition) in the deposition chamber indicated in **Figure S2B**. By applying a bias of (+/-)60 V, all the particles of opposite polarity could thereby be deposited on to the TEM grid by concentrating the particle beam into a spot size equal to the TEM grid diameter. An optimized loading of 1.0 mg cm⁻² MWCNTs, 0.27 mg cm⁻² NG-NPs, 0.13 mg cm⁻² NCB-, 0.050 mg cm⁻² GO-NPs support was used for uniform sub-monolayer coating of the TEM grid (**Figure S1**). The particle spot size can be determined via Eq. 4:

$$r_{spot} = \sqrt{\frac{Q}{\pi V_d}} \quad (4)$$

in which Q is the aerosol flow rate [m³ s⁻¹] and V_d is the particle velocity [m s⁻¹], which can be estimated based on the particle mobility (measured via the DMA) and the electric field applied. The projected 2D coverage of such an electrostatic precipitation deposition can then be estimated via Eq. 5:

$$coverage = \frac{N_p 4\pi r_p^2 t_d}{4\pi r_{spot}^2} \quad (5)$$

in which N_p denotes the particle production rate [s⁻¹], r_p the particle radius [m], and t_d the deposition time [s]. For the electrostatic precipitation experiments, we report coverage in the form of partial monolayers as determined for a 2D projection on a flat surface. The actual coverage is factors smaller due to the added depth-profile of the 3D surface.

Note S4. Experimental part related to cluster immobilization.

Since the clusters produced have >70% of their atoms at the surface, which are highly undercoordinated, they are extremely reactive and agglomerate and sinter easily. Therefore, cluster immobilization is no mean task. Here, we have studied the stability of (bi)metal oxide clusters on various carbonaceous supports: N-doped carbon black NPs (NCBNPs), graphene oxide NPs (GONPs), N-edge functionalized graphite NPs (NGNPs), and finally N-edge functionalized multiwalled carbon nanotubes (NMWCNTs). The synthesis of these substrates is described elsewhere. Here we report the cluster immobilization and stabilization via the electrostatic precipitation deposition study, described in **Note S3**, instead. We observed a deposition equivalent of 0.5 ML of CuO and CuAgO clusters in 2D projection with BF-TEM on all four supports (**Figure S5**). For NCB, GO and NG, coated with CuO, no apparent particles could be observed (**Figure S5A, C-D**), which is a direct result of the low thickness contrast and low density of CuO. Instead, for the NMWCNTs-based sample, particle agglomeration had occurred as particles >20 nm could be distinguished (**Figure S5B**). Interestingly, for the CuAgO particles, a similar effect could be discerned as here larger particles could be observed

likewise (**Figure S5F**). Contrarily, particle agglomerates were absent for the NCB, NG, and GO coated materials with particles <2 nm clearly visible (**Figure S5E, G-H**).

To further investigate the nature of the particles (or the absence thereof) deposited on the various supports as well as their apparent agglomeration when deposited on NMWCNTs, we conducted a STEM-HAADF/EDXS study. Here, we selected one unstable material, MWCNT, and a stable one, NCB, and investigated both the CuO as well as CuAgO functionalization more thoroughly. **Figure S6** shows the outcome of CuO deposition on NCB. Indeed, a homogenous distribution of Cu particles ~1.5 nm can be observed at the particle surface comparing well with the measured size prior to deposition.

Instead, for the mass equivalent CuO deposition on the MWCNTs, larger agglomerates >10 nm are directly visible in the STEM-HAADF image (**Figure S7**). STEM-EDXS further confirms the Cu nature of the particles.

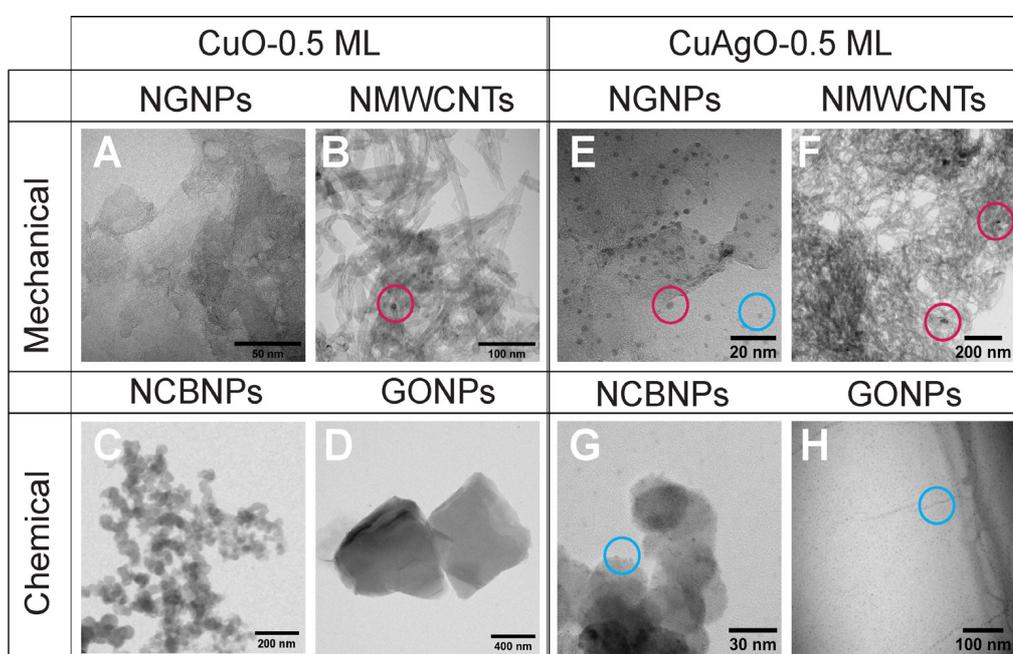


Figure S5. BF-TEM images of the electrostatic precipitation deposition of 0.5 mL equivalent of 1.6 nm CuO and 1.5 nm CuAgO clusters on four different carbonaceous supports. (A-D) NGNPs and NMWCNTs (produced mechanochemically) and NCBNPs and GONPs (produced chemically) coated with CuO clusters, respectively. No apparent particles can be observed with BF-TEM other than in (B). This is due to the small particle size, low relative density of CuO (6.31 g cm^{-3}) and therefore low contrast in bright-field mode. Instead, in (B), particle agglomeration had occurred resulting in the observed particle size $>20 \text{ nm}$. (E-H) NGNPs, NMWCNTs, NCBNPs, and GONPs coated with CuAgO clusters, respectively. Particles $<2 \text{ nm}$ could clearly be observed for NCB, NG and GO based supports and indicated by the blue circles. However, the particle size distribution for the NG-NPs indicated some form of sintering as the mean size shifted from ~ 1.5 to $2.1 \pm 0.6 \text{ nm}$ ($>2 \text{ nm}$ particle indicated by red circle). Further, for the NMWCNTs, particle agglomerates $>20 \text{ nm}$ could be observed similar to the CuO coated system confirming the high surface mobility on carbon nanotubes (red circles, respectively).

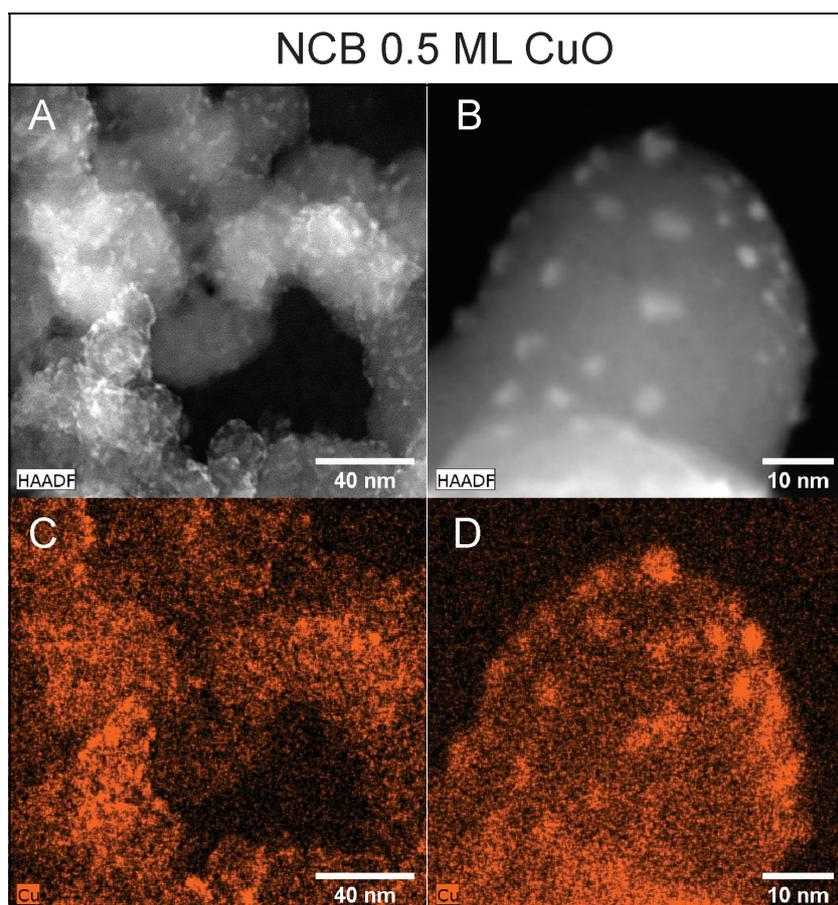


Figure S6. Advanced EM investigation of the 0.5 ML of CuO clusters electrostatically precipitated on the NCB support. (A-B) STEM-HAADF image at 0.45 and 1.25 MX magnification, respectively, showing a homogeneous distribution of higher contrasting particles at the amorphous carbon substrate surface. The average particle size of 1.5 ± 0.5 nm compares well to the 1.6 nm determined by the DMA prior to deposition. (C-D) STEM-EDXS Cu elemental map of the images depicted in (A-B) confirming the Cu nature of the particles.

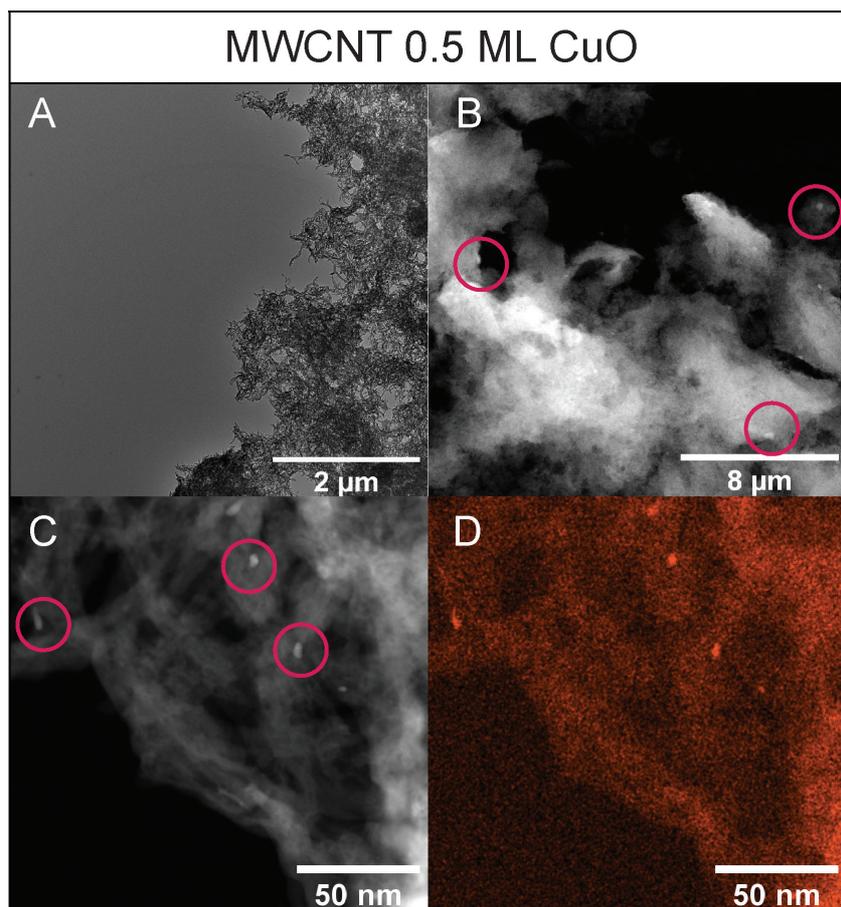


Figure S7. Advanced EM investigation of the 0.5 ML of CuO clusters electrostatically precipitated on the MWCNT support. (A) BF-TEM image of the substrate. (B) STEM-HAADF image of the coated substrate with >10 nm agglomerates visible indicated by the red circles. (C) STEM-HAADF image with clearly identifiable agglomerates. (D) STEM-EDXS elemental map of the image in (C) showing the Cu nature of the agglomerates.

Figure S8 shows the outcome of CuAgO deposition on NCB. The average cluster size determined with STEM-HAADF of 1.4 ± 0.33 nm overlays well with the DMA determined ~ 1.5 nm (**Figure S8A**). Therefore, we can conclude that the particles produced by the spark have been successfully deposited without agglomeration. The high N-content in the NCB samples as well as the high surface area (average C-NP size ~ 50 nm) facilitate immobilization and stabilization of the clusters (**Figure S8B**). STEM-EDXS puts the composition of the CuAgO clusters at $\text{Cu}_{0.42}\text{Ag}_{0.08}\text{O}_{0.5}$ (**Figure S7C**). Further, a second particle mode could be detected that was rich in Ag (**Figure S8D-F**). However, its relative abundance was about two orders smaller and could therefore be neglected in the electrochemical performance considerations (**Figure S8G-F**).

Figure S9 shows the outcome of CuAgO deposition on MWCNTs. Similar to what could be observed in BF-mode, STEM-HAADF pointed towards various agglomerates > 20 nm (**Figure S9A,C**). STEM-EDXS suggested Ag-species as the most mobile as most agglomerates were rich in Ag (**Figure S9B,**

D). Cu instead, showed stronger interaction with the support and remained relatively well dispersed, similar to what had been observed for CuO clusters. Finally, as a control experiment, we acquired a STEM-EDX spectrum confirming the absence of both Cu and Ag in the uncoated MWCNTs (**Figure S9E, F**).

An attempt was made to explain the weaker bonding of the clusters to the MWCNTs by investigating the work function of the supports arguing that stronger bonding should occur for the support with the lowest binding energy (**Figure S10**). Interestingly, the secondary electron cut-offs (SECO) of the support materials, which is equivalent to the work function, could not explain the trend. Following the work function, bonding to the MWCNTs should be second best to NCB supported clusters.

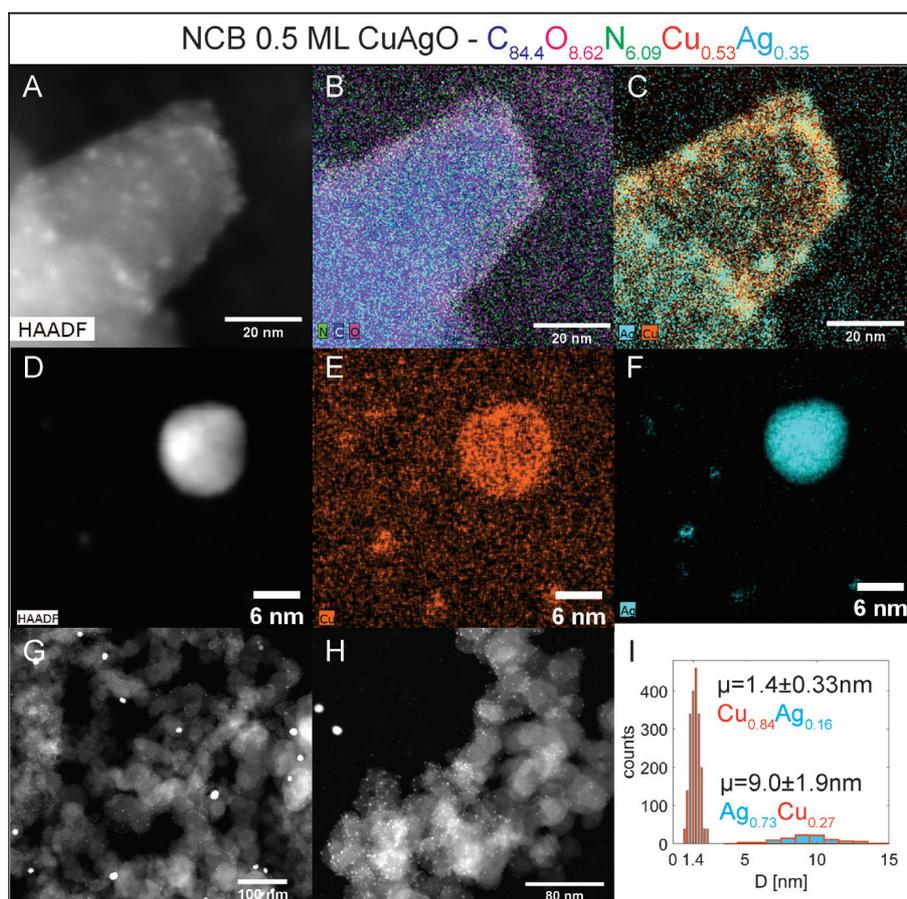


Figure S8. Advanced EM investigation of the 0.5 ML of CuAgO clusters electrostatically precipitated on the NCB support. The TEM grid used was of Au to minimize interference. The composition offered in the title was determined by STEM-EDXS analysis. Note that the grid contains C as well. (A) STEM-HAADF image of the CuAgO clusters with average size of 1.4 ± 0.33 nm. The measured size distribution compares well to the one measured via the DMA at 1.5 nm. (B) STEM-EDXS elemental map of the HAADF image in (A) showing N, C, O, in green, blue, and magenta, respectively. The N doping is as high as 6 at. %. (C) STEM-EDXS elemental map of the HAADF image in (A) of Cu and Ag in orange and turquoise, respectively. Determined Cu:Ag ratio $\sim 5:1$. (D) STEM-HAADF image of large 9 ± 1.9 nm particle. (E) STEM-EDXS elemental map of the HAADF image in (D) showing Cu in orange. (F) STEM-EDXS elemental map of the HAADF image in (D) showing Ag in turquoise. Determined Cu:Ag ratio: $\sim 1:2.7$. This particle represents the second mode that is being produced at the 0.6 kV, 2.5 mA, and 15 lpm spark generator settings. (G) STEM-HAADF low-magnification image showing the relative abundance of the Ag rich particle. (H) STEM-HAADF image showing the high relative abundance of the CuAgO clusters. (I) Quantification of the relative abundance of both particle modes by observing a 630×630 nm area. Nearly 2-order larger abundance of CuAgO clusters vs Ag-rich NP. Average Cu:Ag composition calculated considering both relative abundance and particle mass is 2.1:1, which compares well to the composition determined via XPS (see **Figure S16**, **Table S1**).

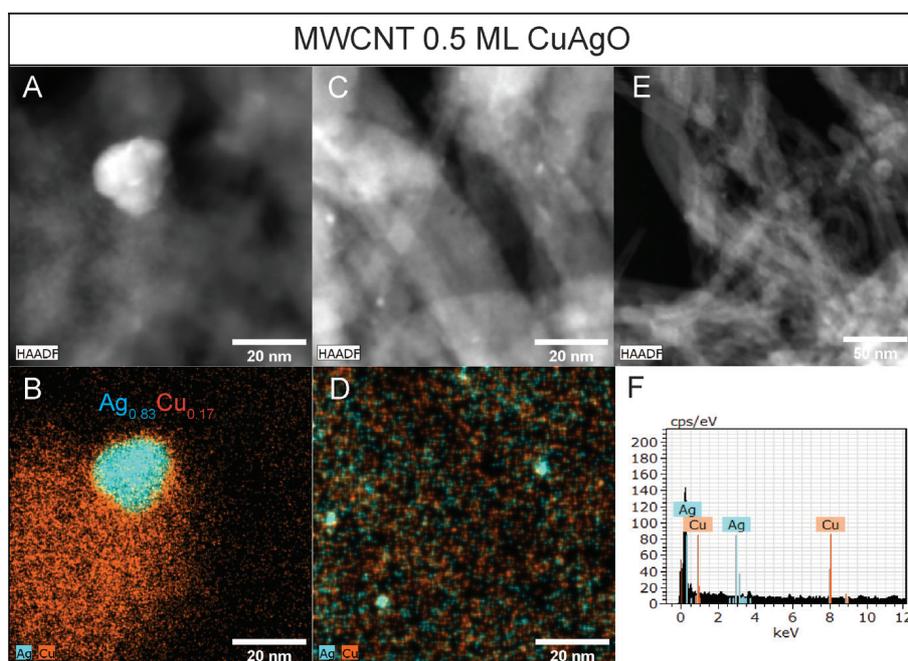


Figure S9. Advanced EM investigation of the 0.5 ML of CuAgO clusters electrostatically precipitated onto the MWCNT support. (A) STEM-HAADF image of agglomerate >20 nm. (B) STEM-EDXS elemental map of the image in (A) with Cu in orange and Ag in turquoise. The particle composition is given in the inset. (C) STEM-HAADF image of > 2 nm particles. (D) STEM-EDXS elemental map of the image in (C), which shows the high Ag content in the particles. (E) STEM-HAADF image of uncoated MWCNTs. (F) STEM-EDXS spectrum of the image in (E) showing the absence of both Cu and Ag prior to deposition.

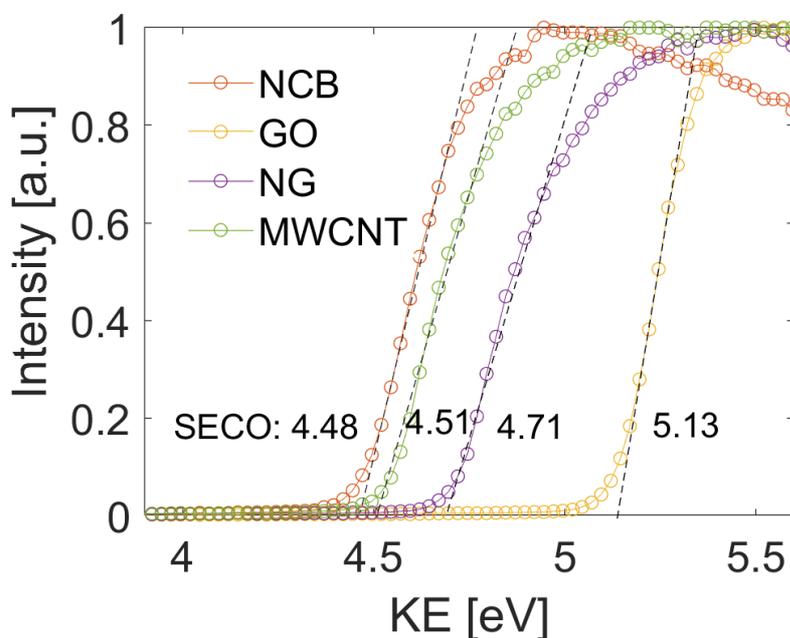


Figure S10. Secondary electron cut-off measured with XPS of the heteroatom doped carbonaceous supports.

Instead, we explain the agglomeration of the CuO/CuAgO clusters on the MWCNT substrate by their poor adhesion. The MWCNTs produced in this study, consist of rolled-up graphene nanosheets with possible amine, imines and amides, bond at their tips. The majority of the structure, however, is highly-crystalline, graphene (**Figure S11**). Dietsche et al. showed that in order to stabilize Ag_{13} clusters on highly-ordered graphite, defects introduced by sputtering were necessary.²⁰ Further, both Cu and Ag are fully oxidized as determined by XPS (**Figure S16**). And Ag clusters ~ 5 nm on (110) TiO_2 have shown to undergo Ostwald ripening at room temperature when exposed to O_2 as determined by STM proposing a potential growth pathway.²¹

It was argued that Ag_2O was the relevant species to undergo surface diffusion due to its higher mobility than its metallic counterpart. This explains the larger Ag-rich agglomerates observed for the CuAgO MWCNTs coated materials vs the CuO coated ones. Upon the failure of Ag_2O to find a stable ligation site, Ag_2O diffuses rapidly over the surface and agglomerates. Instead, the Cu oxides bond relatively well to the surface and stays better dispersed. Nevertheless, for their high relative instability, we have excluded MWCNTs for any further consideration. Likewise, due the shift in particle size distribution of roughly 33% larger of the CuAgO clusters on NG-NP support, we have excluded them as well.

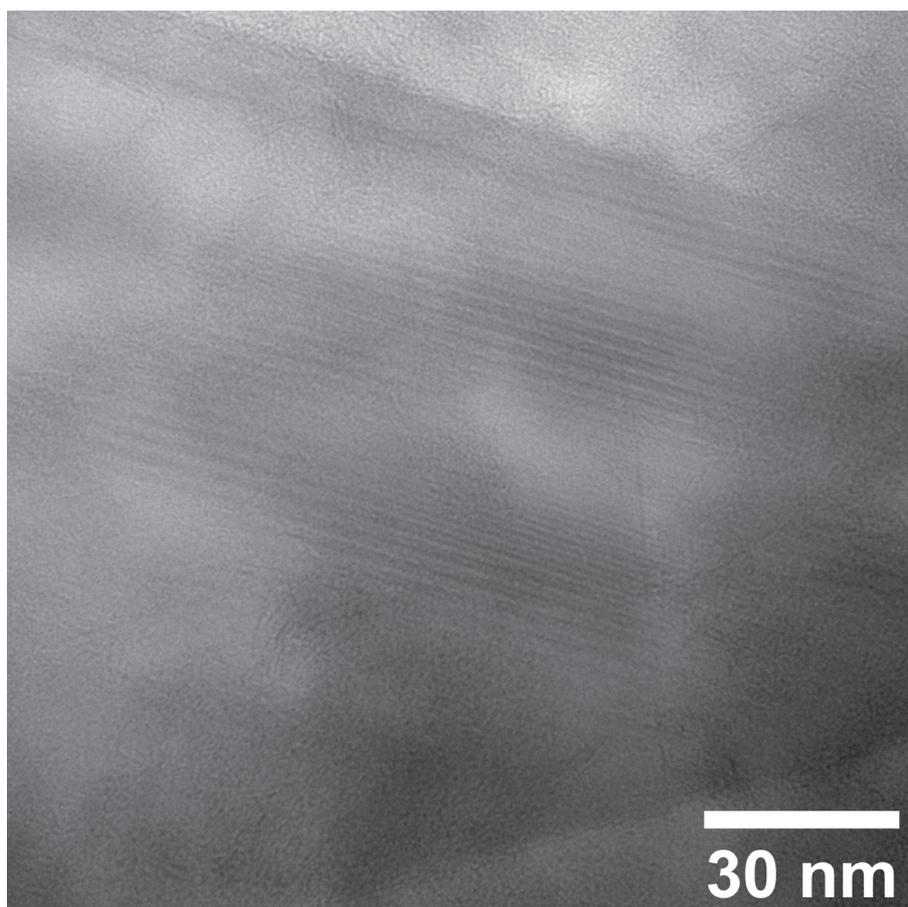


Figure S11. BF-TEM image of the bare MWCNTs. Lattice fringes can be discerned showing the crystalline nature of the nanotubes.

Note S5. Experimental part related to cluster composite electrode production.

In order to test the metal oxide clusters in the electrochemical CO₂ reduction reaction, it is adamant that the cluster carbonaceous support composite will be scaled. Further, for potential flow and membrane assembled electrode cell configurations, the use of a gas diffusion layer support is highly advantageous. Further, to ensure homogeneous cluster coverage and good exposure to the electrolyte, cluster deposition via filtration in which the aerosol gas is directly flowed through a porous support is optimal. Therefore, we designed a Toray TGP-H-60 carbon paper-based gas diffusion electrode with a carbonaceous

support catalyst layer air brushed on top (**Figure S12**).

In order to achieve homogeneous coverage of the carbonaceous heteroatom doped support NPs on the carbon paper, a loading study was performed at different mass loadings for the GO-, NG-, and NCB-NPs based catalyst support inks at 1 mg mL⁻¹ (**Figure S13**).

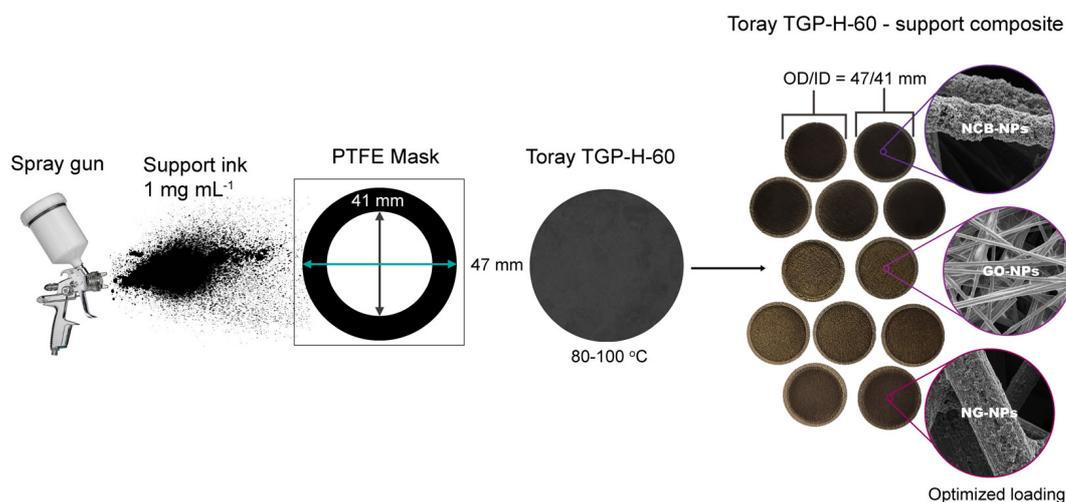


Figure S12. Air brush experiment to produce heteroatom-doped carbonaceous support-carbon paper composites. Ink was consisted of 3:1 isopropanol:H₂O in case of the NCB-, NG-NPs based inks and pure H₂O for the GO-NPs based ink to prevent flocculation. The carbon paper was heated to 80, and 100 °C, respectively to facilitate solvent evaporation. All inks were sonicated for 30 min prior to spraying.

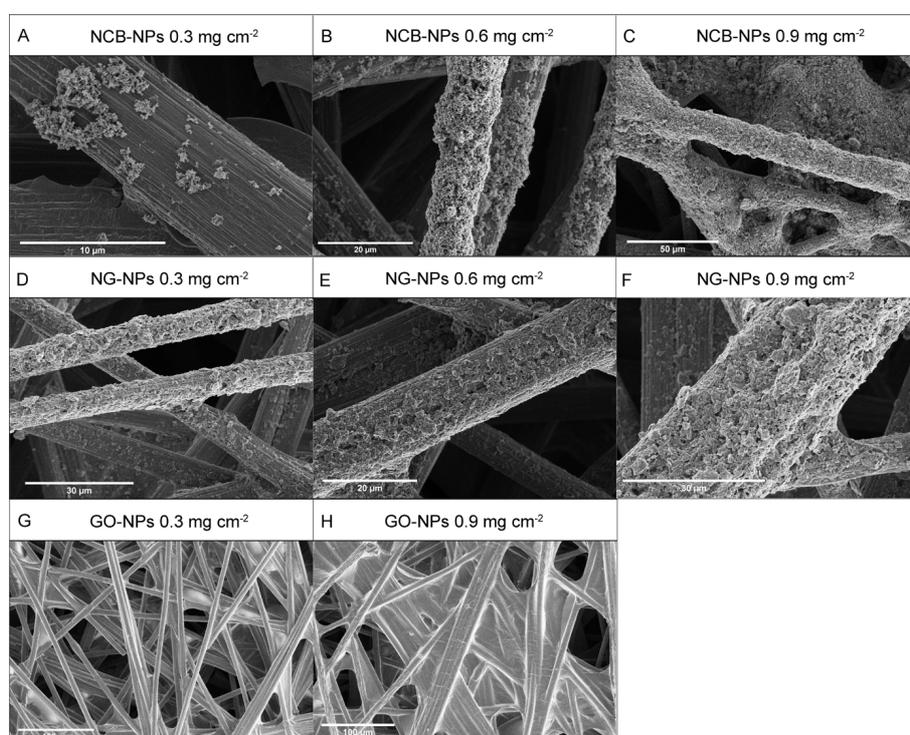


Figure S13. Loading study of the airbrushed heteroatom doped carbonaceous support. (A-C) SEM images of NCB-NPs coated on carbon paper at 0.3, 0.6 and 0.9 mg cm⁻². (D-F) SEM images of NG-NPs coated on carbon paper at 0.3, 0.6 and 0.9 mg cm⁻². (G-H) SEM images of GO-NPs coated on carbon paper at 0.3 and 0.9 mg cm⁻². Optimal loading was achieved at 0.3 mg cm⁻² for the GO-NPs, and 0.6 mg cm⁻² for the NCB-, NG-NPs-based composites in that pore blockage was prevented whilst maintaining good coverage allowing for facile aerosol filtration and electrolyte penetration. All cluster immobilization experiments were performed at the optimized catalyst support loading.

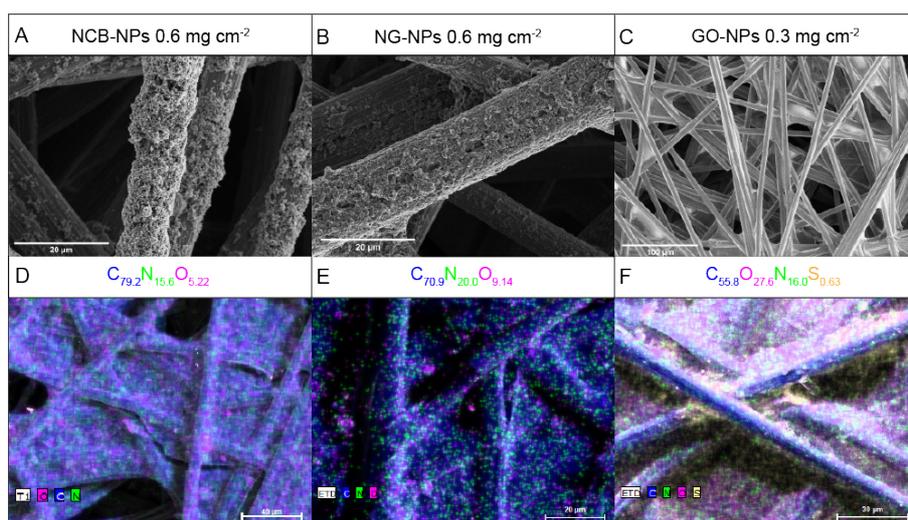


Figure S14. Composition study using SEM-EDXS. (A-C) SEM images of the composite materials produced in **Figure S13**. (D-F) SEM-EDXS elemental maps of the composite materials depicted in A-C in which pixels in blue, green, magenta, and yellow depict C, N, O and S, respectively.

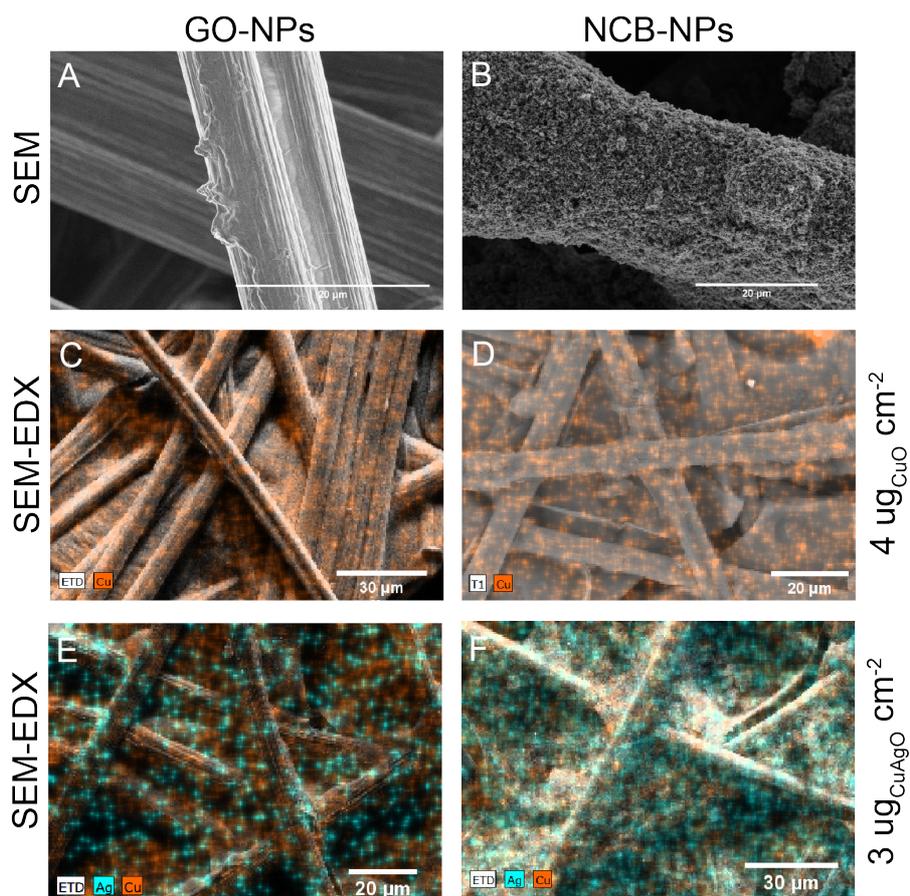


Figure S15. Filtration of metal oxide clusters produced via spark ablation on heteroatom doped carbonaceous support composited. Deposition time in all instances 10 hrs. (A,B) SEM image of the Cu oxide cluster coated GO- and NCB-NP composites showing no clear difference with uncoated samples in **Figure S13**. This is due to the fact that the cluster size is below the limit of detection of SEM. (C-D) SEM-EDXS elemental map of the Cu oxide cluster coated GO-, NCB-NP coated composites, respectively, clearly showing a homogenous Cu signal (in orange) proving the successful coating step. Ablation rate determined mass loading of $4 \text{ ug}_{\text{CuO}} \text{ cm}^{-2}$. (E-F) SEM-EDXS elemental maps of the CuAg oxide cluster coated GO- and NCB-NP coated composite materials, respectively, showing a homogeneous distribution of Cu and Ag indicated in orange and turquoise, respectively. Ablation rate estimated mass loading of $3 \text{ ug}_{\text{CuAgO}} \text{ cm}^{-2}$.

Note S6. Experimental part related to cluster characterization using XPS.

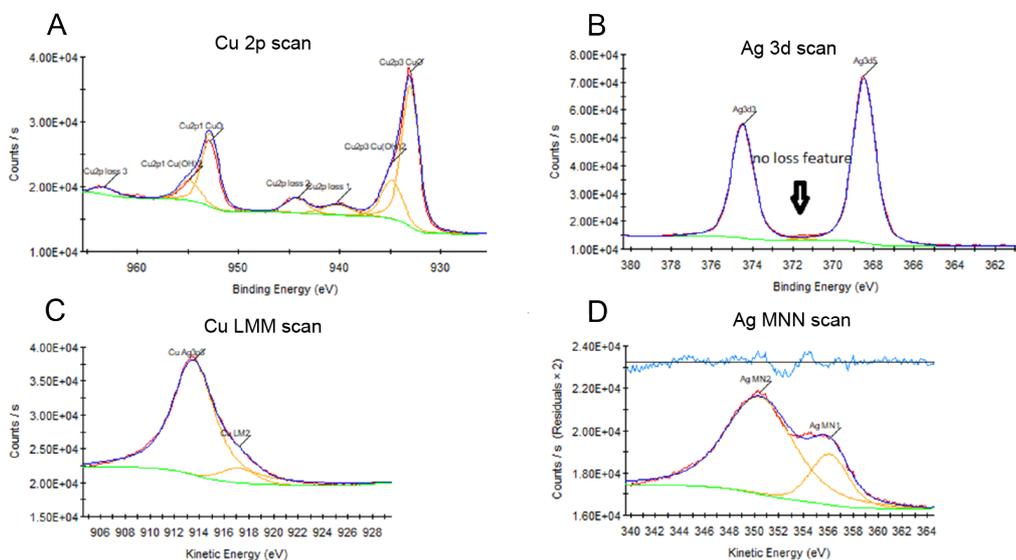
To investigate the oxidation state of both Cu and Ag in the bimetallic clusters excluding the influence of the support we deposited an equivalent amount of CuAg oxide clusters as indicated in **Figure S15** on pure carbon paper and performed XPS (**Figure S16**). To determine the oxidation state after deposition, we performed XPS measurements on the composite 2 hrs (directly) after production (**Figure S16A-D**) and after 7 days (**Figure S16E-H**). Fitting of the Cu 2p and Cu LMM Auger spectrum suggested the presence of both CuO as well as Cu(OH)₂ with the CuO the majority species

at no less than 65 at.%. Determination of the Auger parameter for Ag based on the MNN Auger spectrum of Ag indicated Ag₂O as the produced species. The high relative presence of -OH species in Cu suggest the oxidation of the clusters had already happened prior to deposition meaning in the aerosol. This can be understood from the following. In air, ~21% is O₂ and ~78% N₂. This, leaves <1 % for H₂O. Instead, in Ar, the relative ratio between O₂ and H₂O is ~1:1, explaining the relatively high OH content in the clusters.

CuAgO clusters	CuAg composition
4 μg cm⁻²	
XPS	Cu ₇₈ Ag ₃₂
STEM-EDX	Cu ₇₅ Ag ₃₅

Table S1. Composition of the CuAgO clusters as deposited on pure carbon paper (**Figure S16**) containing two modes of particles: clusters of ~1.5 nm and particles of ~9 nm (**Figure S9**). XPS surface composition and the weighted STEM-EDX composition (Cu₈₄Ag₁₆ and Ag₇₃Cu₂₇ 132:1) shows matching results with <5% error showing the extreme conformity of the particle beam produced with the spark.

2 hrs after deposition



7 days after deposition

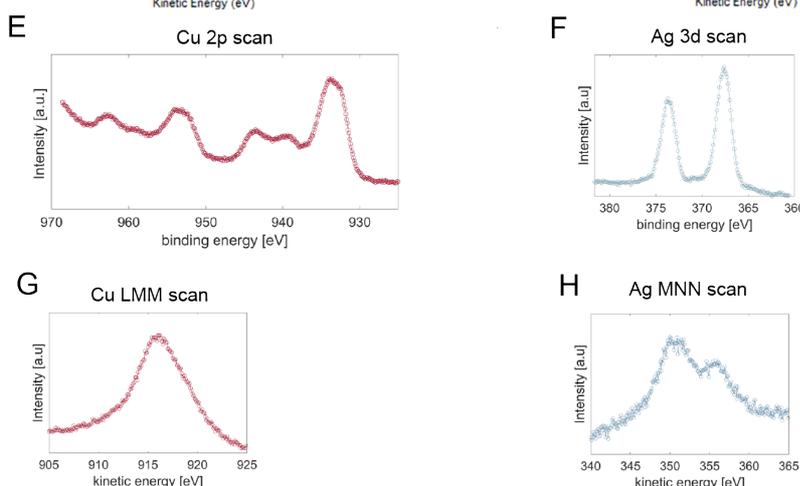


Figure S16. XPS study of the oxidation state of the CuAg oxide clusters deposited on carbon paper, 2 hrs (A-D) and 7 days after deposition (E-H). (A) Cu 2p spectrum of the CuAg oxide clusters. Fitting of the 2p spectrum suggests a combination of both CuO (933 eV) and Cu(OH)₂ (935 eV) species, with the relative composition of CuO between 65-75 at.% and 25-35 at.% for Cu(OH)₂. (B) Ag 3d spectrum showing no loss feature. From the 3d spectrum alone, it is not possible to determine the oxidation state of Ag. (C) Cu LMM Auger spectrum showing a combination of the Ag3p3 peak and the Cu LMM Auger peak. Position of the Cu Auger peak estimated at 917 eV through a fit. (D) Ag Auger spectrum showing the two MNN Ag peaks. The peak position MN1 at 356 eV used to determine the Auger parameter. Auger parameter of Ag of 724, which is much lower than metallic Ag proving the oxidized state of Ag after deposition. (E) Cu 2p spectrum of the CuAg oxide clusters 7 days after production. (F) Ag 3d spectrum 7 days after production showing again no loss feature. (G) Cu LMM Auger spectrum again showing the presence of the Ag3p3 peak. (H) Ag MNN Auger spectrum with the Auger parameter estimated at 718 eV confirming the oxidized state of Ag.

Note S7. Evaluation of the electrochemical performance in the CO₂RR

7.1. Note S7.1. Cathode preparation.

Conical pieces of Toray TGP-60r carbon paper coated with 0.6 or 0.3 mg cm⁻² of NCB or GO respectively and functionalized with ~4 μg cm⁻² Cu(-Ag) clusters were cut out

with a geometrical surface area of 0.5 cm². Finally, 20 μL of 0.83 wt% Nafion dispersed in *iso*-propanol were added as binder.

7.2. Note S7.2. Electrochemical measurements.

The electrodes were evaluated in a commercial gas-tight H-cell from Gaoss Union using constant potential mode controlled by a potentiostat (Autolab PGSTAT302N). All measurements were carried out in 0.1 M KHCO₃, which functioned as both catholyte and electrolyte (25 mL per chamber). Chambers were kept separate by means of a cation exchange (Nafion) membrane. Prior to electrochemical testing, the electrolyte was saturated with CO₂ by bubbling at 25 ml·min⁻¹ for at least 15 min. Also, during any measurement, CO₂ was bubbled through the catholyte continuously to ensure sufficient CO₂ supply during the measurement. A Pt wire was used as counter electrode for the oxygen reduction reaction. An Ag/AgCl electrode was used as

reference. All measurements were carried out at -1.1 V vs RHE. The value of the potential versus Ag/AgCl was converted to the scale of the reversible hydrogen electrode (RHE) using the equation: E (versus RHE) = E (versus Ag/AgCl (3 M KCl)) + 0.21 V + 0.059 * pH. The potential was mathematically compensated for the ohmic resistance that was determined by the electrochemical impedance spectroscopy (EIS). The FEs and currents were repeatedly measured on three individual electrodes for each material evaluated.

Note S7.3. Quantification of the gaseous products

Gas products were analysed online (10 min interval) using a gas chromatography (GC, SRI Instrument 8610C) with the auto-sampling loop (1 ml) connected to CO₂ off-gas of the H-cell catholyte chamber. H₂ was

analysed using thermal conductive detector (TCD) and CO, CH₄, and C₂H₄ were analysed using flame ionization detector (FID) with a methanizer.

7.2. Note S7.2. Electrochemical measurements.

Quantification of the liquid products was achieved according to a previously reported method and a derivation of the Kuhl *et al* method.^{22,23} In brief, the liquid products of all electrodes were quantified using nuclear magnetic resonance (NMR, Bruker 400 MHz AVIII HD). **Figure S17** shows a typical 1D ¹H NMR spectrum obtained for a standard solution containing typical liquid products from the CO₂RR and the internal standards (phenol and DMSO) as indicated by the arrows. The peak area ratio of a given

product to that of the internal standard, as obtained by peak fitting using MestReNova software, was used to determine the concentration of the products. Identical NMR acquisition parameters were used for all measurements. In addition, the water peak was suppressed using the solvent suppression function. The acquisition time of d1 was 5 s and the number of scans was 260. Products with peaks with chemical shifts than larger water (> 5 ppm) were quantified using phenol, all others with DMSO.

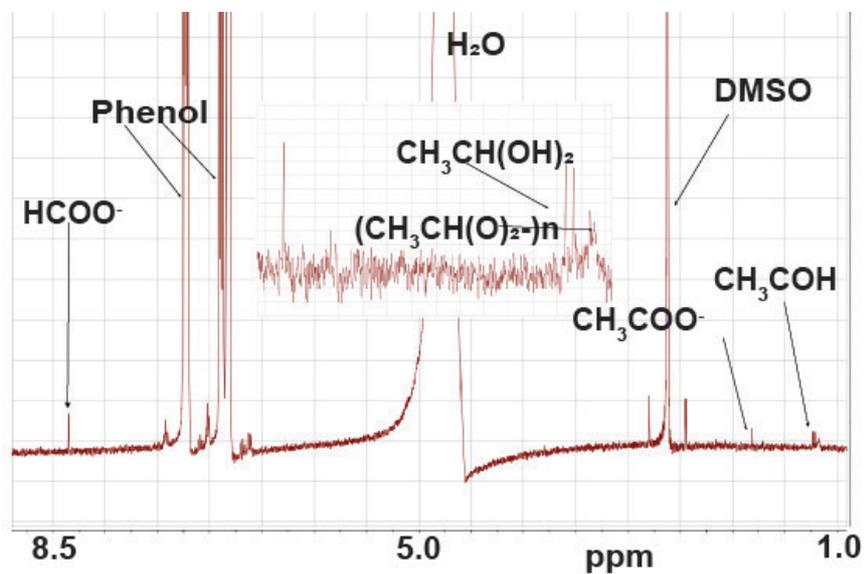


Figure S17. Typical $^1\text{H-NMR}$ spectrum taken of a catholyte aliquot after CO_2RR using a Cu-Ag-NCB-GDL catalyst at 0.9 V vs RHE for 1 hrs. The catholyte contains three CO_2RR products: formate, acetate and acetaldehyde. The acetaldehyde exist a hydrated form²³ and a less soluble aggregate i.e. metaldehyde resulting in peak broadening and shift to lower ppm values. Any multimer of acetaldehyde forms chemically and is base catalyzed. See **Figure S18** for a typical NMR spectrum of metaldehyde.

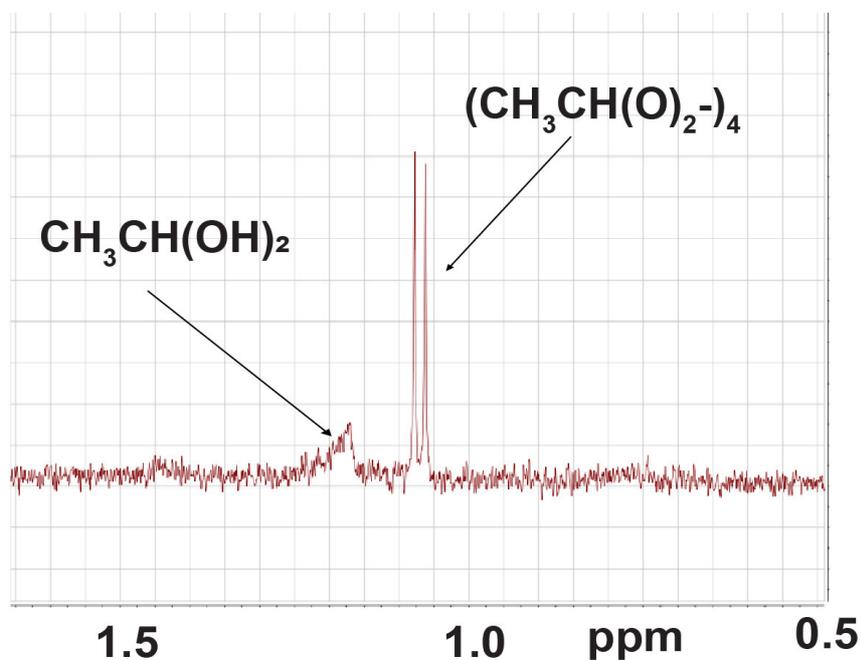


Figure S18. $^1\text{H-NMR}$ spectrum of metaldehyde dissolved in 0.1 M KHCO_3 .

7.5. Note S7.5. Calculation of the faradaic efficiency

The faradaic efficiency (FE) was calculated for gas and liquid products, using

$$\text{FE} = \frac{nFC_i v P}{jRT}$$

and

$$\text{FE} = \frac{nFC_i V}{Q},$$

respectively, where n is the number of transferred electrons to produce one molecule of product i , F is the faradaic

constant, C_i is the concentration of the product as determined by GC or NMR, v is the flow rate of CO_2 , P and T are the pressure (101325 Pa) and temperature (22 °C) of the gas sampled by the GC sample loop, respectively, j is the total current when sampling, R is the gas constant, V is the volume of the electrolyte, and Q is the total charge transferred to produce the target product.

Note S7.6 Determination of the support activity in CO_2RR .

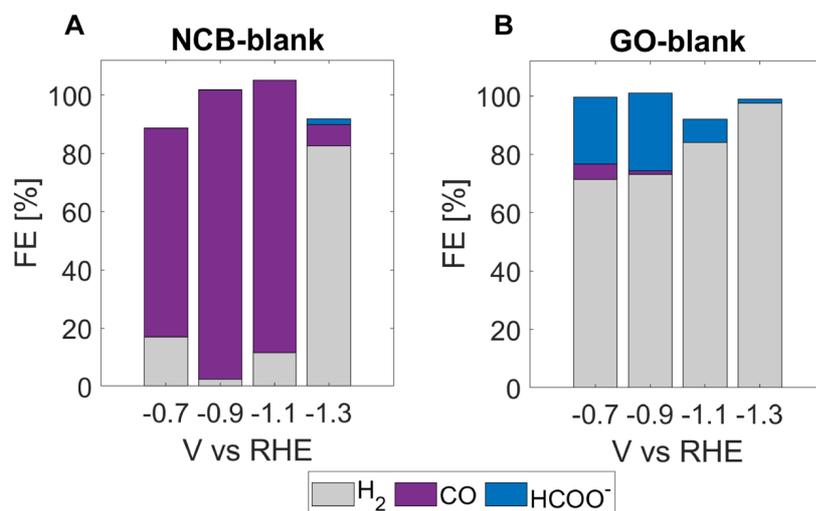


Figure S19. (A) Selectivity as a function of potential of the as-synthesized NCB-GDL composite. (B) Selectivity as a function of potential as the as-synthesized GO-GDL composite. All measurements were performed in CO_2 saturated 0.1 M KHCO_3 . The reaction was let to equilibrate for 10 min before the first sampling of the gas products was performed. An average over 30 min has been reported. Several washing steps with HNO_3 was performed to remove trace metal species from the supports.

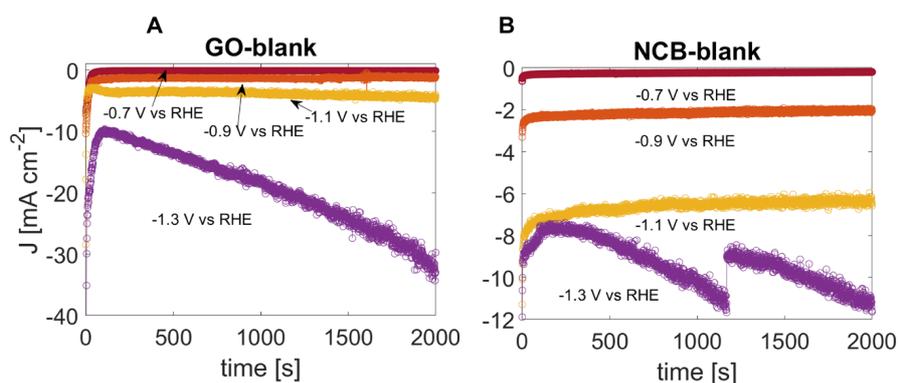


Figure S20. (A) Geometrical current density as a function of potential of the as-synthesized GO-GDL composite. (B) Geometrical current density as a function of potential as the as-synthesized NCB-GDL composite.

	H ₂	CO	CH ₃ CHO	CH ₃ COO ⁻	HCOO ⁻
Cu_NCB_0.5V	16.09	0.00	66.43	9.50	2.50
Cu_NCB_0.6V	46.50	0.00	42.53	4.50	3.08
Cu_NCB_0.7V	30.49	11.49	46.44	10.78	2.15
Cu_NCB_0.8V	64.60	9.17	20.51	1.88	2.46
Cu_NCB_0.9V	7.41	75.75	21.83	1.49	0.79
Cu_NCB_1.1V	35.18	46.02	8.94	1.56	2.00
Cu_NCB_0.5V_STD	16.09	0.00	20.27	1.96	2.50
Cu_NCB_0.6V_STD	11.42	0.00	21.54	1.95	2.87
Cu_NCB_0.7V_STD	21.38	16.25	19.86	4.43	1.58
Cu_NCB_0.8V_STD	12.80	1.98	4.30	0.21	0.82

Table S1. Faradaic efficiencies of Cu-NCB per potential and product.

	H ₂	CO	CH ₃ CHO	CH ₃ COO ⁻	HCOO ⁻
Cu_GO_0.5V	0.00	0.00	92.55	9.18	0.00
Cu_GO_0.6V	56.02	0.00	31.84	5.08	1.69
Cu_GO_0.7V	27.98	0.00	48.46	5.34	5.98
Cu_GO_0.8V	82.60	0.00	19.57	2.81	3.75
Cu_GO_0.9V	60.46	1.03	33.89	2.35	3.74
Cu_GO_1.1V	88.58	2.50	3.20	0.52	2.61
Cu_GO_0.5V_STD	0.00	0.00	1.87	0.02	0.00
Cu_GO_0.6V_STD	2.12	0.00	1.16	1.85	0.60
Cu_GO_0.7V_STD	18.34	0.00	26.81	3.47	2.76

Table S2. Faradaic efficiencies of Cu-GO per potential and product.

	H ₂	CO	CH ₃ CHO	CH ₃ COO ⁻	HCOO ⁻
CuAg_NCB_0.5V	0.00	0.00	88.42	11.34	0.83
CuAg_NCB_0.6V	0.00	0.00	83.45	18.25	2.85
CuAg_NCB_0.7V	15.98	54.36	29.26	4.32	3.04
CuAg_NCB_0.8V	36.32	39.58	15.06	1.92	5.44
CuAg_NCB_0.9V	19.28	71.17	11.34	2.00	1.14
CuAg_NCB_1.1V	39.06	49.72	0.00	1.21	8.99
CuAg_NCB_0.5V_STD	0.00	0.00	0.97	0.40	0.83
CuAg_NCB_0.6V_STD	0.00	0.00	2.66	3.99	0.81
CuAg_NCB_0.7V_STD	0.91	1.12	3.16	0.09	0.44

Table S3. Faradaic efficiencies of Cu-Ag-NCB per potential and product.

	H ₂	CO	CH ₃ CHO	CH ₃ COO ⁻	HCOO ⁻
CuAg_GO_0.5V	0.00	0.00	68.48	4.56	1.88
CuAg_GO_0.6V	57.04	0.00	39.20	0.46	1.10
CuAg_GO_0.7V	23.21	0.00	72.03	7.21	4.04
CuAg_GO_0.8V	72.54	0.00	13.52	4.06	5.51
CuAg_GO_0.9V	70.59	1.98	19.05	5.95	2.21
CuAg_GO_1.1V	88.88	0.25	7.35	0.68	2.09
D					
CuAg_GO_0.5V_ST	0.00	0.00	4.95	0.80	1.62
D					
CuAg_GO_0.6V_ST	0.25	0.00	1.97	0.23	0.88
D					
CuAg_GO_0.7V_ST	3.75	0.00	4.40	7.84	2.30
D					

Table S4. Faradaic efficiencies of Cu-Ag-GO per potential and product.

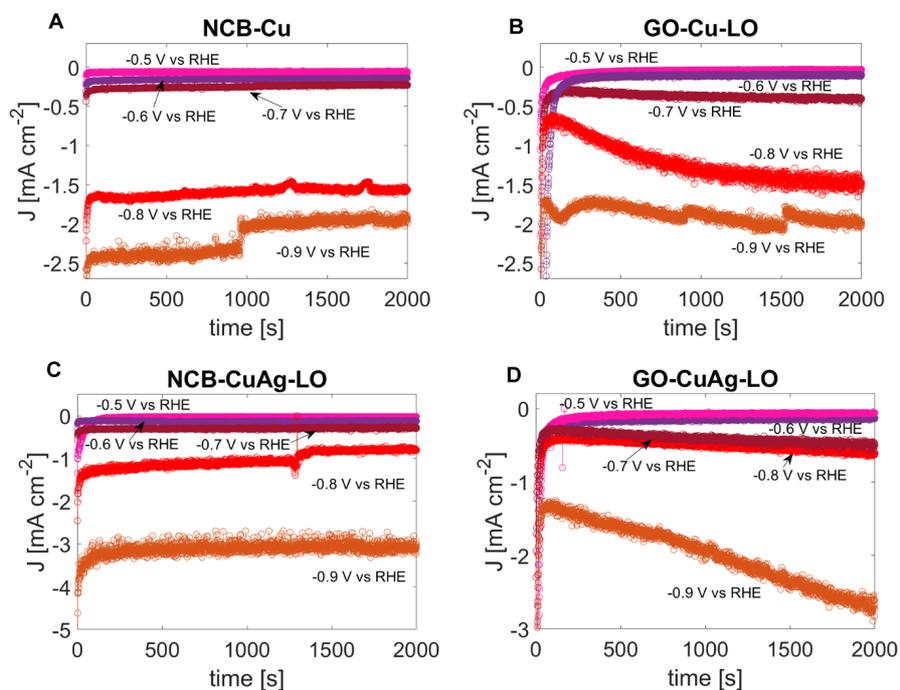


Figure S21. Geometrical current densities as a function of potential for the screened Cu-(ag)-NCB/GO GDL catalysts at low overpotential.

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Chapter 7

Conclusions and perspectives

7.1. Conclusions

With the aim to offer design strategies to improve the selectivity towards liquid fuels of electrocatalysts in the CO₂RR, various well-defined Cu-based electrocatalyst were prepared using wet-chemical and physical processes. Further, they were systematically investigated for their electrochemical performance in CO₂RR, which was correlated to their materials properties as probed via SP-ICP-MS, XAS, STEM-HAADF and other more conventional characterization techniques. Hereby, it could be concluded that alloying Cu with Ag improved the selectivity of Cu towards liquid fuels such as acetic acid, acetaldehyde and ethanol for particles >10 nm, e.g. the bulk. And further, that interfaces of Cu-(Ag) (100) and (111) surfaces have especially high selectivity for liquid fuels, in agreement with what is known for bulk single crystals. Finally, upon the reduction of particle size beyond the size limit in which metallicity breaks down, the cluster size regime, electrocatalyst performances differ distinctly from the bulk and can be by nature of a more precisely defined active site (or series of active sites) have much higher selectivity for specific products than for bulk catalysts.

In Chapter 2, three decades worth of experimental data on the CO₂RR were critically reviewed. From here it was concluded that:

- 1) metal nanoparticle catalyst >10 nm behave as bulk materials (electronics and facet controlled reactivity) but can benefit from higher surface to mass ratios,
- 2) ultrasmall particles (1 nm ≤ X ≤ 10 nm) may have significantly increased activities in comparison to bulk materials as based on their higher degree of undercoordination but may be negatively affected in CO₂RR performance by enhancement of the parasitic HER ,
- 3) cluster catalysts can produce hydrocarbons and perform C-C coupling and can show uniquely high selectivity for multicarbon products, and
- 4) single-atom catalysts cannot form C-C bonds but do show high selectivities for single carbon products such as CH₄, MeOH, CO and HCOO⁻.

In Chapter 3, facilitated by Chapter 2, a selection of catalyst from potentially promising size regimes (NP > 10 nm and clusters < 1 nm) was made forming the basis of this thesis.

In Chapter 4, the full picture of the ensemble of multimetallic NPs was made accessible by means of the development of a novel protocol, based on SP-ICP-MS, in which composition distribution could be obtained at the single-particle level but with ensemble representative statistics in a matter of minutes. This allowed to study the chemistry of a galvanic exchange reaction that made it possible to introduce Ag and Pd in Cu lattices of shaped NPs. The method was successfully applied to four shapes of NPs (Au spheres and Cu cubes, truncated octahedra and tetrahedra) and three Cu-based surface-alloy NPs (CuAg, CuPd and CuPdAg). The author argues that this technique can find use in materials science, materials chemistry, (nano)physics, (nano) photonics, catalysis and electrochemistry.

In Chapter 5, facilitated by the work developed in Chapter 4, a low-temperature non-equilibrium synthesis of shape-controlled NSA with up to three components, was designed independently of component miscibility. This facilitated the deeper understanding and deconvolution of the effect of facet and composition in the CO₂RR to show improved selectivity

of Cu-Ag alloys towards C₂₊ liquid fuels. Further, machine learning was used to guide the synthesis of Cu-Ag-Pd NSAs with high C₂₊ selectivity and phase stability. The author expects the low-temperature non-equilibrium synthesis to be advantageous for researchers seeking nanomaterials of specific spatial atomic arrangements in a range of applications.

In Chapter 6, a scalable production and immobilization method was discussed for Cu-based bimetallic clusters of <150 atoms, which have unique catalytic properties for electrochemical conversion of CO₂ to acetaldehyde with high selectivity (>90%). Further, this type of catalyst also exhibits resistance against potential cycling due to its in situ formed metallic nature, which remains even after air exposure and is a unique property of cluster catalysts. The author argues that this production method offers a platform technology for screening different catalysts for various electrochemical reactions beyond CO₂RR such as nitrogen reduction reaction and OER.

7.2. Perspectives

Although the results discussed in this thesis offer significant improvements in design strategies for electrocatalysts with enhanced CO₂RR selectivity towards liquid fuels over the conventional, achievements were solely made at the lab scale and, therefore, using a limited range of reaction environments. For their application in CO₂RR as a mature technology, performance metrics will need to be assessed at various length scales and

under various reaction conditions beyond the discussed. Therefore, the author attempts to provide a perspective on which specific metrics will need to be reevaluated at more industrially relevant conditions to assess the technology readiness level of the obtained results and discussed in the previous. Below such perspectives are provided.

7.2.2. Catalyst stability as a function of reaction environment

The performance in various electrolytes and pH environments has not yet been established for the Cu-based catalyst mentioned i.e. only 0.1 M KHCO₃ electrolyte (pH 6.8) has been tested. Therefore, further scientific objectives could be to establish catalyst performance as a function of pH and the nature of the electrolyte i.e. KOH, CsOH, NaOH, CsHCO₃ and NaHCO₃ at various ionic strengths. As it has been reported that the nature of the electrolyte, its pH and the specific cation all influence CO₂RR performance, which carries disadvantages and advantages relative to an aimed at product, electrolyte screening will need to be attempted with a specific product in

mind.¹ Further, current densities reported have been limited due to the requirement of CO₂ to dissolve to achieve electrochemical conversion in the presently used H-cell configuration and the overall low solubility of CO₂ in aqueous solutions. Therefore, extension of the performance screening of the discussed catalysts in different gas-fed reaction designs will be needed to determine and evaluate structure-activity relationships at more industrially relevant current densities. Two types of reactor design are particularly of interest, namely the zero-gap cell and the solid-state device of which some specifics are discussed below.^{2,3}

7.2.3. Electrolyzer design

In the field of CO₂ electrolysis, two major schools of thought exist with respect to the electrolyzer design (**Figure 39**) that could enable industrial scale. The first, is based on the so called zero-gap electrolyzer design in which the cathode and anode are sandwiched in between an ion exchange membrane (**Figure 39A**).² The second, is based on a solid-state device in which the cathode is operated without contact to any liquid electrolyte. Instead a solid polymer electrolyte is used to shuttle ions to perform CO₂ electrolysis (**Figure 39B**).³

The zero-gap electrolyzer design has two major advantages: 1) the sandwich structure allows to reduce the cell resistance by making the cell thinner thereby lowering the overall cell potential and improve the energy efficiency and 2) it easily

allows for stacking of the cells offering an easy avenue to increase electrode surface area, pressurized operation and increase conversion. However, the zero-gap design has two major disadvantages that need consideration: 1) it requires alkaline anolyte to run the reaction at high current densities, which traps CO₂ as carbonates, which lessens the conversion and floods the cathode overtime i.e. stops the reaction and 2) in case of liquid products, cross-over via the ion exchange membrane may occur resulting in the need for purification steps and even loss of product via reoxidation at the anode.

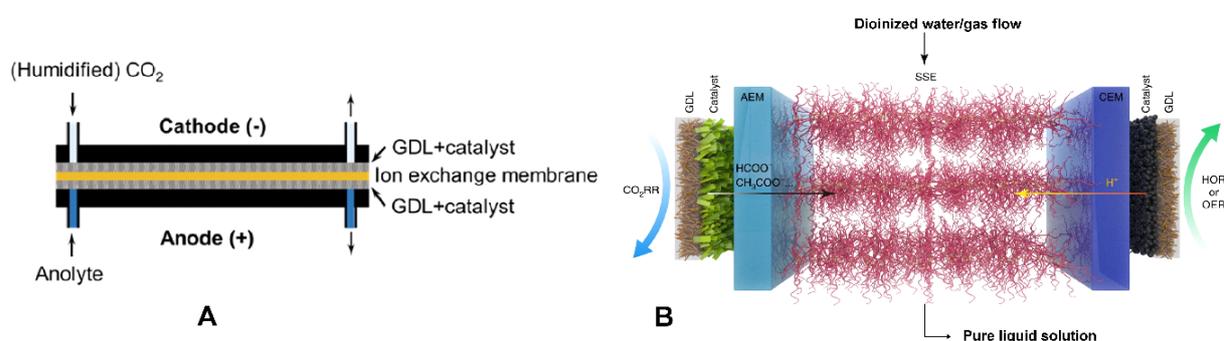


Figure 39. (A) Zero-gap cell with the ion exchange membrane either cation exchange membrane (CEM) or anion exchange membrane (AEM). (B) A solid-state device in which ions shuttling occurs through a solid-state electrolyte (SSE). Adapted and reprinted with permission from Ref. ² and Ref. ³.

Since this thesis discusses by and large the production of liquid fuels, salt formation may be a significant issue as OH⁻ formation and reaction with CO₂ to form carbonates is relatively large for C-C coupled products. In example, in case of acetaldehyde three moles of carbonate could cross-over per one mole of acetaldehyde formed enhancing the rate of salt formation 3-fold as compared to CO evolution and could significantly reduce CO₂ conversion. This may in turn significantly thwart long-term operation of the zero-gap design and would require further scrutiny. Potential avenues to address these issues are purging of the cathode with pure H₂O and or switching of the electrolyte to pure H₂O with periodically infused cations to maintain high selectivity and conversion.^{4,5} Further, cross-over of liquid product through the ion exchange membrane to the anode could result in significant loss of product. Also, here optimization would be needed of which optimized electrolyte flow and or operation at elevated temperatures may offer some lenience.

An alternatively solution could be sought in

the solid-state device design as it has two major operational advantages over the zero-gap design: 1) since the cathode is never into direct contact with liquid electrolyte, flooding is not possible. Further, degradation processes based on corrosion/dissolution well-known for Cu based catalysts⁶ are strongly inhibited extending the life time of the catalyst.⁷ And 2) cross-over of products to the anode side is prevented by a steady-stream of gas or water vapor through the solid-electrolyte layer collecting the products before reoxidation can occur. On top of that, cross-over of CO₃²⁻ can be circumvented by its recombination with H⁺ to form CO₂ which can then be reused, thereby, extending its conversion.⁸ Also, several disadvantages exist regarding this technology: 1) it lacks maturity, i.e. its components, i.e., solid electrolyte, although commercially available, have never been used for electrolysis (originate from battery tech) and, therefore, the durability cannot be assessed, 2) cations are absent in the solid-state device, which may reduce CO₂RR over HER selectivity, and 3) the AEM, SSE, CEM three-component configuration limits

the cell thinness and increases thereby the overall cell potential.

Although major advantages and disadvantages exist for either cell design, performance metrics of the catalyst discussed in this thesis would require extension on and revalidation of in either type of reactor designs before their technology readiness level can be assessed beyond the lab scale. Therefore, future studies should be aimed at testing the developed catalysts in such gas-fed electrolyzers to confirm obtained results and raise the technology readiness level to the pilot scale.

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- 2022 High-throughput Sizing, Counting and Elemental Analysis of Anisotropic Multimetallic Nanoparticles with Single-Particle Inductively Coupled Plasma Mass Spectrometry **Koolen, C. D.**; Torrent, L.; Agarwal, A.; Meili-Borovinskaya, O.; Gasilova, N.; Li, M.; Luo, W.; Züttel, A, *ACS Nano*, **2022**.
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- 2023 Scalable synthesis of CuAg oxide clusters via spark ablation for the highly selective electrochemical conversion of CO₂ to acetaldehyde. **Koolen, C.D.**; Zijlstra, B.; Winzely, M.; Zhang, J.; Pfeiffer, T.; Vrijburg, W.; Li, M.; Boshuizen, B.; Agarwal, A.; Ko, Y.; Bornet, A.; Herranz Salaner, J.; Safonova, O.; Schmidt-Ott, A.; Luo, W.; Züttel, A., *in preparation*.
- 2023 Low-temperature non-equilibrium synthesis of anisotropic multimetallic nanosurface alloys for the electrochemical CO₂ reduction reaction, Koolen, C.D.; Oveisi, E.; Zhang, J.; Li, M.; Pedersen, J.K.; Rossmeisl, J.; Luo, W.; Züttel, A., *submitted to Nature Synthesis*.

Patents

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2018	Niels Bohr Institute Travel Grant (15,000 DKK), Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark.
2018	Röntgen-Ångström-Cluster Travel Grant (20,000 SEK), Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany.
2017	Erasmus plus mobility grant (€ 2,000), University of Amsterdam, Amsterdam, the Netherlands.
2015	Bronze medal best Pharmaceutical Sciences Bachelor project, VU University, Amsterdam, the Netherlands.
2016 – 2014	National Scholarship of the Netherlands (€ 12,000), Ministry of Education, Culture and Science, Hoofddorp, the Netherlands.

Schools (only PhD level courses) and Conferences

2022	ACS Fall Meeting, Chicago, United States of America.
2021	ILMAC 2021, Basel, Switzerland.
2019	NanoGe Fall Meeting, Berlin, Germany.
2018	Graduate School on Neutron Scattering including final exam (two weeks), The Nordic Neutron Science Programme and the Swedish Neutron Education for Science & Society Programme, Tartu, Estonia.
2018	RACIRI Summer School including poster presentation (one week), Advanced Materials Design at X-ray and Neutron Facilities, Röntgen-Angström-Cluster/loffe-Röntgen-Institute, Rügen, Germany.

Notable experiences and volunteering

Present – 2021	Toastmaster, Toastmaster International Lausanne, Lausanne, Switzerland.
2018 – 2017	Member of the Board, Lunds Universitets Roddklub, Malmö, Sweden.
2017 – 2016	Commis de Cuisine at Suitehotel & Restaurant Posthoorn (one Michelin star), Monnickendam, the Netherlands.
2013 – 2012	Fundraiser for several Dutch NGO's such as 'Het Longfonds', Amsterdam, the Netherlands.

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