Developing the Chemistry of Colloidal Cu Nanocrystals to Advance the CO$_2$ Electrochemical Reduction

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Abstract: The ability to tailor make materials with atomic scale precision is crucial for understanding the sensitivities of their performance parameters and for achieving the design specification corresponding to optimal device operation. Herein, this topic is discussed in the context of catalysis. The electrochemical CO$_2$ reduction reaction (CO$_2$RR) holds the promise to close the carbon cycle by storing renewable energies in chemical feedstocks, yet it suffers from the lack of efficient and selective catalysts. This article highlights how colloidal chemistry can contribute to tackle this compelling issue by designing shape-controlled nanocatalysts. In particular, two case studies relative to copper nanocrystals are discussed.

Keywords: CO$_2$ reduction reaction · Colloidal chemistry · Nanocrystals

Raffaella Buonsanti received her master degree in Chemistry from the University of Bari, Italy. After being awarded her PhD in Nanochemistry from the University of Salento working at the National Nanotechnology Laboratory, she spent almost six years at Lawrence Berkeley National Laboratory, first as a postdoctoral researcher and project scientist at the Molecular Foundry, later as a staff scientist at the Joint Center of Artificial Photosynthesis. Since 2015, she is a tenure-track Assistant Professor in the Institute of Chemical Sciences and Engineering at the École Polytechnique Fédérale de Lausanne. She leads a broad multidisciplinary program which spans from materials chemistry and nanoscience to catalysis, electrochemistry and sustainability. Her team is interested in the synthetic development of nanocrystals and their use as electrocatalysts to drive the conversion of small molecules and as materials to advance different energy technologies.

1. Introduction

Advances in many renewable and sustainable technologies (*i.e.* batteries, solar cells, catalysis, opto-electronic devices) critically depend on our ability to design and realize nanomaterials with optimal properties. The ability to tailor materials with tunable morphological characteristics in an unrestricted compositional range is key for achieving the most favourable design specifications and for providing understanding of the sensitivities of performance parameters.

Over the past 40 years, the rich tunability of colloidal nanocrystals (NCs) has enabled the discovery of new phenomena as well as providing technological solutions. Colloidal NCs are constituted by an inorganic core surrounded by a shell of ligands. The latter confers the NCs with solubility in a large variety of solvents;

thus colloidal NCs come as an easily processable ink. Quantum dots are one of the most significant examples of colloidal NCs.[1] Their tunable size-dependent optical properties have made them ideal candidates for a wide range of applications, including display and lighting devices. Nowadays, they are included in the high-end products of several manufacturers, such as Samsung. Noble metal NCs, and particularly gold, provide another example.[2] For these nanomaterials, size and shape define their surface plasmon resonance absorption properties, which are important for detecting many organic moieties, including small molecules and proteins in commercial devices based on surface enhanced resonance Raman spectroscopy (SERS). Colloidal NCs also enable many emerging technologies, including Mid-IR and NIR detectors, third generation solar cells, NIR electrochromic windows, brain imaging and so on.[3]

In the field of heterogeneous catalysis, these materials have not only demonstrated catalytic performance comparable with their conventional counterparts but also improved properties especially when selectivity is concerned, to the point that industry has started to commercialize colloidal catalysts for hydrogenation reactions.[4–6]

Despite their contribution to many different fields, one of the current big challenges in colloidal chemistry is that synthesis by design is not possible, so it is difficult to target underexplored classes of materials, which are often those required for applications.

Colloidal synthesis is a low temperature bottom-up approach where metal precursors are combined with ligands in either aqueous or organic media. Based on the classical nucleation theory and the La Mer diagram, the precursors first convert into 'monomers', which can be thought as reaction intermediates.[7,8] As the concentration of the monomers reaches the critical limiting super-saturation, nucleation occurs and growth follows. General consensus is that the ligands contribute to size and shape control

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by modulating the surface energy of the nuclei and growing NCs. However, very little is known about the chemical nature of the monomers, how the metal precursors evolve into the monomers and, more generally, what are the chemical transformations involved into the NC formation.

To identify reaction intermediates forming during the synthesis of colloidal NCs is not trivial. They can be entities of different chemical nature (*i.e.* molecular clusters, coordination polymers, secondary nanoparticles), therefore a multimodal approach must be employed (*i.e.* combined mass spectrometry, NMR, X-rays, electron microscopy) and the results often need to be corroborated by theoretical calculations. Furthermore, many intermediates are metastable species, therefore *in situ* studies of NC synthesis are highly desirable.[8–10]

While demanding, these efforts are worth it as the substitution of the current empirical approach with a rational choice of the synthetic pathway has the potential of greatly enhancing our control of the NC features and functionality, thus accelerating progress in solving disparate environmental and technological challenges.

In this article, two case studies from our group which demonstrate the validity of such a statement are discussed. They both focus on the synthetic development of Cu NCs as tunable and controlled electrocatalysts for the conversion of CO_2 into added-value products.

2. The Electrochemical CO_2 Reduction Reaction (CO_2RR)

The transformation of small molecules into more complex chemicals is one of the enabling foundations of our modern society. The idea of using renewable energy to drive these conversions is expected to play a key role in our advancement towards sustainability. The electrochemical reduction of CO_2 into energy carriers and chemical feedstocks, which are nowadays extracted from petroleum, is an attractive solution to mitigate the rising atmospheric CO_2 levels while providing long-term storage for excess energy from renewable sources.[11,12] One of the current issues is to find catalysts which render this conversion selective towards one specific product.[11,12]

Copper is the only single metal catalyst able to generate high energy dense hydrocarbons and alcohols, going beyond the simple CO molecule.[11,12] At the same time, polycrystalline copper foil produces more than 16 different products, which would represent a separation nightmare for an actual technology.[13] Studies on copper single crystals have evidenced the existence of structure-dependent reaction selectivity; for example, the (100) and (111) surfaces were found to promote ethylene and methane formation, respectively.[14–16] Surface chemistry studies on single crystals are essential in catalysis; at the same time they are often performed in conditions that are far from those under which an actual electrochemical reactor would operate. To make shape-controlled copper NCs is highly desirable in order to link surface science studies to catalyst behaviour under realistic conditions. Colloidal chemistry emerges as the ideal synthesis technique to address this need.

3. Challenges in the Synthesis of Non-noble Metal Nanocrystals

Non-noble metal NCs, including Mn, Fe, Co, Ni and Cu, possess interesting properties and are sought after for different applications, spanning from alternative plasmonics to batteries and catalysis. At the same time, their synthetic development is lagging substantially behind that of noble metal NCs, which implies that shape control is currently limited.[17] One of the reasons behind this delayed development is their tendency to oxidize. Most of the synthetic development for noble metals has been carried out in water where varying the power of the reducing agent provides a way to tune the reaction kinetics and the final NC shape. To synthesize non-noble metal NCs in water is possible, however only

strong reducing agents can be used and this imposes restrictions to size and shape tunability (*i.e.* small spherical Cu NCs form when reducing the metal precursor with sodium borohydride). Synthesis in organic solvent should then be preferred but this is underdeveloped for metal NCs.

4. Shape-controlled Cu Nanocrystals: Their Synthesis and Behaviour as CO_2RR Electrocatalysts

4.1 *Insights into the Reaction Mechanism to Predict Synthetic Pathways*

To understand the crucial parameters governing the formation of Cu NCs in a typical organic reaction environment, we studied their synthesis by *in situ* X-ray absorption spectroscopy (XAS) in a custom-made flask reactor (Fig. 1) combined with *ex situ* techniques, which included NMR, MS, XRD and TEM.[18]
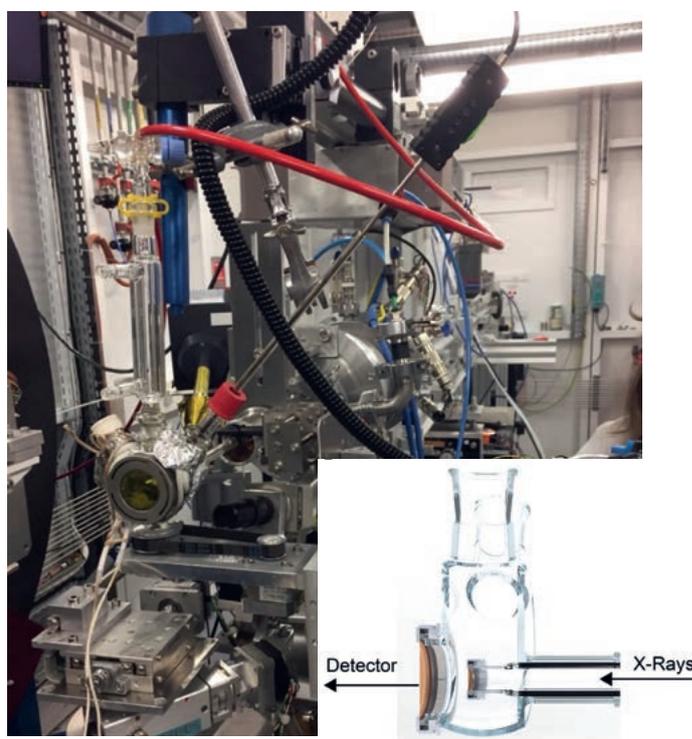

Fig. 1. Customized reactor for *in situ* studies of nanocrystal synthesis. Adapted with permission from ref. [18]. Copyright (2019) American Chemical Society.

In particular, we focused on the reaction of copper bromide (CuBr) in oleylamine (OLAM), which forms spheres or cubes in the presence of trioctylphospine (TOP) or trioctylphosphine oxide (TOPO), respectively. The reaction scheme is reported in Fig. 2A. Based on current understanding, the attainment of the two different shapes would be explained *via* the different binding strength of the TOP and TOPO towards the NC facets, specifically TOPO stabilizing the (100) facet to form cubes. However, this reasoning does not hold because Cu cubes can be obtained also in the presence of TOP when the reaction conditions are properly tuned.

In situ extended X-ray absorption fine structure (EXAFS) combined with mass spectroscopy (MS) and nuclear magnetic resonance spectroscopy (NMR) showed that {CuBr(TOP)$_2$}$_2$ and CuBr(OLAM)$_2$(TOPO) complexes form during the plateau at 80 °C (Fig. 2B). *In situ* X-ray absorption near edge structure (XANES) evidenced that they both undergo disproportionation reactions during the heating ramp. However, the formation of

Fig. 2. (A) Synthesis scheme of Cu nanospheres and Cu nanocubes obtained by reacting CuBr and OLAM with TOP and TOPO, respectively; (B) Complexes forming during Stage I of the synthesis; (C) Intensities of the Cu(0), Cu(I), and Cu(II) pre-edges in the TOP synthesis, normalized by the highest value observed during the ramp; (D) Intensities of the Cu(0), Cu(I), and Cu(II) pre-edges in the TOPO synthesis, normalized by the highest value measured. Adapted with permission from ref. [18]. Copyright (2019) American Chemical Society.
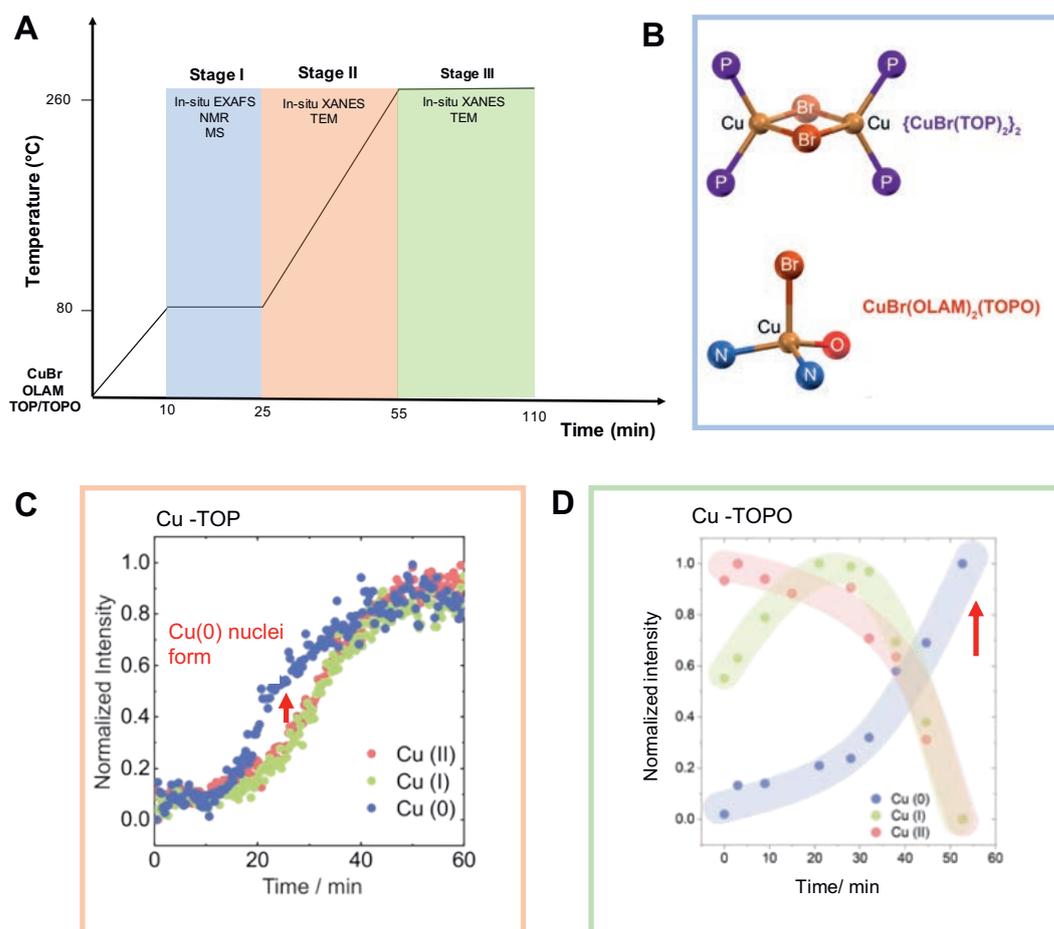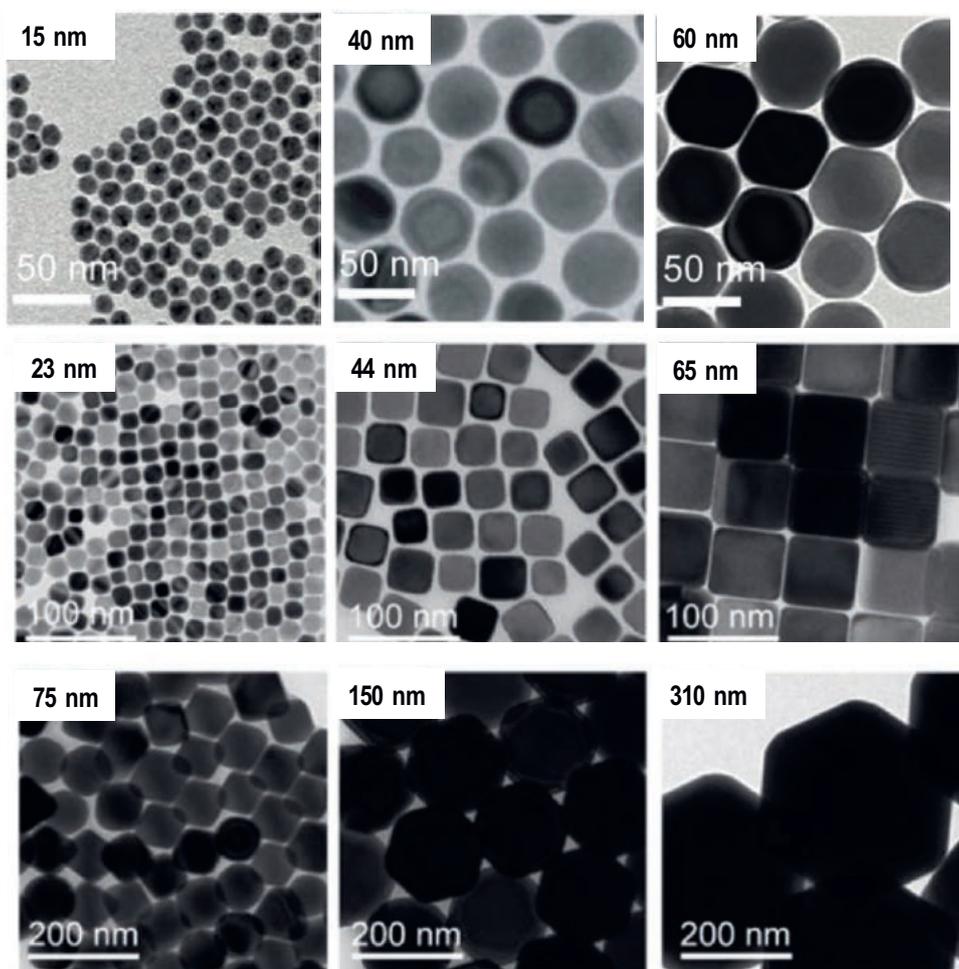

Fig. 3. Representative TEM images of the shape-controlled Cu nanocrystals (nanospheres, nano-cubes and nano-octahedra) with different sizes obtained by varying the reaction conditions, having learned that the disproportionation kinetics govern the outcome of the reaction. Adapted from ref. [22] and from ref. [24] by permission of The Royal Society of Chemistry.

Cu(0) nuclei occurs during this heating ramp for the synthesis including the Cu-TOP complex, which is indicated by the deviation from equilibrium of the Cu(0) signal in the XANES spectra (Fig. 2C). Rapid nucleation occurs instead at 260 °C for the synthesis with the Cu-TOPO complex as a sudden increase of the Cu(0) signal was detected (Fig. 2D). Thermodynamic considerations (*i.e.* free energy of disproportionation and metal–ligand bond stability) cannot explain these findings; therefore kinetics must come into play. For the bimetallic TOP complex, the electron transfer is more favoured considering the proximity of the two Cu(I) centres. Instead, the disproportionation is slower in the synthesis with TOPO, since two equivalents of the monometallic complex should first approach one another and then associate. The faster kinetics of disproportionation of the Cu-TOP account for the nucleation at lower temperature. It should be kept in mind that the nucleation is exergonic, therefore it will drive the disproportionation forward once it happens.

The consumption of Cu(0) at lower temperature generates an overall lower Cu(0) flux during the growth in the synthesis with TOP compared to the synthesis with TOPO. As the nuclei form as truncated octahedra (*i.e.* spheres), which is the thermodynamically more stable shape for face-centred cubic metals, the shape won't change for a low Cu (0) flux during the growth, as the atoms have sufficient time to surface diffuse after deposition; thus, spherical Cu NCs form.[19,20] Instead, the high Cu(0) flux during the synthesis with TOPO will lead to a faster growth rate of the less stable (111) surface which will eventually disappear from the surface of the growing Cu NCs, finally forming the metastable Cu nanocubes.[19,20] Having established that the disproportionation rate of the copper complexes governs the attainable NC shapes, we succeeded in obtaining Cu NCs as spheres of different sizes, cubes of different sizes, octahedra of different sizes (Fig. 3) and also tetrahedra, which have never been shown before.

4.2 Shape-controlled Cu NCs as Selective CO$_2$RR Electrocatalysts.

Having obtained a decently sized library of Cu NCs, we exploited their functionality as electrocatalysts for CO$_2$RR. First, Cu nanocubes (Cu$_{cub}$) of three different average sizes, namely 24 nm, 44 nm and 63 nm, were studied (Fig. 4A).[21,22] A prior study had compared nanostructured Cu constituted by cuboidal particles, preferentially exposing (100) facets, to copper foil. This catalyst had shown preferential selectivity towards ethylene, which was consistent with the studies on single crystal mentioned above.[23] However, no further information was obtained. Our size-dependent study revealed that not only shape is important but also size, in a way which was neither expected nor predictable. Indeed, the NCs with edge length around 44 nm showed the best performance.[21] First of all, the hydrogen evolution reaction (HER), which competes with CO$_2$RR being typically kinetically favoured, was suppressed down to a faradaic efficiency (FE) of only 20%. Furthermore, a FE for ethylene as high as 40% was achieved, which was among the highest values at the time of publication. We then moved to test the size-dependent behaviour of the Cu octahedra (Cu$_{oct}$) (Fig. 4B).[24] The smallest synthesized (75 nm) Cu$_{oh}$ demonstrated an overall CO$_2$RR selectivity of 77% with a CH$_4$ faradaic efficiency (FE) of 55%. While the major (111) facets direct selectivity towards CH$_4$, consistently with the single crystal study, again we revealed that size plays a crucial role in directing selectivity.

In addition to the more trivial surface-to-volume ratio, size tunes the ratio between exposed surface facets, particularly (110)/(100) and (110)/(111) for the Cu$_{cub}$ and for the Cu$_{oct}$, respectively. This parameter indicates that step-sites critically contribute to direct reaction pathways. DFT calculations have subsequently shown that the (110)/(100) interface favours C–C coupling, which suggests that the Cu$_{cub}$ with an average 40 nm size provides an optimal population of these surface sites to eventually maximize ethylene selectivity.[25]

The studies discussed up to this point aimed to learning about the intrinsic catalytic properties of the Cu NCs. As such, the testing of the catalysts was performed in a so-called H-cell, which is a suitable set-up to access this fundamental understanding. At the same time, the conditions under which the catalysts operate (*i.e.* current density, local microenvironment, mass transport) in a H-cell are still far from those of a commercial electrolyzer. An open debate in the community exists regarding the possibility of translating fundamental studies to commercially relevant conditions.[26] To address this question, the Cu NC catalysts were tested in a gas-fed flow cell, which allows to implement commercially
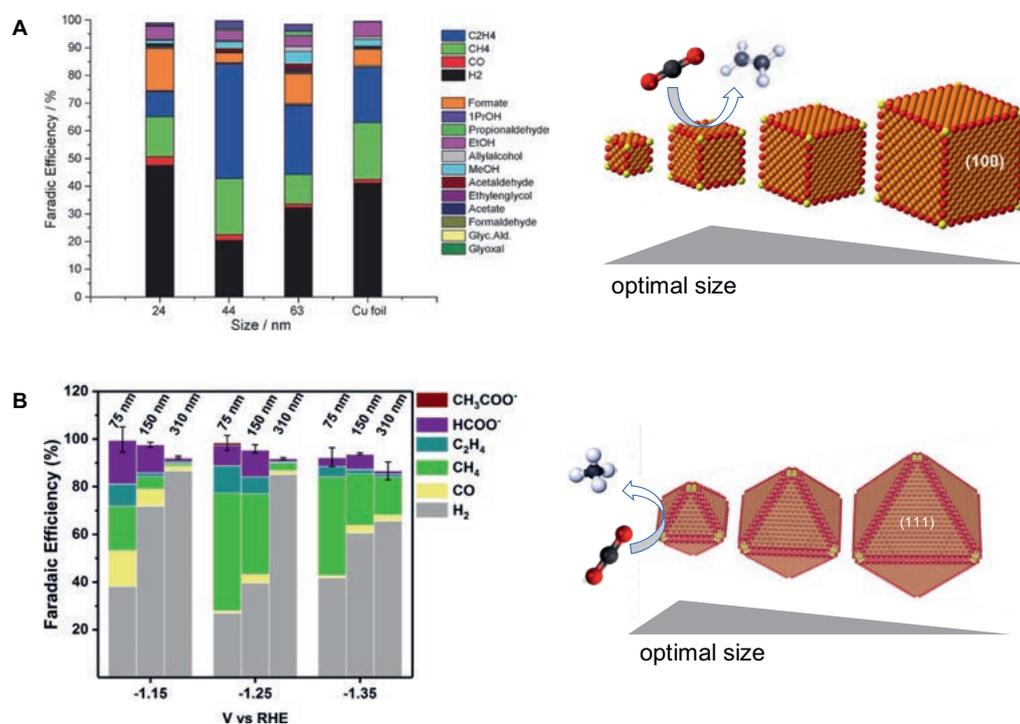

Fig. 4. (A) FEs for reaction products at –1.1 VRHE in 0.1 M KHCO$_3$ for Cucub of different sizes, along with a schematic illustration of the main conclusion, being optimal C-C coupling for samples with edge length of around 40 nm. Adapted from ref. [21]. Copyright 2016, Wiley. (B) Potential dependent FEs for reaction products in 0.1 M KHCO$_3$ for Cu$_{oct}$ of different sizes, along with a schematic illustration of the main conclusion, being higher FE for methane at for samples with edge length of around 75 nm. Adapted from ref. [24] by permission of The Royal Society of Chemistry.

relevant current density.[27] Overall, the intrinsic selectivity of the catalysts was maintained with even enhanced HER suppression. Specifically, ethylene mass activities between 200 mA/mg and 700 mA/mg in a potential range between –0.65 V and –0.75 V vs RHE with selectivity ~57% were obtained for the 40 nm Cu_{cub}. The methane current densities for the Cu_{oct} were exceptionally large and varied from 1.45 A/mg to 2.5 A/mg in the potential range of –0.93 V to –0.96 V vs RHE with selectivities between 51% and 41%. The latter is a very interesting fundamental result which illustrates the power of catalyst design even in gas-fed electrolyzers, as activity towards methane is expected and has generally been shown to be suppressed under high bulk and local pH conditions. These results illustrate that Cu NCs could be ideal model systems but might also provide a concrete solution as the CO_2RR electrolyzes become established as an actual technology.

5. Size-tailored Cu Nanospheres: Insights into the Reaction Intermediates during Synthesis and into their Reconstruction during CO_2RR

5.1 Coordination Polymer Lamellae as Reaction Intermediates

Classical nucleation theory predicts the direct conversion of monomers into nuclei through a thermodynamic energy barrier which depends on the high surface-to-volume ratio of the nuclei. However, studies across the literature evidence that this theory overlooks the complexity of the free energy landscapes and of the reaction dynamics underlying the NC synthesis. In fact, additional local minima in the free-energy landscape can exist and be occupied by intermediates, i.e. pre-nucleation structures which can lower the nucleation barrier compared to a classical nucleation pathway where direct molecule-to-solid conversion is assumed.[8]

In this context, we have learned that coordination polymer lamellae act as intermediates for the formation of Cu nanospheres (Cu NSs).[28] The synthesis involves copper acetate (Cu(OAc)), trioctylamine (TOA) and tetradecylphosphonic acid (TDPA). Similarly to Fig. 2A, the temperature profile of the reaction consists of a plateau at 180 °C, followed by a heating ramp up to 270 °C where the reaction is kept for 30 minutes. In situ X-ray diffraction (XRD), small angle X-ray scattering (SAXS) and XANES provided consistent evidence for the formation of layered copper phosphonate chains forming between the Cu precursor and the TDPA at lower temperatures, followed by the reduction to metallic Cu by the TOA during the heating ramp (Fig. 5A–C). These results indicated that the lamellae might act as concentration hot spots for Cu atomic species, which causes a burst of nucleation and therefore the formation on monodispersed particles (Fig. 5D,E).

Having learned that the lamellae are the reaction intermediates for the formation of the Cu NSs, we could obtain Cu NSs of different sizes by tuning the concentration of pre-formed lamellae in the reaction mixture, and these NSs possessed a superior monodispersity compared to those obtained by simply
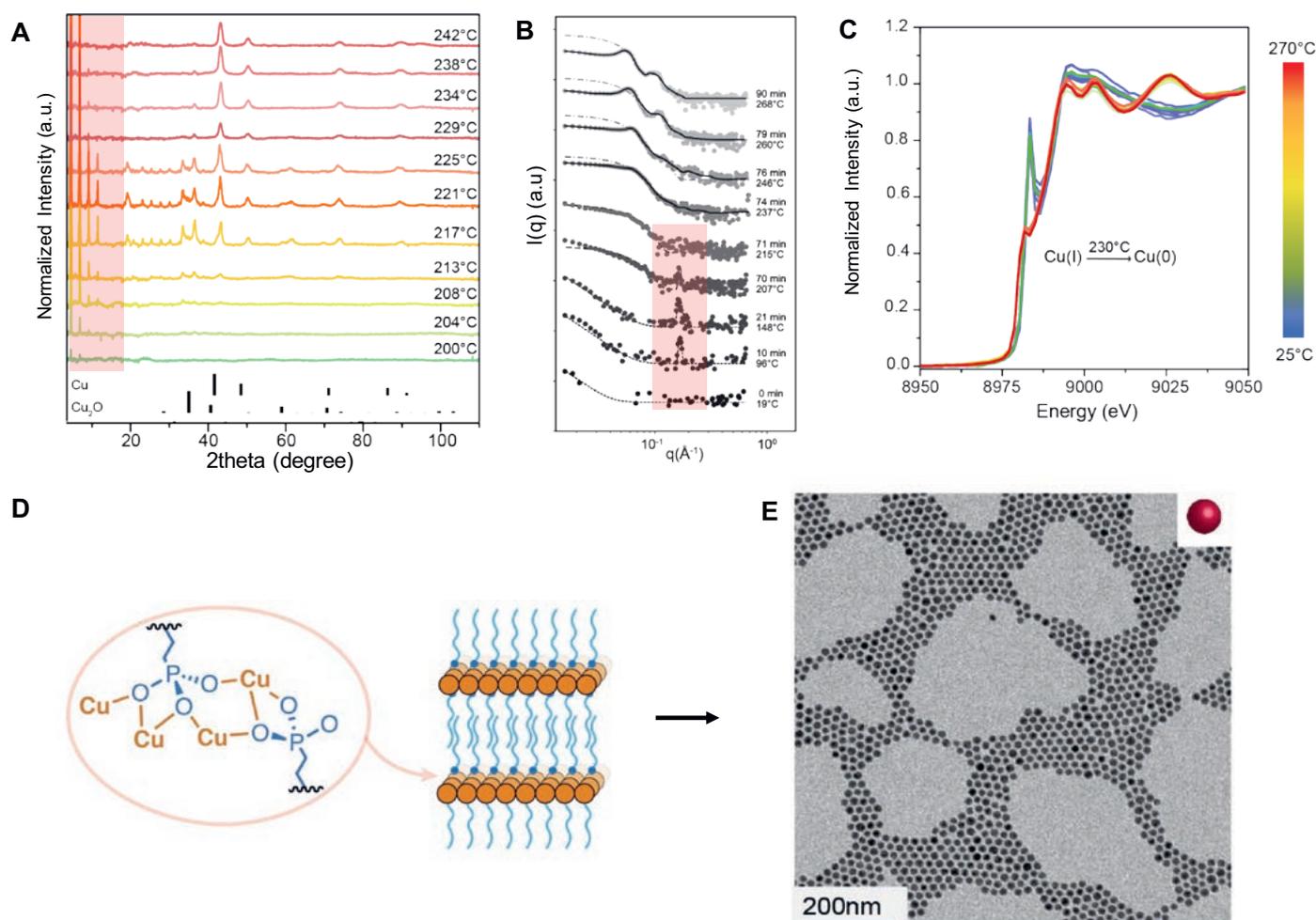

Fig. 5. (A-C) XRD patterns, selected SAXS data and Cu K-edge spectra recorded at different time points during the synthesis of the Cu NSs; (D) Layered copper phosphonates act as reaction intermediate for Cu NSs; (E) Representative TEM image of the copper nanospheres obtained as the reduction product. Adapted from ref. [28]. Copyright 2020, Wiley.
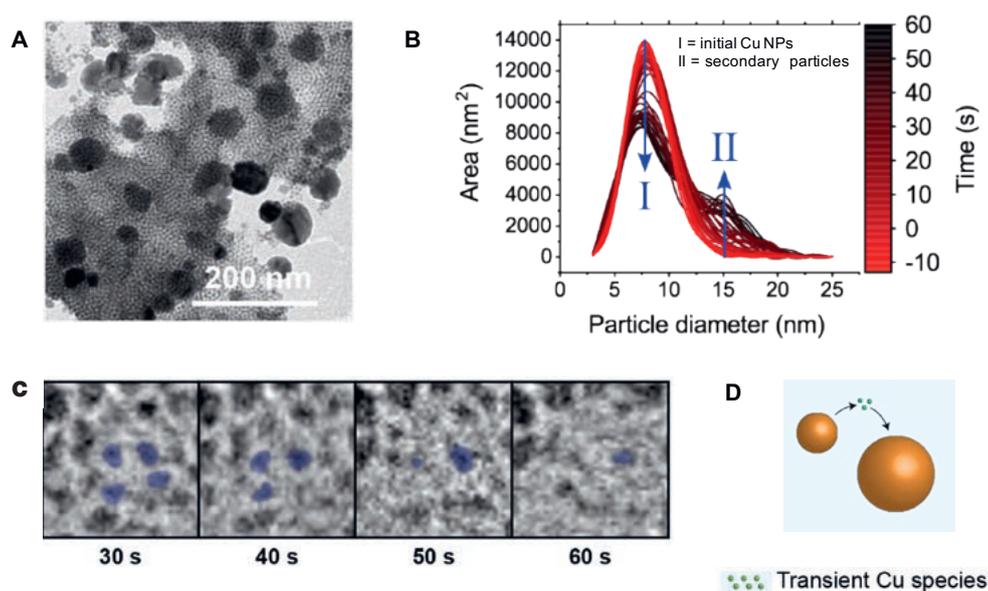
Fig. 6. (A) Catalyst morphology after applying linear sweep voltammogram from open circuit voltage to –0.8V vs RHE at 50 mV/s to 8nm Cu NSs; (B) evolution of the area weighted particle size distribution; (D) magnified images depicting the shrinking process of the primary 8 nm Cu NSs (blue); (E) dissolution of the smaller particles into transient species, of unknown nature to date, that feeds the growth of larger nanoparticles under constant applied potential during the cell operation. Adapted from ref. [32]. Copyright 2020, Wiley.

increasing the TDPA concentration as suggested by the previous literature study.[28,29]

5.2 *Understanding Catalyst Reconstruction during CO$_2$RR by Real-time Monitoring of Cu Nanospheres*

Size, morphology and surface sites of electrocatalysts have a major impact on their performance. Understanding how, when, and why these parameters change under operating conditions is of uttermost importance for designing stable, active, and selective catalysts. Well-defined and homogeneous NCs are ideal model systems to study such reconstruction processes. The Cu$_{cub}$ and Cu$_{oct}$ with sizes above 20 nm do not undergo substantial structural changes for at least one hour of electrolysis.[21,22,24] Instead, Cu catalysts of smaller sizes, like the 8 nm Cu nanospheres, undergo reconstruction already during the start-up phase.[29-31] This process can lead to active cubic catalysts or to less active Cu aggregates. To understand the chemistry behind it is important to eventually learn how to obtain stable catalysts or how to direct reconstruction processes towards the most active form of the catalysts.

With the aid of *in situ* TEM and *operando* X-ray spectroscopy, we investigated the reconstruction of the 8 nm Cu NSs into larger Cu particles (up to around 15 nm) during the CO$_2$RR start-up phase (Fig. 6A).[32] Thanks to the initial size monodispersity of the sample, we could perform an accurate statistical analysis of the size distribution over time from the TEM movies (Fig. 6B). Particles were observed to shrink and disappear (Fig. 6C). These results revealed that a potential-driven dissolution and redeposition, instead of the most commonly observed coalescence, is the mechanism responsible for the change in morphology of the electrocatalyst. The observed solution-mediated process is rather surprising at the negative potentials required by the CO$_2$ reduction reaction, where metallic Cu is the thermodynamically stable phase. While the process is certainly accelerated by the nanocrystalline nature of the investigated catalyst, it is relevant for all the Cu-based CO$_2$RR catalysts. The exact nature of the transient species mediating the observed process remains yet to be discovered. Similarly, like our approach to the synthesis of Cu NCs, the idea here is that learning about the intermediate species will allow us eventually manipulate catalyst reconstruction during operation.

6. Conclusions

This contribution has discussed two examples that highlight the importance of understanding the chemistry behind the formation of NCs to achieve a material tunability which was not accessible before. In the first case study, learning that the disproportionation rate of Cu-ligand complexes regulates the growth regime and therefore the shape provided access to an unprecedented size and shape control of Cu spheres, cubes, octahedra and to synthesized Cu tetrahedra. The study of their catalytic properties for CO$_2$RR has revealed the existence of optimal sizes of cubes and octahedra to achieve state-of-the art selectivity for ethylene and methane, respectively, even at commercially relevant current density. This discovery is particularly important as it has shown the importance of facet ratios to tune selectivity of copper-based catalysts in CO$_2$RR. In the second example, the identification of the copper polymer lamellae as the reaction intermediate was crucial to obtain highly monodispersed Cu spheres. Such homogeneity helped to identify a unique reconstruction mechanism of copper electrodes during CO$_2$RR which is undergoing further investigation.

Looking towards the future, continuous efforts in synthetic development to expand the library of Cu shapes currently accessible are foreseen. For example, Cu NCs with high index facets and Cu nanocages will be some of the targets, being highly desirable for CO$_2$RR selectivity. To develop the chemistry of other non-noble metal NCs, including Mn, Co, Fe, Ni, which are attractive for various catalytic transformations, is the longer-term goal.

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