Facet-Controlled Synthetic Strategy of Cu$_2$O-Based Crystals for Catalysis and Sensing

Yang Shang and Lin Guo*

Shape-dependent catalysis and sensing behaviours are primarily focused on nanocrystals enclosed by low-index facets, especially the three basic facets ([100], [111], and [110]). Several novel strategies have recently exploded by tailoring the original nanocrystals to greatly improve the catalysis and sensing performances. In this Review, we firstly introduce the synthesis of a variety of Cu$_2$O nanocrystals, including the three basic Cu$_2$O nanocrystals (cubes, octahedra and rhombic dodecahedra, enclosed by the [100], [111], and [110] facets, respectively), and Cu$_2$O nanocrystals enclosed by high-index planes. We then discuss in detail the three main facet-controlled synthetic strategies (deposition, etching and templating) to fabricate Cu$_2$O-based nanocrystals with heterogeneous, etched, or hollow structures, including a number of important concepts involved in those facet-controlled routes, such as the selective adsorption of capping agents for protecting special facets, and the impacts of surface energy and active sites on reaction activity trends. Finally, we highlight the facet-dependent properties of the Cu$_2$O and Cu$_2$O-based nanocrystals for applications in photocatalysis, gas catalysis, organocatalysis and sensing, as well as the relationship between their structures and properties. We also summarize and comment upon future facet-related directions.

1. Introduction

In addition to the shapes of nanocrystals (NCs), their surface conditions (surface energies and electronic structures) also determine their physical and chemical properties.[1] Facets with distinctive crystallographic feature possess different atomic terminated characters, which have shown big differences in catalysis and sensing.[2–9] Over the past decades, the understanding, design, and optimization of metal oxide NCs enclosed by well-defined facets has been widely explored.[7,10–16] It is noteworthy that, although high-index facets that have high-density atomic edges with corners and plentiful unsaturated active sites are promising for catalysis and sensing applications, those facets are often unstable, and hardly obtained by traditional chemical methods.[17–23] Thus, the shape-dependent catalysis and sensing behaviours is primarily focused on NCs enclosed by low-index facets, especially the three basic facets (i.e., the [100], [111], and [110] facets).[8–9,12–16,24–34] For instance, by employing hydrofluoric acid as a capping agent (CA), H. G. Yang et al.[34] were the first to obtain uniform anatase TiO$_2$ single crystals with a high percentage (47%) of highly reactive {001} facets, which possessed promising applications in sensors, solar cells and photocatalysis. Besides the various routes for the synthesis of NCs, several novel strategies have recently exploded by carving, modifying, or transforming the original NCs that greatly improve the catalysis and sensing performances.[6,27,30,33,35–52] For example, X. Chen et al.[31] disordered the surface layers of nanophas TiO$_2$ by hydrogenation. The disorder-engineering substantially improved the solar photocatalytic performances of TiO$_2$. R. Long et al.[30] fabricated a metal–semiconductor hybrid structure in which Pd nanocubes exposed with [100] facets were deposited on TiO$_2$ supports. By changing the light intensity irradiated on Pd–TiO$_2$ heterogeneous structures, the charge condition of the Pd surface could be rationally modulated, and thus the function of Pd nanocubes in organic oxidation reactions and O$_2$ activation could be tailored. Our group[35] synthesized Ni–Co amorphous double hydroxides nanocages with tunable Ni/Co molar ratio by using Cu$_2$O octahedra as templates. The obtained amorphous NiCo$_{2.7}$(OH)$_x$ nanocages displayed outstanding applications in electrochemical water oxidation.

In this context, the inexpensive, non-toxic and abundantly available Cu$_2$O nanomaterials, with unique optical and electrical properties,[6,8,10,53–58] have recently aroused general attention, due to their outstanding morphology-dependent applications in catalysis (gas oxidation),[3,13,17,59–61] CO$_2$ reduction,[62–63] organocatalysis,[14,15,34,32,40,50,66] electrocatalysis,[20,67–68] and photocatalysis,[16,69–76] sensing (gas sensors),[8,79–83] ion detection,[29] and surface-enhanced Raman scattering (SERS).[84–89] as adsorbents,[7,90] biotoxicity,[26,91–92] as chemical templates,[35,38,45,47–49,52,93–96] and energy-related processes (water
splitting,[97–100] solar energy conversion[101,102] and lithium-ion batteries[25,103]. Compared to Cu2O nanowires[72,81,104–106] or nanorods,[83,107] nanospheres,[53,64,76,82,84,87,90,108,109] hollow structures,[42,57,67,79,94,95,110–114] self-assembled superstructures,[8,115,116] and Cu2O polyhedra enclosed by low-index planes,[2,3,7–9,14,25,26,29,32,55,57,66,68,75,91,92,123–129] the preparation of Cu2O polyhedra enclosed by low-index planes is simple and large-scale. Even more importantly, several novel facet-controlled routes, including carving,[42,44,110,130–132] modifying[36,40,50,70,73,133] and converting,[35,38,45,47–49,52,60,93,134] have been recently carried out on the basis of the well-defined facets of Cu2O NCs, especially in cubic, octahedral, and rhombic dodecahedral crystals (the three basic Cu2O crystals, enclosed by the {100}, {111}, and {110} low-index facets, denoted as c-Cu2O, o-Cu2O and d-Cu2O, respectively), to tailor their facet-dependent properties. It is noteworthy that although smaller NCs possess higher activities in catalysis and sensing than larger NCs, the reported activity of smaller Cu2O NCs[8,32,68] remain ≈1 order of magnitude lower than those of larger Cu2O NCs; thus, larger Cu2O NCs are often used as precursors for further carving, modifying and transforming.

In this review, we comprehensively summarized the recent progresses in facet-controlled synthetic strategies for the preparation of Cu2O-based NCs as well as tailoring their facet-dependent properties of catalysis and sensing. We begin with a brief discussion of solution phase synthetic strategy of the three basic Cu2O NCs (c-Cu2O, o-Cu2O and d-Cu2O) and Cu2O NCs enclosed by high-index planes, as well as the key role of CA for controlling their crystallographic facets. We then introduce in detail the three main facet-controlled synthetic strategies (deposition, etching and template) on the Cu2O NCs to fabricate Cu2O-based NCs with heterogeneous, etched, or hollow structures, and discuss in detail a number of important concepts involved in those facet-controlled routes, including the selective adsorption of CA for protecting special facets, and the impacts of surface energy and active sites on reaction activity trends. Finally, we summarize the exciting facet-dependent properties of Cu2O and Cu2O-based NCs for applications of photocatalysis, gas catalysis, organocatalysis and sensing, as well as the relationship between their structures and properties. We expect that this review will inspire facet-controlled methodologies, and more examples of these facet-dependent properties should be continuously explored, endowing nanomaterials with excellent properties for numerous applications.

2. Basic Growth Strategies for Cu2O Polyhedra

Cu2O crystallizes in a cubic structure. A tetrahedron of Cu atoms encircle every O atom, and every Cu atom possesses two neighboring O atoms as illustrated in the model of unit cell[123] (Figure 1a). For the {100}, {111} and {110} facets, the three

---

**Yang Shang** was born in Beijing, China in 1986. He received his Ph.D. in Materials Science and Engineering from Beihang University under the supervision of Prof. Lin Guo in 2015. Since then, he has worked as a postdoctoral in Prof. Lin Guo’s group. His research interests focus on controlled synthesis of copper and copper-compound micro–nano materials for applications in catalysis and sensing.

**Lin Guo** received his Ph.D. in Materials Science and Engineering from Beijing Institute of Technology in 1997. He joined Beihang University in 2000 and now is Professor and Vice Dean at the School of Chemistry and Environment in Beihang University. His research interests include development of novel strategies to design functional micro–nano materials for catalysis and energy applications.
low-index facets of Cu₂O crystals, it is well established that the surface energy is closely related to the density of under-coordinated Cu atoms.[75] The atomic arrangements along three low-index facets of Cu₂O are illustrated in Figure 1b–d. Only O atoms are terminated in the {100} facet, leading to electric neutrality (Figure 1b). [44] By contrast, Cu atoms at the {111} facet are coordinated unsaturated. Each two Cu atoms have a dangling bond perpendicular to the {111} facet illustrated by the pink circles in Figure 1c, which make them positively charged. [19] Similarly, the {110} facet has the same terminated Cu atoms with dangling Cu atoms (illustrated by the pink circles in Figure 1d), while the number of dangling Cu atoms on {110} plane per unit surface area is approximately 1.5 times higher than that on {111} plane. [75] Thus, the {110} facet should be more positively charged than the {111} facet, and the surface energies of Cu₂O are in the following order: \( \gamma_{\{100\}} < \gamma_{\{111\}} < \gamma_{\{110\}} \).

However, the conditions of high-index facets of Cu₂O NCs are distinctly different. For example, the {311}, {522} and {211} facets can be displayed by a terrace \( \times \) step as \( 2 \{100\} \times \{111\} \), \( 3 \{100\} \times 2 \{111\} \), and \( \{100\} \times \{111\} \), respectively. That is, they possess two {100} terraces and one {111} step, three {100} terraces and two {111} steps, and one {100} terrace and one {111} step, respectively (Figure 2). [135] Therefore, compared to low index {100} and {111} facets, the numerous kinks and steps endow those high-index facets with higher surface energies.

Cu₂O crystals with clean facets were primarily synthesized through solution phase synthesis (hydrothermal and solvothermal process) [7,8,7,5,75,101,107,122,124] because that route could delicately tailor the exposed facets of crystals, through controlling the nucleation and growth behaviours (especially growth rates in different directions) of crystals. [136,137] The Wulff construction determines the equilibrium or natural morphologies of crystals, because minimizing the total surface energies mainly lead the shape evolution of crystal. [123] Based on the Gibbs–Wulff’s theorem, the facets with higher surface energies always grow rapidly and finally decrease or vanish from the ultimate morphologies, while the crystal facets with lower surface energies grow slowly and are preserved in the final structure. [91] However, selective surface stabilization of appropriate organic or inorganic additives (molecules or ions) as CA can effectively decrease the surface energies and retard the crystal growth along their normal orientations (Figure 3). [5,7] CAs tend to selectively adsorb on the surface with higher surface energy, which consequently lead to delicately tuning of the percentages of different facets of crystals. [7,138]

To date, CAs have played an important role on shape-controlled synthesis of NCs [137–142] and there are many successful examples in preparing Cu₂O NCs. [7,8,7,5,75,107,122,125,143] We will introduce some classic synthetic routes of Cu₂O NCs enclosed by low-index facets. For instance, by using the preferential adsorption of polyvinylpyrrolidone (PVP) on the {111} facets, our group [7] successfully achieved the systematic morphology evolution from c-Cu₂O to o-Cu₂O (Figure 4a), which was in accordance with the identical evolution in shapes of cubic-structured crystal depending on the ratio \( R \) (the growth rate ratio of \( <100> \) to \( <111> \)). [144] The negatively charged O atoms of “=O” in PVP (Figure 4b) would strongly interact with the positively charged dangling Cu atoms on {111} facet to stabilize the crystal surfaces. The ratio of the surface area of {111} to {100} could be controlled by increasing the concentration of PVP (Figure 4c). It is worth noting that {110} facets could not be obtained by only using PVP as CA. The reason is that the relatively strong adsorption of PVP is not enough to reduce the growth rate of {110} facets. Interestingly, L. Gao et al. [125] reported that, by employing oleic acid with stronger adsorption ability as the CA, rhombic dodecahedron Cu₂O NCs totally enclosed by {110} facets could be obtained. With the increasing concentrations of oleic acid, the morphologies...
of Cu₂O crystals were evolved from c-Cu₂O, o-Cu₂O, {110} truncated o-Cu₂O, to d-Cu₂O. During this process, oleic acid firstly adsorbed on the {111} facets to form o-Cu₂O; with continuous increasing of the concentration of oleic acid, the oleic acid began to adsorb on the {110} crystal planes. The area of the {110} surface was ever increasing, while the {111} surfaces gradually disappeared. Finally, d-Cu₂O enclosed by {110} facets were synthesized. By using sodium dodecyl sulfate (SDS) as CA, M. H. Huang et al. synthesized a succession of Cu₂O NCs with morphology evolution from c-Cu₂O to d-Cu₂O (Figure 5). The adding NH₂OH·HCl played a dual role in reducing Cu(OH)₂ to Cu₂O and controlling the pH. By increasing the amount of NH₂OH·HCl, the gradually decreased solution pH that caused by the HCl released from NH₂OH·HCl would retard the formation rate of Cu₂O. The rate for growing c-Cu₂O was within 1 min, but that for d-Cu₂O was decreased to 60 min.

This suggested that a slower growth rate contributed to the generation of d-Cu₂O. Furthermore, a slower growth rate, namely a kinetic-controlled process is essential for obtaining high-index facets. C. Wang et al. reported 50-facet Cu₂O polyhedral micro-crystals partially enclosed by {311} high-index facets.

Figure 4. a) SEM of the Cu₂O polyhedral NCs depending of the ratio R (the ratio of the growth rate along <100> to that of <111>), and the corresponding 3D structures. Scale bar = 300 nm. b) The molecular formula of PVP. c) PVP adsorption during the growth process of Cu₂O NCs. Reproduced with permission.[7] Copyright 2009, Royal Society of Chemistry.

Figure 5. SEM images and the corresponding geometry models with shape evolution from c-Cu₂O to d-Cu₂O. Reproduced with permission.[75] Copyright 2012, American Chemical Society.
concentration of copper salts as well as a weak reducing agent contributed to the kinetic-controlled process, and the decreased viscosities caused by the extra ethanol may improve the diffusions of the reactants. Those above factors finally contributed to the generation of the novel configurations. So far, another shape of 50-facet Cu$_2$O architectures with {311}, {522}, {211} facets,\(^\text{[135]}\) 50-facet and 74-facet Cu$_2$O polyhedra with {211}, {522} and {744} facets\(^\text{[117]}\) and 30-facet Cu$_2$O polyhedra with {332} facets\(^\text{[121]}\) could also be obtained through different kinetic-controlled process by changing the concentration of reactants.

To sum up, by using CA or kinetic-controlled process, Cu$_2$O polyhedra with smooth surfaces could be easily obtained, which lays a solid foundation for further tailoring and investigation of the facet-dependent performance.

3. Facet-Controlled Deposition

Recently, numerous studies are focused on the formation of heterogeneous structures by rational growing supported substances (typically noble metal nanoparticles) on the support (typically metal oxides), since metal oxides can not only serve as a support for a better dispersibility of disperse metal nanoparticles (NPs), but also enhance the catalytic abilities by interacting with the metal NPs.\(^\text{[6,27,30,33,36,40,50,61,145–147]}\) Despite many successful examples on the synthesis of heterogeneous structures, it is noteworthy that the spatially controllable deposition of noble metal NPs on metal oxide support is a significant topic. For example, R. G. Li et al.\(^\text{[27]}\) demonstrated that for the monoclinic BiVO$_4$ enclosed by {110} and {010} facets, photogenerated holes and electrons were transferred to the {110} and {010} surfaces for oxidation and reduction reactions respectively, due to the different energy levels of the two facets. When MnO$_x$ (oxidation co-catalyst) and Pt (reduction co-catalyst) were preferentially deposited by light-induced deposition onto the {110} and {010} facets of BiVO$_4$, the performances of photocatalytic water splitting were significantly improved. They further optimized the experiments to design two highly efficient photocatalyst systems (M/MnO$_x$/BiVO$_4$ and M/Co$_3$O$_4$/BiVO$_4$, where M stands for noble metals).\(^\text{[6]}\) Besides the intrinsic nature of separation of charge between the two facets, the synergetic effect of those catalysts also played a significant role in enhancing photocatalytic performances. So far, lots of Cu$_2$O-based heterogeneous structures have been reported,\(^\text{[33,36,40,50,61,70,76–78,89,108,148]}\) and the synthetic routes mainly focused on light-induced deposition\(^\text{[33,70]}\) or galvanic deposition.\(^\text{[28,36,40,50,76,89,148]}\) In this section, we plan to discuss the site-selective deposition of noble NPs on the preferential faces, edges, or corners of Cu$_2$O crystals.

K. S. Choi et al.\(^\text{[126]}\) synthesized o-Cu$_2$O by employing the preferential adsorption of SDS on {111} facets (Figure 6a, left). They then demonstrated that the selective adsorption of SDS could be used for preferentially blocking the nucleation of Au NPs on these planes (Figure 6a, right).\(^\text{[133]}\) In the presence of SDS, Au NPs only electrodeposited on the {100} facets of truncated octahedral Cu$_2$O; however, Au NPs would form on both {100} and {111} facets in the absence of SDS. By contrast, galvanic or light-induced process can control the site-selective deposition in the absence of CAs. X. W. Liu\(^\text{[28]}\) reported that during the in situ reduction of AuCl$_4^-$ precursors, a galvanic process occurred that Au NPs selectively grew on {111} facets of Cu$_2$O truncated octahedra and cuboctahedra (Figure 6b), which can be formulated as shown in Eq. (1):

\[
\text{HgAuCl}_4 + e^- \rightarrow \text{Au} + \text{HgCl}_2
\]

Figure 6. a) Using selective adsorption of SDS for controlling morphology (left) and for Au preferential deposition (right). Reproduced with permission.\(^\text{[133]}\) Copyright 2009, American Chemical Society. b) Selective growth of Au NPs on {111} facets of Cu$_2$O microcrystals. Reproduced with permission.\(^\text{[28]}\) Copyright 2011, American Chemical Society. c) Illustration of the shape evolution of the preferential growth of Au NPs on o-Cu$_2$O. Reproduced with permission.\(^\text{[144]}\) Copyright 2013, Royal Society of Chemistry.
The galvanic deposition selectively occurred on the \{111\} facet of Cu$_2$O since that metallic component prefers to nucleate on highly active surface sites or defects with a large curvature, in which the \{111\} facet is more active than \{100\} facet due to the higher surface energy. By changing the concentration of the AuCl$_4^-$ precursor, the density and size of Au NPs can also be controlled. Unlike galvanic deposition, light-induced deposition can lead to a distinct selectivity. After light illumination, the photogenerated electrons preferred to transfer from bulk to \{100\} surface of c-Cu$_2$O, which was contributed to reduce metal ions to pure metal. In contrast, the photoexcited holes mostly accumulated on the \{111\} facet that inhibited the reduction of metal ions.

Edges and corners with a large curvature also play a key role in selective growth. M. L. Du et al.\cite{148} reported a sequential growth process of Au NPs on o-Cu$_2$O. With the increasing concentration of AuCl$_4^-$ ions, Au NPs were sequentially deposited on the corners, edges and facets of o-Cu$_2$O (Figure 6c). The surface energy distribution follows the order of corners > crystal edges > \{111\} facets, and results in selective growth and evolution of the heterogeneous structures.

4. Facet-Controlled Etching

Recently, much effort is dedicated to a so-called “top-down” engineering approach that delicately modifies crystals to create more highly active sites by etching and crystal cut, for the purpose of improvement the physical and functional properties of crystals.\cite{43,46,51,68,149–154} (In this section, the “top-down” means crystal carving without phase transformation; while the “top-down” in the next section refers to total phase transformation from Cu$_2$O to various hollow structures.) To date, various metal or alloys (Ag,\cite{151} Rh,\cite{152} Pd,\cite{153} Pd-Pt,\cite{139} Pt,\cite{155} and Pt$_x$Ni$_y$\cite{150} etc.) and metal oxide (Cu$_2$O,\cite{42,44,60,66,85,110,113,130,132} TiO$_2$,\cite{13,51} etc.)
Fe$_2$O$_3$, and ZnO etc.) NCs with sophisticated structures have been fabricated through a chemical "top-down" route. The first step is partial dissolution of the mother-crystal, namely via a surface etching process, in which the etching agent (ions or molecules) chelates to exposed facets by cations, and then leads the chelated surfaces to dissolve.

A subsequent step of surface recrystallization on the residual surfaces of mother-particles may occur, which make the mother-particles roughen or convert to more stable facets. In other words, if the surface recrystallization process does not happen, the continuous surface etching process would contribute to the transformation from the mother-crystal particles to hollow or branch structures.

In the absence of CAs, when many kinds of facets are exposed on the surface of a precursor, the etching will proceed with facet selectivity beginning with the facet(s) with the highest active sites. Although Ag$_2$O has an identical cuprite crystal structure, the order of facet stability for Ag$_2$O to chemical etching by NH$_3$ and NaOH is {111} > {110} > {100}.

In other words, if the surface recrystallization process does not happen, the continuous surface etching process would contribute to the transformation from the mother-crystal particles to hollow or branch structures.

In the absence of CAs, when many kinds of facets are exposed on the surface of a precursor, the etching will proceed with facet selectivity beginning with the facet(s) with the highest active sites. Although Ag$_2$O has an identical cuprite crystal structure, the order of facet stability for Ag$_2$O to chemical etching by NH$_3$ and NaOH is {111} > {110} > {100}.

The drastically different facet stability is caused by the pH of the reaction system. The {111} and {100} facet of Ag$_2$O are terminated with Ag atoms and O atoms, respectively, while the {110} facet consists of rows of surface O and Ag atoms. Under alkaline condition, OH$^-$ ions would strongly interact with Ag atoms on {111} facets and protect them from etching by NH$_3$, while a protecting ionic layer does not exist for the {100} facets, leading to their dissolution by NH$_3$. However, in an acidic environment, the {110} and {111} facets of Ag$_2$O with high surface energy are unstable, and those facets would transform into {100} facets with low surface energy.

An appropriate CA (ions or molecules) could selectively adsorb on special facets to avoid dissolution. Thus, the existing CA is a critical factor when inferring the reacted facet in the initiation of an etching process. For example, using phosphate ions as CA selectively protected the {110} facet of Fe$_2$O$_3$ NCs; the etching by oxalic acid preferentially occurred along the [001] direction. Hence, the Fe$_2$O$_3$ NCs with minor {001} and major {110} facets would transform into Fe$_2$O$_3$ discs with minor {110} and major {010} facets. We intend to conclude the face-dependent etching on Cu$_2$O NCs, and study the formation mechanisms, including preferential adsorption, etching, and others.

CA adsorption is conducive to the selective etching on different positions of Cu$_2$O NCs. M. H. Huang et al. obtained Cu$_2$O nanocages and nanoframes with empty {100} or {110} facets from Cu$_2$O truncated rhombic dodecahedra. Because SDS selectively adsorbed and protected the {110} facets, the etching process occurred prior to the {100} facets. Thus, truncated rhombic dodecahedral Cu$_2$O nanoframes consisting of empty {100} facets and {110} skeleton facets (type-I nanoframe) were formed first (Figure 7a). Then, {100} facets were filled during the further reaction, generating nanocages. By adding ethanol and subsequent sonication of the reaction system, the adsorbed SDS on {110} facets of the nanocages was detached.
which conduced preferential etching of the {110} facets via HCl, leading to the generation of elliptical pores on {110} facets (type-II nanoframes in Figure 7a).

In order to obtain more delicate structures, a “pre-synthesis strategy” has been widely used to carve NCs involving a two-stage route where NCs acted as precursors for subsequent etching. H. B. Yang et al. [42] reported other Cu$_2$O nanocages and nanoframes with empty {100} facets from truncated octahedral Cu$_2$O precursors (Figure 7b). The capping PVP preferentially adsorbed onto the {111} facets of the Cu$_2$O polyhedra and “freezes” the {111} planes; thus, the subsequent oxidative etching selectively occurred on the {100} facets. Similarly, S. D. Sun et al. [130] reported the branching growth of Cu$_2$O NCs via selective oxidative etching with ethanol solution (Figure 7c). As for o-Cu$_2$O, the adsorption energies ($E$) are in the following order: $E_{\text{apex}} > E_{\text{edge}} > E_{\text{facet}}$, according to the different numbers of coordinated O atoms. Hence, the relative order of ethanol molecules adsorbed on o-Cu$_2$O should be facet $<$ edge $<$ apex. Therefore, the selective oxidative etching was reversed to the order of adsorption, from the centre of {111} facets, edges, to apexes.

Without CAs, the {111} or {110} facets with higher surface energy are etched prior to the {100} facet. Q. Hua et al. [111] reported the facet-dependent oxidative dissolution of c-Cu$_2$O, o-Cu$_2$O and d-Cu$_2$O NCs in NH$_3$ solution. The relative stability of different Cu$_2$O crystal facets in NH$_3$ solution in the sequence of {110} $<$ {111} $<$ {100} that was reversed to the order of the surfaces energies. When changing to a weak acid solution [132] instead of the aqueous ammonia, the stability of Cu$_2$O facets also followed the order of [100] $>$ [111] $>$ [110], which determined the extent of oxidative dissolution. Stable {100} facets were preserved, but unstable {110} and {111} facets were etched with newly formed {100} facets (Figure 7e). Using truncated octahedron Cu$_2$O NCs exposed with {100} and {111} facets as precursors, our group [44] created Cu$_2$O jagged polyhedra totally enclosed by {100} facets, with numerous {111} corners and {110} edges (Figure 7d). Due to the Cu dangling bonds, O$_2$ molecules strongly interacted with the {111} facet, making those facets easily dissolve. The selective oxidative etching only occurred on the {111} facets. New {100} facets emerged from the {111} facets by etching, while the original {100} facets remained unchanged.

5. Sacrificial Templates

Due to the large surface area, low density, good surface permeability, and high loading capacity, the shape-controllable synthesis of hollow/cage-like nanostructures, even with non-spherical shapes and regular interiors, has received extensive attention in recent years because of their widespread applications. A template-assisted synthetic strategy is straightforward for the preparation of nanocages and the possible creation of nonspherical nanostructures. The following steps occur during the template synthesis of cage-like/hollow nanostructures: i) synthesizing template, ii) using template to create target structure, iii) removing template (if necessary). Recently, one “top-down” synthetic route has been extensively studied by using the low-cost and highly chemically reactive Cu$_2$O NCs.
(cubes, octahedra, and other highly symmetrical structures) as the sacrificial template, to create various hollow, non-spherical nanostructures, including hollow metal oxides,[15, 18, 45, 47–49, 52] hollow copper sulfide (Cu₇S₄),[93, 158–162] and hollow metals or alloys.[134, 163–165] In this section, we summarize the recent progress in Cu₂O sacrificial templates, and discuss the three major routes as shown in Figure 8 (galvanic replacement, the Kirkendall effect, and coordinating etching).

5.1. Galvanic Replacement

Galvanic replacement is an electro-chemical process, in which the sacrificial template is oxidized and dissolved in the solution; meanwhile another metal ion with a higher reduction potential would be reduced and deposited on the surface of the template, and finally inherits the original structure.[19] For example, due to the lower standard reduction potential of Cu²⁺/Cu₂O (0.203 V vs standard hydrogen electrode (SHE)) than that of the Fe³⁺/Fe²⁺ pair (0.77 V vs SHE), Fe(III) ions could instantly oxidize a Cu₂O template at room temperature. This redox reaction is showed in Eq. (2)[49]:

\[ \text{Cu}_2\text{O} + 2\text{Fe}^{3+} + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + 2\text{Fe}^{2+} + \text{H}_2\text{O} \]  

(2)

Amorphous Fe(OH)ₓ nanoboxes (Figure 9a1) with thin and smooth shells perfectly duplicated the shape of c-Cu₂O templates. After an annealing process, polycrystalline α-Fe₂O₃ nanoboxes were obtained (Figure 9a2). Fe(OH)ₓ box-in-box structures could be created through further redox etching of the Cu₂O/Fe(OH)ₓ core/shell (Figure 9a3). Due to the higher standard reduction potential of Pd²⁺/Pd (0.987 V vs SHE) and PtCl₆²⁻/Pt (0.735 V vs SHE) pairs, Cu₂O polyhedra could also use for the preparation of nonspherical metal mesocages. F. Hong et al.[134] synthesized noble metal alloy mesocages (Pd, Pt and Pt/Pd) with many morphologies (cube, octahedron, “star”). Figure 9b illustrates the generation process of metal mesocages from c-Cu₂O.

Galvanic replacement has facet selectivity when the surface of template possesses more than one type of facet.[139] Similar to the etching process, galvanic replacement also begins with the facet(s) with the highest surface energy. Certainly, the surface energies of facets can also be altered and even reverse their order via the adsorption of CA.[139] Using PVP to stabilize the [111] facets of Cu₇O truncated octahedra, Y. S. Kang et al.[166] obtained metal oxide hollow structures by controlling the galvanic replacement occurring on the {100} facets (Figure 9c). In contrast, galvanic replacement and subsequent selective deposition would happen on the [111] facet of Cu₇O crystals without the protection of PVP, leading to the formation of hierarchical structures (Figure 9cii).

5.2. The Kirkendall Effect

The Kirkendall effect is defined as the migration of the boundary layer between two materials when the two materials have different interdiffusion rates. Due to the faster diffusion rate, voids would be formed in the inner component, which is the most defining feature of the Kirkendall effect.[39] Over the past decade, the Kirkendall effect has become a promising route for creating micro–nano materials with hollow structures.[167, 168] Compared to the mono-stoichiometric Cu₂O, copper sulfides (Cu₇S₄) at room temperature possess at least five stable phases: i.e., chalcocite (Cu₂S), djurite (Cu₁.95S), digenite (Cu₁.8S), anilite (Cu₁.75S), and covellite (CuS).[93] Their unique electrical and optical properties derive from the valence states and complicated structures.[93, 96] The Cu₂O-template route (Figure 8b) is a facile and straightforward by adding sulfur sources (i.e., Na₂S solution, thioacetamide, and thiourea) into the Cu₂O suspension, in which Cu₂O template is transformed into Cu₂O/Cu₇S₄ core/shell structures at once because of the minimal solubility product constant Ksp of Cu₇S₄ (Ksp ≈ 10⁻⁴⁸).[93]

Finally, the Cu₂O core is dissolved completely, and the Cu₇S₄ shell is kept to the formation of hollow structures.

By using Cu₂O crystals as templates, D. S. Xu et al.[93] first created non-spherical Cu₇S₄ mesocages (including cubic, octahedral and multi-pod) with single-crystalline shells. Figure 10a is a typical TEM image of cubic Cu₇S₄ cages. Through a replacement reaction between S²⁻ in solution and O in the Cu₂O lattices, Cu₂O/Cu₇S₄ core/shell structures were firstly formed; Cu₇S₄ mesocages obtained through a subsequently removing the residual Cu₂O by ammonia. It is noteworthy

![Figure 10](image-url)
that the compositions can be adjusted from Cu$_2$S to Cu$_{1.75}$S through controlling the reaction atmospheres from N$_2$ to air as shown in Eq. (3) and Eq. (4), respectively.

$$\text{S}^2^- + \text{Cu}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH}^- + \text{Cu}_2\text{S} \quad (3)$$

$$16\text{S}^{2-} + 14\text{Cu}_2\text{O} + 16\text{H}_2\text{O} + \text{O}_2 \rightarrow 32\text{OH}^- + 4\text{Cu}_2\text{S} \quad (4)$$

Guided by the above mechanisms, W. X. Zhang et al. synthesized double-walled Cu$_7$S$_4$ nanoboxes by two consecutive cycles that repeatedly produced Cu$_7$S$_4$ layers in Na$_2$S solution and dissolved the Cu$_2$O core in NH$_3$ solution (Figure 10b). Using polyhedral 26-facet Cu$_2$O microcrystals as the templates, S. D. Sun et al. synthesized 26-facet CuS microcages with different types of shells (Figure 10c–e). Interestingly, the three pairs of square {100} facets and the four pairs of triangular {111} facets became rough with self-assembled nanoplate, however, the six pairs of rectangular {110} facets remained smooth. Further TEM analysis demonstrated that the {100}, {111} and {110} facets of CuS microcage were transformed into mesocrystal, nano-twin and single crystal, respectively colored blue, red, and yellow in the simulated structure shown in Figure 10e. The formation of different shells is attributed to the different crystallographic structures of {100}, {111} and {110} facets of Cu$_2$O crystals. The {110} and {111} facets with dangling Cu atoms could be protected by negatively charged agents, while the neutral {100} facet had weak protection. Thus, the rate of the Kirkendall process between S and O atoms was different in each surface, leading to different shells.

5.3. Coordinating Eetching

Coordinating dissolution is commonly used for dissolving insoluble materials. For instance, by using certain ligands (CN$^-$, SCN$^-$, S$_2$O$_3^{2-}$, Cl$^-$ or NH$_3$ etc.) coordinate Cu$_2$O polyhedra, various transition metal hydroxides, or oxides with hollow structures could be obtained, perfectly imitating the geometry of the Cu$_2$O template. Z. Y. Wang et al. synthesized uniform SnO$_2$ nanoboxes by combining precisely controlled hydrolysis of SnCl$_4$ and simultaneous coordinating etching of the c-Cu$_2$O templates. During this process, insoluble CuCl intermediate was immediately formed, and dissolved in NaCl solution via coordinating with excess Cl$^-$ to form soluble [CuCl$_{x-1}$]$^{2-x}$

$$\text{SnO}_2 + \text{H}_2\text{O} \rightarrow \text{Sn}^{4+} + \text{Cl}^{-} + 2\text{OH}^-$$

Eventually, outward evacuation of [CuCl$_{x-1}$]$^{2-x}$ and inward diffusion of Sn$^{4+}$ and Cl$^-$ through the SnO$_2$ shell lead to formation of intact SnO$_2$ shells and the consumption of Cu$_2$O templates. Based on the Pearson’s hard and soft acid–base (HSAB) principle, stable complexes could be formed through the interaction of hard bases with hard acids, and soft bases with soft acids. As a soft acid, Cu$^+$ within the Cu$_2$O templates prefer a soft base ligand (S$_2$O$_3^{2-}$, CN$^-$, SCN$^-$) to a hard base (Cl$^-$, NH$_3$) as the coordinating etchant. Recently, our group put forward a general route to create metal hydroxides (MHs, M = Mn, Fe, Co, Ni, and Zn) nanocages by employing o-Cu$_2$O as the sacrificial template at room temperature.

$$\text{Cu}_2\text{O} + x\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow [\text{Cu}_y\text{S}_x\text{O}_{3y}]^{2-x} + 2\text{OH}^- \quad (5)$$

$$\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \Leftrightarrow \text{HS}_2\text{O}_3 + \text{OH}^- \quad (6)$$

$$\text{M}^{2+} + \text{OH}^- \rightarrow \text{M(OH)}_2 \quad (7)$$

The strategy was well designed by using Na$_2$S$_2$O$_3$ as the coordinating etchant. S$_2$O$_3^{2-}$ would coordinate etching Cu$_2$O and

Figure 11. SEM, TEM, and SAED images of the a) Mn(OH)$_2$, b) Fe(OH)$_2$, c) Co(OH)$_2$, d) Ni(OH)$_2$, and e) Zn(OH)$_2$ nanocages. Parts (x$_1$) (x = a–e) and (x$_2$) display typical SEM and TEM images of MH nanocages, respectively; part (x$_3$) displays high-magnification SEM images of part (x$_1$); part (x$_4$) is the corresponding SAED patterns. The scale bars in parts (x$_1$), (x$_2$), and (x$_3$) are 100, 20, and 100 nm, respectively. Reproduced with permission. Copyright 2013, American Chemical Society.
form soluble $\left[Cu_2(S_2O_3)\right]_{x=2-4}$, because the soft–hard interaction of Cu$^{2+}$–O$^{2-}$ within Cu$_2$O was weakened compared to the soft–soft interaction of Cu$^{2+}$–S$_2$O$_3^{2-}$ (Eq. (5)). Due to the unstable interaction of borderline acid–soft base (M$^{2+}$–S$_2$O$_3^{2-}$), metal ions (M$^{2+}$) were free in the solution. The OH$^-$ ions that originated from Cu$_2$O etching (Eq. (5)) and some S$_2$O$_3^{2-}$ hydrolysis (Eq. (6)) lead to the generation of M(OH)$_2$ (Eq. (7)). The above routes could be concluded as “coordinating etching and precipitating”, which is shown as Step 1 in Figure 8c. The two simultaneous reactions ensure that the shell of M(OH)$_2$ perfectly kept the original shape of o-Cu$_2$O (Step 2 in Figure 8c). Through simple thermal treatment, those polyhedral amorphous MHs nanocages could dehydrate into polycrystalline metal oxide (MO) porous nanocages (Step 3 in Figure 8c).

Well-defined MH nanocages (Mn(OH)$_2$, Fe(OH)$_2$, Co(OH)$_2$, Ni(OH)$_2$, and Zn(OH)$_2$) could be produced according the CEP route (Figure 11). The as-prepared MH nanocages kept the shape of the o-Cu$_2$O template with an edge length of ~500 nm (Figure 11x; x = a–e), and small NPs consisted of the MH shell (Figure 11x,j). TEM images of MH nanocages (Figure 11x,j) clearly illustrated their hollow characteristic, and the SAED patterns (Figure 11x,d) demonstrated their amorphous in nature. According to this strategy, amorphous Ni(OH)$_2$ nanoboxes$^{[32]}$ (Figure 12a), Co(OH)$_2$/reduced graphene oxide$^{[45]}$ (Figure 12b) and Ni–Co amorphous double hydroxides$^{[35]}$ (Figure 12c,d) can also be obtained by minor revised this method, and illustrate excellent performances in the realm of sensor and energy.

6. Applications in Catalysis and Sensing

To date, the applications of Cu$_2$O have mainly been in the realms of catalysis and sensing. In this section, we will focus on the facet-dependent performances of the three basic Cu$_2$O NCs and such Cu$_2$O-based NCs for applications of photocatalysis, gas catalysis, organocatalysis, and sensing as well as the relationship between their structures and properties.

6.1. Photocatalysis

The requirement of sustainable energy and reduction of environmental pollution has driven considerable research efforts in photodegradation of pollutants and water splitting by employing abundant solar energy.$^{[169]}$ Cu$_2$O with bandgap of 2.1 eV are expected to be promising materials in visible-light photocatalytic degradation.$^{[69]}$ and great studies have been devoted to the controlled synthesis of Cu$_2$O with their morphology-dependent photocatalytic activities.$^{[13,36,44,73,114,147]}$ During the photocatalytic process, one of the key factors for the catalyst is “catching” the organic pollutants, since that would offer the catalyst more opportunities to contact and catalyze those pollutants.$^{[34,75]}$ Our group$^{[7]}$ demonstrated that the adsorption ability of methyl orange (MO), one of the industrial pollutants, to the different shapes of Cu$_2$O NCs followed the sequence of octahedra > cuboctahedra > cubes. The exposed {111} facets of o-Cu$_2$O had positively charged “Cu” atoms that inclined to interact with the negatively charged groups –SO$_3^-$ in MO molecules. This suggested that Cu$_2$O (111) facets would strongly interact with the molecules possessing negatively charged groups, and then effectively photodecompose these molecules; while the (111) facets interact weakly with the positively charged molecules, and lead to a poor photodegradation activities. As expected, M. H. Huang et al.$^{[128]}$ verified that the photocatalytic activity of o-Cu$_2$O was higher than that of o-Cu$_2$O. Furthermore, the photocatalytic activities of extended hexapods Cu$_2$O NCs with more {111} facets were more effective and active than o-Cu$_2$O (Figure 13a). Subsequently, they synthesized d-Cu$_2$O NCs with only exposed {110} facets,$^{[79]}$ which exhibited an excellent photocatalytic activities for the photodegradation of MO because of the high density of Cu atoms on the surface (Figure 13b). T. R. Zhang et al.$^{[135]}$ demonstrated the photocatalytic activities of Cu$_2$O microcrystals: c-Cu$_2$O with {100} facet <o-Cu$_2$O with {111} facet < 50-facet polyhedral with {211} facet = 50-facet polyhedral with {522} facet = 50-facet polyhedral with {311} facet (Figure 13c). The larger number of atomic steps and kinks in these high-index facets contributed to the more efficient photodegradation than those of the c-Cu$_2$O and o-Cu$_2$O.

Figure 12. a) Typical TEM image of Ni(OH)$_2$ nanobox with thin shell and well-defined interior. Reproduced with permission.$^{[32]}$ b) Typical TEM image of Co(OH)$_2$/rGO with secondary structures. Reproduced with permission.$^{[45]}$ Copyright 2014, American Chemical Society. c) A typical TEM image of NiCo$_2$O$_4$(OH)$_2$ double hydroxides nanocages, and d) their corresponding EDS measurements. Reproduced with permission.$^{[35]}$ Inset of a–c) is the SAED pattern of each hydroxides nanocages.
A more efficient photogenerated electron–hole (e\(^{-}/\)h\(^{+}\)) pair separation would contribute to the improvement of photocatalytic activity. Besides the strong interaction between MO and the \{111\} corners and \{110\} edges of Cu\(_2\)O jagged polyhedron (Figure 14a,b), the OH\(^{-}\) ions also selectively adsorb onto these corners and edges with higher energy. Thus, a faster e\(^{-}/\)h\(^{+}\) separation will accelerate the production of the \cdot\text{OH} free radicals and then enhance their photocatalytic activities. Compared to the precursor of Cu\(_2\)O truncated octahedron, the Cu\(_2\)O jagged polyhedron displayed a better photocatalytic performance in the degradation of MO (Figure 14c).\(^{[44]}\) After 75 min, MO was only degraded to 60% by the Cu\(_2\)O precursor, while MO was even degraded to 82% by jagged Cu\(_2\)O.

Furthermore, another important factor for photodecomposition reactions is the rapid transportation to the surfaces of photogenerated charges. A Schottky barrier could be formed at the metal–semiconductor interface that reduces the recombination of the photogenerated e\(^{-}/\)h\(^{+}\) pairs, and then improve photocatalytic efficiency.\(^{[30,33,36]}\) Y. J. Xiong et al.\(^{[33]}\) designed a p-type metal–semiconductor (Pd–Cu\(_2\)O) heterostructure, and demonstrated that the synergistic effect between charge spatial separation and Schottky barrier contributed to the efficient hydrogen production from pure water (Figure 15). Due to the low work function of \{111\} facet, no Schottky barrier is formed at the Pd–Cu\(_2\)O\{111\} interface; instead, an anti-blocking layer would be formed at that interface that increase the recombination of e\(^{-}/\)h\(^{+}\) pairs (Figure 15a). In contrast, since the high work function of \{100\} facet, e\(^{-}/\)h\(^{+}\) pairs would be well separated at the Cu\(_2\)O\{100\}-Pd interface (Figure 15b). The hydrogen production of Pd–Cu\(_2\)O cubes with proper Pd load capacity over 4 h was 2.20 mmol g\(^{-1}\), which was dramatically higher than other Cu\(_2\)O counterparts (Figure 15c).
6.2. Gas Catalysis

Cu₂O crystals have been actively studied in gas catalysis, and showed facet-dependent catalytic performance. W. X. Huang et al. evaluated the CO oxidation of uniform c-Cu₂O and o-Cu₂O. HRTEM images (Figure 16a,b) demonstrated that the surfaces of c-Cu₂O and o-Cu₂O were all oxidized to CuO thin films during the CO oxidation (denoted as CuO/c-Cu₂O and CuO/o-Cu₂O, respectively). CuO/c-Cu₂O became active at 190 ºC and achieved the conversion rate of 49.1% CO at 240 ºC, while CuO/o-Cu₂O became active at 140 ºC and achieved the conversion rate of 93.2% CO at 240 ºC (Figure 16c). The activation energies of CuO/c-Cu₂O and CuO/o-Cu₂O oxidized CO were calculated to be 110.0 ± 6.4 and 73.4 ± 2.6 kJ mol⁻¹ respectively, as shown in the Arrhenius plot of Figure 16d. Density functional theory (DFT) calculation suggested that CuO thin films grow on {111} and {100} facets with different surface compositions and structures (Figure 16e,f). Three-coordinated O (O₃c) and three-coordinated Cu (Cu₃c) atoms were terminated at the CuO overlayer on [111] facet (Figure 16e); by contrast, only O₂c atoms were terminated at the {100} facet (Figure 16f).

Further DFT calculation results demonstrated that there were significant differences in the reaction process and active sites during the process of CuO/c-Cu₂O and CuO/o-Cu₂O oxidized CO (Figure 16g). For the surface of CuO/o-Cu₂O (Figure 16g), individual CO or O₂ molecules were weakly adsorbed on the sites of Cu₃c, while these two molecules could be strongly co-adsorbed on the sites of O₃c and Cu₃c, and then a COO(a) surface intermediate (SI) was formed. Subsequently, the COO(a) SI disintegrated into O₂ and a O(a) adatom, with an activation energy (Eₐ) of 0.37 eV. Finally, CO reacted with O(a) adatom to produce CO₂ with an Eₐ of 0.17 eV; thus, a cycle of catalytic process has completed. For the surface of CuO/c-Cu₂O (Figure 16h), O₂ molecules could not adsorb on the sites of O₃c, while CO could be strongly adsorbed onto the sites of O₂c and a CO₂(a) SI was formed. Next, the CO₂(a) SI disintegrated to generate CO₂, and an oxygen vacancy (OV) was created in CuO with a Eₐ of 1.15 eV. Subsequently, O₂ molecules could adsorb on OV in CuO to produce O₂(a). Finally, CO reacted with O₂(a) to produce CO₂ with a Eₐ of 0.67 eV; thus, a cycle of catalytic process has completed, and the OV has refilled. Therefore, DFT calculation results were in accordance with experimental results, which demonstrated that CO oxidation catalyzed by CuO/o-Cu₂O proceeded with a lower Eₐ (the disintegration of the COO(a), 0.37 eV) than that catalyzed by CuO/c-Cu₂O (the disintegration of the CO₂(a) SI, 1.15 eV).

W. X. Huang et al. further reported the facet-dependent performances in catalyzing propylene oxidation by using CA-free c-Cu₂O, o-Cu₂O, and d-Cu₂O. c-Cu₂O exposed by {100} facets were most selective for CO₂; O₂-Cu₂O exposed {111} facets were most selective for acrolein; d-Cu₂O exposed by {110} facets were most selective for propylene oxide (Figure 17a). All the three Cu₂O NCs became active at 170 ºC, and the conversion rate of C₃H₆ rose with the increase of reaction temperature (Figure 17 b1-b3). In addition, the efficiency of C₃H₆ conversion was followed the order o-Cu₂O > c-Cu₂O > d-Cu₂O. The specific reaction rate of propylene for various Cu₂O NCs also followed the order o-Cu₂O > c-Cu₂O > d-Cu₂O (Figure 17 b4). o-Cu₂O are more active in catalyzing C₃H₆ oxidation with O₂ than c-Cu₂O and d-Cu₂O. The (111) plane was terminated with three-coordinated unsaturated O (O₃CSU) in the first layer, and one-coordinated unsaturated Cu (Cu₁CSU) and coordinated saturated (Cu₃CSU) in the second layer in a 1:3 ratio. The (100) plane was terminated with two-coordinated OCSU in the first layer, and CUCSU in the second layer. The (110) plane was terminated with three-coordinated OCSU and CUCSU in the first layer, and CUCSU in the second layer. DFT calculations explained the adsorption of C₃H₆ on (111), (100), and (110) facets (Figure 17b). For the (111) facet (Figure 17c), Cu₃CSU-C₃H₆(a) was formed through the selective adsorption of C₃H₆ molecules at the site of Cu₃CSU (C=C stretching frequency (νC=C) of 1560 cm⁻¹)

Figure 15. a1,b1) Scheme of the photogenerated charge transfer in the Pd-Cu₂O cubic-octahedron and Pd-Cu₂O cubes, respectively. a2,b2) SEM image of Cu₂O cubic-octahedron and Cu₂O cubes with Pd selectively loaded on the {111} and {100} surface, respectively. The molar ratio of Pd/Cu₂O in b2 is 8 x 10⁻³. c) H₂ production from pure water irradiation for 4 h by employing various photocatalysts under visible-light (λ > 400 nm). “Cubo-oct” denotes cubic-octahedron, and the concentrations represent the molar ratio of Pd/Cu₂O. Reproduced with permission. © 2015 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
with an adsorption energy \(E_{\text{ads}}\) of \(-1.53\) eV. For the (100) facet (Figure 17c), \(O_{\text{CUS}}-O_{\text{CUS}}-C_{\text{H}}(a)\) was formed through the selective adsorption of \(C_{3}H_{6}\) molecules at the site of two neighboring two-coordinated \(O_{\text{CUS}}\) (\(v_{\text{ce}} = 1453\) cm\(^{-1}\)) with an \(E_{\text{ads}}\) of \(-2.85\) eV. For the (110) facet (Figure 17c), \(C_{3}H_{6}\) adsorbed on the three-coordinated \(O_{\text{CUS}}\), and \(Cu_{\text{CSA}}\) sites to form \(Cu_{\text{CSA}}-O_{\text{CUS}}-C_{\text{H}}(a)\) (\(v_{\text{ce}} = 1437\) cm\(^{-1}\)), and on \(O_{\text{CUS}}\) site to generate \(O_{\text{CUS}}-C_{\text{H}}(a)\) (\(v_{\text{ce}} = 1574\) cm\(^{-1}\)). The \(E_{\text{ads}}\) for the two sites of (110) facet was similar.

In addition, different SI produced on each \(Cu_{3}O\) NCS. On the \(Cu_{3}O\) (111) surface, the distance of \(C=C\) bond (\(d_{\text{C=C}}\) in \(Cu_{\text{CUS}}-C_{\text{H}}(a)\)) was calculated to be 1.37 Å, while \(d_{\text{C=C}}\) in \(C_{3}H_{6}\) molecule was 1.34 Å. Therefore, the stable \(C=C\) bond of \(Cu_{\text{CUS}}-C_{\text{H}}(a)\) can be kept in the subsequent reactions, which was in favor of the generation of acrolein. On the \(Cu_{3}O\)(100) surface, \(d_{\text{C=C}}\) in \(O_{\text{CUS}}-O_{\text{CUS}}-C_{\text{H}}(a)\) was 1.59 Å; hence, the weakened \(C=C\) bond would be cleaved by propylene combusting. DFT calculation results (Figure 18a) demonstrated that the \(E_{f}\) for the combustion of \(O_{\text{CUS}}-O_{\text{CUS}}-C_{\text{H}}(a)\) to adsorb \(C_{3}H_{6}(a)\) and the disintegration of \(O_{\text{CUS}}-O_{\text{CUS}}-C_{\text{H}}(a)\) into adsorbed \(CH_{2}(a)\) and \(CHCH_{3}(a)\) was 2.09 and 1.02 eV, respectively. This result suggested that propylene was in favor of...
combustion, which was in accordance with the experiments of \( c\)-CuO\(_2\). On the Cu\(_2\)O(110) surface, \( d_{\text{CC}}\) in \( \text{O}_{\text{CUS}}\text{C}-\text{C}_3\text{H}_6(a)\) was 1.36 Å, which was considered to the generation of acrolein; while the weakened C=C bond in \( \text{Cu}_{\text{CSA}}\text{O}_{\text{CUS}}\text{C}-\text{C}_3\text{H}_6(a)\) with a distance of 1.50 Å inclined to break during the reactions. DFT calculations results (Figure 18b) suggested that the \( E_c\) for the combustion of \( \text{O}_{\text{CUA}}\text{O}_{\text{CUS}}\text{C}-\text{C}_3\text{H}_6(a)\) to adsorb \( \text{CH}_3\text{H}_2(a)\) and the disintegration of \( \text{O}_{\text{CUA}}\text{O}_{\text{CUS}}\text{C}-\text{C}_3\text{H}_6(a)\) into adsorbed \( \text{CH}_2(a)\) and \( \text{CHCH}_3(a)\) was 1.28 and 2.08 eV, respectively. This result suggested that propylene was in favor of epoxidation, which was in accordance with the experiments of \( d\)-CuO. The distinction in reactivities between \( \text{Cu}_{\text{CSA}}\text{O}_{\text{CUS}}\text{C}-\text{C}_3\text{H}_6(a)\) on Cu\(_2\)O(110) and \( \text{O}_{\text{CUS}}\text{C}-\text{C}_3\text{H}_6(a)\) on Cu\(_2\)O(100) is three-coordinated \( \text{O}_{\text{CUS}}\) on (110) facet and two-coordinated \( \text{O}_{\text{CUS}}\) on (100) facet. Three-coordinated \( \text{O}_{\text{CUS}}\) is less electrophilic than two-coordinated \( \text{O}_{\text{CUS}}\), which is to the disadvantage of the breakage of the C=C bond in propylene.

Compared to low-index facets, the high-index facets have higher catalytic activities due to the more atomic steps and kinks. C. Wang et al.\cite{} evaluated the CO oxidation of \( d\)-CuO polyhedra. Due to the presence of high-index \{311\} planes on their surfaces, the 50-facet Cu\(_2\)O microcrystal showed the highest specific catalytic rate \((8.8 \times 10^{-6} \text{ mol m}^{-2} \text{ vol} \text{s}^{-1})\), which was markedly higher than \( d\)-CuO, \( o\)-CuO, \( c\)-CuO, and rhombicuboctahedron (Figure 19a). Z. X. Xie et al.\cite{} investigated the CO oxidation of truncated concave \( o\)-Cu\(_2\)O enclosed mainly by high-index surfaces \{332\} facets with high-density atomic steps (Figure 19b, inset). Truncated concave \( o\)-Cu\(_2\)O \{332\} + \{100\} displayed the highest catalytic activity, which became active at 170 °C and reached a CO conversion rate of 50.4% at 220 °C. Truncated \( o\)-Cu\(_2\)O \{111\} + \{100\} became active at 170 °C with a lower CO conversion, and reached a CO conversion of 39.8% at 220 °C. However, \( c\)-Cu\(_2\)O illustrated the lowest catalytic activity that \( c\)-Cu\(_2\)O only became active at 190 °C and reached a CO conversion of 31.9% at 220 °C (Figure 19b).

### 6.3. Organocatalysis

Numerous important products (optical devices, drugs, materials, etc.) commercialized or in the stage of development, have aromatic C=N and aromatic C=C bonds that can be coupled by organocatalysts through cross-coupling reactions.\cite{} Thus, scaling up production of these bonds with any novel and basic technology is greatly significant for industry.\cite{} Over the last decade, the research focus on coupling of C=N and C=C bonds has gradually moved from the high-cost Pd-catalyst to the low-cost Cu-catalyst.\cite{} Recently, Cu\(_2\)O (NC form or bulk) has been reported as excellent catalysts for cross-coupling reactions.\cite{} The facet-dependent organocatalysis activity of \( c\)-Cu\(_2\)O, \( o\)-Cu\(_2\)O, and \( d\)-Cu\(_2\)O NCs was firstly evaluated by M. H. Huang et al.\cite{} based on the synthesis of 1,2,3-triazoles\cite{} and the regioselective synthesis of 3,5-disubstituted isoxazoles.\cite{} To compare the catalytic activities of each Cu\(_2\)O NCs, all the three NCs were used with identical surface area (Table 1). \( d\)-Cu\(_2\)O displayed the most efficient catalytic activity, with shortest reaction times and the highest product yields, followed by \( o\)-Cu\(_2\)O and the least active \( c\)-Cu\(_2\)O. These results demonstrate that delicate facet controlling of Cu\(_2\)O NCs can greatly improve the organocatalytic efficiency. Subsequently, M. H. Huang et al.\cite{} developed a capping-free synthetic approach for the synthesis of sub-100 nm Cu\(_2\)O NCs with morphology evolution from \( c\)-Cu\(_2\)O to \( o\)-Cu\(_2\)O. All the Cu\(_2\)O NCs illustrated high yields.
within short reaction times, o-Cu$_2$O was the most excellent catalyst that could catalyse the cycloaddition reaction in just 2 h with high yields.

L. L. Li et al. [66] employed monodisperse o-Cu$_2$O, d-Cu$_2$O, and octadecahedra to catalyse aerobic oxidative coupling of phenylacetylene and arylboronic acids. During the catalytic reaction, those NCs showed high yields but different crystal surface stability. After three catalytic cycles, o-Cu$_2$O were seriously etched and aggregated beyond recognition, as well as their yield dropping from 94% to 32%. By contrast, no change was observed in the {110} facets of d-Cu$_2$O and octadecahedra during the reaction. Interestingly, Cu$_2$O octadecahedra had the best catalytic activity upon recycling, and the yield of aerobic oxidative coupling was increased from 89% to 97%. The reason was that the {100} facets of Cu$_2$O octadecahedra were more prone to etching than the {110} facets during this catalytic reaction, and the Cu$_2$O octadecahedra were gradually oxidized and etched to high-active concaves (Figure 20a). However, the in-depth etching mechanism still requires further study. A metal–metal oxide interface formed after deposition of noble metal onto metal oxide, and the hybrid structure displayed superior catalytic performances to the physical mixtures or single domains. [30,33,36,40,145] L. L. Li et al. [40] further improved the experimental route by selective depositing noble metals on the concave Cu$_2$O NCs. Pd atoms only grew on cavities (Figure 20 b, inset), but Ag$^0$ majorly nucleated on edges and vertices (Figure 20 c, inset). During the aerobic oxidative arylation of phenylacetylene, the hybrid nanoconcaves exhibited more excellent catalytic activities than the single component or physical mixtures (Figure 20 b,c). XPS spectra combined DFT calculation results verified the improvement of catalytic activities attributed to the synergistic effect, in which e$^-$ migrated from the noble metal to Cu$_2$O.

6.4. Sensing

H. C. Zeng et al. [8] evaluated the ethanol sensing ability of Cu$_2$O self-assembled 3D superlattices (~10 nm) and disassembled nanocubes (~20 nm), and the corresponding TEM images were shown in Figure 21 a, b, respectively. The organized Cu$_2$O illustrated a better sensing capability than the
disassembled Cu$_2$O (Figure 21c). Without ethanol molecules, the defects on the surface of Cu$_2$O would adsorb O$_2$ from air and negatively charged O$^-$, O$_2^-$, and O$_3^-$ are produced. A localized accumulation of holes were formed that separated from e$^-$ near the surfaces of Cu$_2$O. When Cu$_2$O was exposed to ethanol/air mixtures, e$^-$ was produced from the redox reactions between adsorbed O$_2$ on the surface and ethanol that would be transferred into conduction band of Cu$_2$O. And then, e$^-$ and h$^+$ would be recombined that lead to decrease the concentration of carrier. Due to the higher ratio of surface to bulk, a greater carrier depletion layer would be formed of the self-assembled c-Cu$_2$O when exposed to ethanol. That layer, in cooperation with a relatively small contact potential, would result in a distinct improvement of sensitivity (Figure 21d).

Our group$^{[60]}$ evaluated the CO sensing performance of Cu$_2$O–CuO composite microframes at the working temperature of 240 ºC. As the concentration of CO increased, the Cu$_2$O–CuO composite microframes illustrated excellent CO sensing performance with highest sensitivity and shortest response time, followed by the pure CuO microcubes and the pure Cu$_2$O microcubes (Figure 22).

In the presence of o-anisidine and graphene oxide, H. M. Fan et al.$^{[81]}$ synthesized reduced graphene oxide (rGO)–conjugated Cu$_2$O nanowire (NW) composite mesocrystals. The obtained mesocrystals with marked octahedral shape and eight [111] facets were composed of highly oriented nanowires. They further compared the NO$_2$ sensing performance of Cu$_2$O NW, rGO and rGO–Cu$_2$O mesocrystals at room temperature. In the presence of NO$_2$, all the

Table 1. The catalytic abilities of Cu$_2$O NCs for the synthesis of 3-(4-nitrophenyl)-5-phenylisoxazole.

| Entry | Catalyst                  | BET surface area/m$^2$ g$^{-1}$ | Amount used (mg) | Time (h) | Yield$^a$ |
|-------|---------------------------|---------------------------------|------------------|----------|-----------|
| 1     | Cu$_2$O (nanocubes)       | 2.84                            | 1                | 7        | 82        |
| 2     | Cu$_2$O (octahedra)       | 0.56                            | 5                | 5        | 89        |
| 3     | Cu$_2$O (rhombic dodecahedra) | 1.35                         | 2                | 2        | 95        |

Note: Reagents and conditions: 1a (5.0 × 10$^{-2}$ g, 2.5 × 10$^{-4}$ mol), 2a (2.6 × 10$^{-2}$ g, 2.5 × 10$^{-4}$ mol), Et$_3$N (7.5 × 10$^{-2}$ g, 7.5 × 10$^{-4}$ mol), and EtOH (3 × 10$^{-1}$ L). $^a$Isolated yields Reproduced with permission.$^{[24]}$ Copyright 2013, Royal Society of Chemistry.

Figure 20. a) Shape evolution of the three different Cu$_2$O NCs during the aerobic oxidative arylation of phenylacetylene. Reproduced with permission.$^{[66]}$ Catalytic activities of b) Pd-Cu$_2$O and c) Ag-Cu$_2$O nanconcave in the aerobic oxidative arylation of phenylacetylene. Inset of (b) and (c) is the typical SEM images of Pd-Cu$_2$O and Ag-Cu$_2$O, respectively. Reproduced with permission.$^{[40]}$
three samples exhibited an increased sensitivity with the increasing concentration of NO\(_2\) (Figure 23a,b). The sensitivities of rGO–Cu\(_2\)O, Cu\(_2\)O NW, and rGO at 2.0 ppm were 67.8%, 44.5%, and 22.5%, respectively. And the limits of detection (LOD) were calculated as 64, 81, and 82 ppb for rGO–Cu\(_2\)O, Cu\(_2\)O NW, and rGO, respectively. The improved sensing performance of the rGO–Cu\(_2\)O mesocrystals was attributed to their high specific surface area and enhanced conductivity. When rGO–Cu\(_2\)O was exposed to NO\(_2\), the NO\(_2\) molecule could obtain e\(^-\) from the “activated” surface O ion, and the rGO with excellent electrical conductivity could effectively transfer electrons that promoted the h\(^+\) conductivity in the Cu\(_2\)O (Figure 23c). Furthermore, because of the porous and highly anisotropic structure of NW mesocrystals cooperated with the rGO, the rGO–Cu\(_2\)O possessed larger surface accessibility for contacting NO\(_2\).

Recently, S. H. Yu et al.\[^{29}\] investigated the facet-dependent stripping behaviour in the determination of Pb\(^{2+}\) by using c-Cu\(_2\)O, o-Cu\(_2\)O, and d-Cu\(_2\)O through square wave stripping voltammetry (SWASV). At –0.65 V, all three samples illustrated sharp stripping peaks of Pb\(^{2+}\) with different detection limit and sensitivity (Figure 24a). The o-Cu\(_2\)O modified electrode illustrated the lowest detection limit of 0.066 × 10\(^{-6}\) M (Figure 24a2) and highest sensitivity of 178 ± 20.3 μA μm\(^{-1}\) cm\(^{-2}\) (Figure 24a4), followed by c-Cu\(_2\)O of 0.076 × 10\(^{-6}\) M (Figure 24a1) and 127 ± 14.4 μA μm\(^{-1}\) cm\(^{-2}\) (Figure 24a4), and d-Cu\(_2\)O of 0.103 × 10\(^{-6}\) M (Figure 24a3) and 90.1 ± 13.4 μA μm\(^{-1}\) cm\(^{-2}\) (Figure 24a4). It suggested that the order of stripping response of Pb\(^{2+}\) on Cu\(_2\)O microcrystal facets was found to follow the sequence \{111\} > \{100\} > \{110\}.

DFT calculations were employed to investigate the adsorption mechanism of Pb\(^{2+}\) on Cu\(_2\)O. Figure 24b depicted the conditions of Pb\(^{2+}\) adsorption on different Cu\(_2\)O surfaces. When Pb\(^{2+}\) adsorbed on \{111\} surface (Pb/Cu\(_2\)O \{111\}) (Figure 24b1), one O atom coordinated with Pb\(^{2+}\), and the distance of Pb–O bond was 2.188 Å. When for the \{100\} surface (Figure 24b2), two O atoms coordinated with Pb\(^{2+}\), and the distance of Pb–O bond was 2.260 and 2.223 Å. Figure 24b3 showed the Pb/Cu\(_2\)O \{110\} that one Cu atom and one O atom coordinated with Pb\(^{2+}\), because the Cu and O atoms were in the identical plane in top layer, and the distances of Pb–Cu and Pb–O bond were 2.685 Å and 2.183 Å. The shorter distance of Pb–O in Pb/Cu\(_2\)O \{111\} contributed to the strong adsorption with the Cu\(_2\)O surface. Furthermore, the adsorption Gibbs free energy of Pb(II) on \{100\}, \{110\} and \{111\} facets were calculated as 4.952, 4.761 and 5.742 eV, respectively. These calculated results demonstrate the stronger Pb\(^{2+}\) adsorption ability of \{111\} facet, followed by the \{100\} and \{110\} facet, which agreed quite well with the electrochemical performance.

7. Conclusion and outlook

Through numerous examples, we have demonstrated that facet-controlled synthetic strategies provide remarkably facile and convenient approaches to the preparation of Cu\(_2\)O-based NCs with heterogeneous, etched, or hollow structures. These routes depend on the different surface atomic structure of Cu\(_2\)O NCs, in which the selective adsorption of CAs could protect special

![Figure 21](image1.png)

Figure 21. TEM images of a) Cu\(_2\)O self-assembled 3D supercrystals and b) disassembled nanocubes. c) Their corresponding sensitivities toward ethanol sensing measured under identical situations. d) The schematic diagrams of 1D array of c-Cu\(_2\)O toward ethanol sensing, where \(E_F\), \(E_V\), and \(E_C\) are Fermi energy, valence band energy, and conduction band energy, respectively. Reproduced with permission.\[^{8}\] Copyright 2010, American Chemical Society.

![Figure 22](image2.png)

Figure 22. The normalized resistance of CO exposure on (I) Cu\(_2\)O-CuO microframes, (II) pure CuO cubes and (III) pure Cu\(_2\)O cubes. Inset is a typical TEM image of the Cu\(_2\)O-CuO microframe. Reproduced with permission.\[^{60}\] Copyright 2013, Royal Society of Chemistry.
facets, and the surface energy and active sites would determine the reaction activity trend. The facet-dependent properties of the Cu$_2$O NCs and such Cu$_2$O-based NCs have been investigated, especially in the realm of photocatalysis, gas catalysis, organocatalysis and sensing. Due to different crystal surface structures, the Cu$_2$O NCs exhibit distinct facet-dependent properties; a subsequently rational design and synthesis of Cu$_2$O-based NCs could tailor and optimize their facet-dependent performances. Although the controllable synthesis of NCs and their derivatives has seen considerable progress and development in the last decade, the next requirements for NCs with excellent performance are the development of more simple and convenient synthetic routes to tailor NCs with ideal components and structures.

The progress we have summarized also opens the door for in-detail studies in catalysis and sensing. Due to their well-defined facets, shape-controlled NCs can provide smooth surfaces for further delicate carving, modifying, or transforming; a deep insight into the relationship between structures and properties will be obtained by combining with theoretical calculations and simulations of the catalysis and sensing process. This perception will enable further delicate tailoring of NCs, and bridge the gap between structures and properties, so that traditional trial-and-error pattern to obtain functional NCs would be instead replaced by ingenious design and controllable synthesis.

Finally, it is should be envisaged that the facet-dependent properties of Cu$_2$O-based NCs could also apply to other realms. For instance, our group$^{[92]}$ found that o-Cu$_2$O NCs displayed a higher oxidative stress to D. magna than that of c-Cu$_2$O due to its higher reactivity. M. H. Huang et al.$^{[9]}$ investigated the facet-dependent electrical properties of the three basic Cu$_2$O NCs. o-Cu$_2$O is highly conductive, c-Cu$_2$O is moderately conductive, and d-Cu$_2$O is nonconductive. A thin surface layer having different degrees of band bending contributed to the different conductivities. Interestingly, a diode-like response was obtained when electrical connection was made on two different facets of a rhombicuboctahedron. D. F. Xue et al.$^{[25]}$ evaluated Li-ion battery anode performances and showed that c-Cu$_2$O had the highest capacity among Cu$_2$O polyhedra (the sequence of electroactivity is \{110\} < \{111\} < \{100\}), because \{100\} facets had high electroactivities toward redox reactions. Thus, more instances of the facet-dependent properties should be continuously explored, endowing nanomaterials with excellent performances for numerous applications.

Figure 23. a) Response of Cu$_2$O NW, rGO-Cu$_2$O, and rGO with the increasing concentration of NO$_2$. b) The sensitivities for detection of NO$_2$ on Cu$_2$O NW, rGO-Cu$_2$O, and rGO. c) The mechanism of rGO-Cu$_2$O toward NO$_2$ sensing. Reproduced with permission.$^{[81]}$ Copyright 2012, American Chemical Society.
Acknowledgements

This project is supported by the National Basic Research Program of China (2014CB931802), the National Natural Science Foundation of China (51272012, 21471013) and China Postdoctoral Science Foundation Funded Project (2015M570916).

Received: May 5, 2015
Revised: July 1, 2015
Published online: August 14, 2015

References

[1] C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, Chem. Rev. 2005, 105, 1025.
[2] H. Bao, W. Zhang, Q. Hua, Z. Jiang, J. Yang, W. Huang, Angew. Chem. Int. Ed. 2011, 50, 12294.
[3] Q. Hua, T. Cao, X. K. Gu, J. Lu, Z. Jiang, X. Pan, L. Luo, W. X. Li, W. Huang, Angew. Chem. Int. Ed. 2014, 53, 4856.
[4] M. H. Huang, S. Rej, S.-C. Hsu, Chem. Commun. 2014, 50, 1634.
[5] G. Liu, C. Y. Jimmy, G. Q. M. Lu, H.-M. Cheng, Chem. Commun. 2011, 47, 6763.
[6] R. Li, H. Han, F. Zhang, D. Wang, C. Li, Energy Environ. Sci. 2014, 7, 1369.
[7] D.-F. Zhang, H. Zhang, L. Guo, K. Zheng, X.-D. Han, Z. Zhang, J. Mater. Chem. 2009, 19, 5220.
[8] K. X. Yao, X. M. Yin, T. H. Wang, H. C. Zeng, J. Am. Chem. Soc. 2010, 132, 6131.
[9] C.-S. Tan, S.-C. Hsu, W.-H. Ke, L.-J. Chen, M. H. Huang, Nano Lett. 2015, 15, 2155.
[10] M. H. Huang, P. H. Lin, Adv. Funct. Mater. 2012, 22, 14.
[11] K. Zhou, Y. Li, Angew. Chem. Int. Ed. 2012, 51, 602.
[12] H. Wang, J. Gao, T. Guo, R. Wang, L. Guo, Y. Liu, J. Li, Chem. Commun. 2012, 48, 275.
[13] Y. Wang, H. Zhang, Y. Han, P. Liu, X. Yao, H. Zhao, Chem. Commun. 2011, 47, 2829.
[14] K. Chanda, S. Rej, M. H. Huang, Chem. Eur. J. 2013, 19, 16036.
[15] H. Wang, X. Lang, J. Gao, W. Liu, D. Wu, Y. Wu, L. Guo, J. Li, Chem. Eur. J. 2012, 18, 4620.
[16] H. Wang, J. Yang, X. Li, H. Zhang, J. Li, L. Guo, Small 2012, 8, 2802.
[17] M. Leng, M. Liu, Y. Zhang, Z. Wang, C. Yu, X. Yang, H. Zhang, C. Wang, J. Am. Chem. Soc. 2010, 132, 17084.
[18] Z.-Y. Zhou, N. Tian, J.-T. Li, I. Broadwell, S.-G. Sun, Chem. Soc. Rev. 2011, 40, 4167.
[19] Z.-Y. Jiang, Q. Kuang, Z.-X. Xie, L.-S. Zheng, Adv. Funct. Mater. 2010, 20, 3634.
[20] H. B. Jiang, Q. Cuan, C. Z. Wen, J. Xing, D. Wu, X.-Q. Gong, C. Li, H. G. Yang, Angew. Chem. Int. Ed. 2011, 50, 3764.
[21] J. Yin, Z. Yu, F. Gao, J. Wang, H. Pang, Q. Lu, Angew. Chem. Int. Ed. 2010, 49, 6328.
[22] X. Han, M. Jin, S. Xie, Q. Kuang, Z. Jiang, Y. Jiang, Z. Xie, L. Zheng, Angew. Chem. Int. Ed. 2009, 48, 9180.
[23] X. Wang, X. Han, S. Xie, Q. Kuang, Y. Jiang, S. Zhang, X. Mu, G. Chen, Z. Xie, L. Zheng, Chem. Eur. J. 2012, 18, 2283.
[24] K. Chanda, S. Rej, M. H. Huang, Nanoscale 2013, 5, 12494.
[25] K. Chanda, S. Song, D. Xue, CrystEngComm 2015, 17, 2110.
[26] W. Fan, Z. Shi, X. Yang, M. Cui, X. Wang, D. Zhang, H. Liu, L. Guo, Water Res. 2012, 46, 5981.
[27] R. Li, F. Zhang, D. Wang, J. Yang, M. Li, J. Zhu, X. Zhou, H. Han, C. Li, Nat. Commun. 2013, 4, 1432.
[28] X.-W. Liu, Langmuir 2011, 27, 9100.
[29] Z.-G. Liu, Y.-F. Sun, W.-K. Chen, Y. Kong, Z. Jin, X. Chen, X. Zheng, J.-H. Liu, X.-J. Huang, S.-H. Yu, Small 2015, 11, 2493.
[30] R. Long, K. Mao, M. Gong, S. Zhou, J. Hu, M. Zhi, Y. You, S. Bai, J. Jiang, Q. Zhang, X. Wu, Y. Xiong, Angew. Chem. Int. Ed. 2014, 53, 3205.
[31] L.-M. Lyu, M. H. Huang, J. Phys. Chem. C 2011, 115, 17768.
[32] Y.-H. Tsai, K. Chanda, Y.-T. Chu, C.-Y. Chiu, M. H. Huang, Nanoscale 2014, 6, 8704.
[33] L. Wang, J. Ge, A. Wang, M. Deng, X. Wang, S. Bai, R. Li, J. Jiang, Q. Zhang, Y. Luo, Y. Xiong, Angew. Chem. Int. Ed. 2014, 53, 5107.
[34] H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, Nature 2008, 453, 638.

Figure 24. a1–a4) Typical SWASV responses of a1) c-Cu2O, a2) o-Cu2O, and a3) d-Cu2O to detect Pb(II) in optimal situations. The corresponding linear fitting was inset in (a1), (a2) and (a3), respectively. a4) Sensitivities for SWASV detection of Pb(II) on bare GCE, d-Cu2O, c-Cu2O, and o-Cu2O modified GCE. Inset of (a4) shows SWASV responses of 1.4 × 10^−6 mol/L Pb(II) on bare GCE (black line), o-Cu2O (red line), c-Cu2O (blue line), and d-Cu2O (pink line) modified GCE. b1–b3) Top and side views of optimized adsorption models of Pb(II) on different Cu2O NCs simulated by DFT. Reproduced with permission.[29]
