Electrochemical Synthesis of Cu$_2$O Concave Octahedrons with High-Index Facets and Enhanced Photoelectrochemical Activity

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ABSTRACT: High-index-faceted nano-/microcrystals exhibit enhanced catalytic activity and can thus serve as new-generation catalysts owing to their high density of low-coordinated atoms, leading to significantly enhanced catalytic activity. In this study, an effective electrochemical approach termed cyclic scanning electrodeposition (CSE) was developed to convert a thin Cu film into Cu$_2$O concave octahedrons enclosed by 24 {344} high-index facets at room temperature with high yield and high throughput. The formation mechanism and the role of each ion in the electrolyte were systematically studied, which facilitated the design of a high-index-faceted metal/metal oxide through CSE. We also presented a general formula to identify the structure of an individual crystal enclosed by {khh} high-index facets based on the crystals oriented along three low-index zone axes and imaged by transmission electron microscopy. Experimental results demonstrated the Cu$_2$O concave octahedrons to be highly efficient, cost-effective catalysts for photoelectrochemical hydrogen production. This new technology is a promising route for the synthesis of metal or metal oxide crystals with high activity and has a great potential for several advanced applications, such as clean energy conversion.

KEYWORDS: high index, Cu$_2$O, shape-controlled, concave, photoelectrochemical

INTRODUCTION

The development of clean energy conversion processes, such as hydrogen production, electricity generation through fuel cells, and CO$_2$ conversion, relies on a series of electrochemical processes. A major challenge for these technologies is the development of cost-effective and robust catalysts that can effectively catalyze the reactions on the electrode surface. Inorganic microcrystals with high-index facets have attracted considerable attention as potential new-generation catalysts because their high density of low-coordinated atoms (steps, ledges, and kinks) results in considerably enhanced catalytic activity.¹⁻³

Synthesis of high-index-faceted microcrystals is challenging because the rate of crystal growth in the direction perpendicular to the high-index plane is considerably faster than that along the low-index plane, thereby causing rapid disappearance of the high-index facets during crystal formation. Recently, there has been a growing interest in the controlled execution of concave structures because their negative curvatures are generally enclosed by high-index facets.² For example, Pt concave nanocubes enclosed by {720} facets exhibited an enhanced electrocatalytic activity 2–4 times higher than that of the Pt cubes and Pt cuboctahedra for oxygen reduction reaction and formic acid oxidation.⁵ Truncated concave octahedral Cu$_2$O microcrystals enclosed by 24 {332} facets and 6 {100} facets exhibited 20% improvement in the catalytic oxidation of CO compared with cubic Cu$_2$O microcrystals.⁵

Several synthetic methods for synthesizing anisotropic concave metallic or metallic oxide microcrystals have been developed. These methods can be classified into two strategies: selective etching and controlled overgrowth.⁴,⁷ In selective etching, etchants perform at different etching rates on different crystallographic planes, and capping agents are used to selectively passivate the specific planes, resulting in a concave structure. In controlled overgrowth, crystal growth is kinetically controlled in a nonequilibrium condition, leading to preferential and directional growth to form a concave structure. However, these synthesis methods typically require complicated procedures, including seed preparation, intermediate purification, and removal of adsorbates (e.g., organic additives, capping agents, and surfactants). Consequently, fabrication is time-consuming (10⁻72 h), and even a subtle change in the reaction temperature or the concentration of adsorbates results in a low production yield with different morphologies.⁸⁻¹⁰ Using adsorbates may block active sites and introduce heterogeneous impurities, leading to degraded catalytic activity.

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Moreover, adsorbates have different binding affinities to different metals or metal oxides; therefore, it is challenging to formulate a generic rule for selecting adsorbates for the design of targeted crystals. Although the aforementioned methods are well-established in a laboratory environment, they remain unsuitable for industrial production. Therefore, an industrial technique must be developed for the design of different morphologies and the controlled execution of high-index-faceted microcrystals.

Electrochemical deposition is a widely used industrial process because of its inherent low cost and high throughput. This process has also been recently developed to grow metal microcrystals by controlling potential waveforms and using ions or organic additives. In this study, a new electrochemical approach termed cyclic scanning electrodeposition (CSE) was developed to effectively convert Cu films into Cu$_2$O concave octahedrons by 24 \{344\} high-index facets at room temperature with a high yield. The formation mechanism and roles of Ni$^{2+}$, SO$_4^{2-}$, and CH$_3$COO$^-$ in the electrolyte were systematically studied, which provided a design rule to tune Cu$_2$O with various shapes through CSE. The effectiveness of the high-index-faceted Cu$_2$O microcrystals was demonstrated, and an enhanced catalytic activity was observed in photoelectrochemical (PEC) hydrogen production.

**RESULTS AND DISCUSSION**

**Electrochemical Synthesis of High-Index-Faceted Cu$_2$O Concave Octahedrons.** Figure 1 is a schematic of the formation of concave octahedral Cu$_2$O microcrystals on the substrates. An MPS layer is formed on the substrate, and a Cu layer is then electroplated on the MPS-grafted substrate in the Cu electrolyte. During CSE, the Cu layer is stripped from the substrate in an electrolyte comprising CH$_3$COONa, NiSO$_4$, and Na$_2$SO$_4$ in the forward anodic scan, and Cu$^{2+}$ ions are re-electroplated to form concave octahedral Cu$_2$O microcrystals in the reversed cathodic scan.

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**Figure 1.** Schematic of the formation of concave octahedral Cu$_2$O microcrystals on the substrates. An MPS layer is formed on the substrate, and a Cu layer is then electroplated on the MPS-grafted substrate in the Cu electrolyte. During CSE, the Cu layer is stripped from the substrate in an electrolyte comprising CH$_3$COONa, NiSO$_4$, and Na$_2$SO$_4$ in the forward anodic scan, and Cu$^{2+}$ ions are re-electroplated to form concave octahedral Cu$_2$O microcrystals in the reversed cathodic scan.

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**Figure 2.** SEM images of (a) a Cu layer coated on the MPS-grafted substrate, (b) concave octahedral Cu$_2$O microcrystals formed on the substrate through CSE, and (c) a single concave octahedral Cu$_2$O microcrystal.
field-emission scanning electron microscopy (FE-SEM) images of Cu2O concave octahedron in three orientations, suggesting that the concave octahedrons are in an octagonal symmetry and enclosed by 24 identical facets. According to Steno’s law, Miller indices of high-index facets can be identified by a conjunction of the angle between the facets viewed along an appropriate zone axis.20 Figure 3a2−c2 illustrates the schematic model of a concave octahedron in [111], [110], and [100] zone axes corresponding to the featured projection angles from the three orientations, respectively, where the 24 quadrangular planes are all {344} high-index facets. To confirm the high-index planes, the Cu2O concave octahedron oriented in the zone axes was examined through transmission electron microscopy (TEM) and selective area electron diffraction (SAED). Considering the first row in Figure 3 as an example, the six spots in a six-fold symmetry correspond to the {110} reflections (d-spacing, 3.0 Å) of a Cu2O crystal (Figure 3a4), indicating that the zone axis in Figure 3a3 was [111]. The projection angle of edge-on facets delineated with a red outline was then compared with the schematic model viewed in the same direction. It is noteworthy that the projection angles in the TEM image are in good agreement with the theoretical values of the angles in the {344} model (the deficient apex of the Cu2O microcrystal was due to the transferring of Cu2O microcrystals from the substrate to the Ni grid when preparing the TEM sample). A comparison between the TEM images and the schematic model in the three primary zone axes confirmed that the concave octahedrons are enclosed by 24 {344} high-index facets.10,21

Three-dimensional (3D) and two-dimensional (2D) atomic models of the Cu2O crystal are shown in Figure 4. The atomic model projected from the [110] zone axis demonstrates that the {344} facet is periodically composed of three units of {111} on the terrace and one unit of {110} at the step (Figure 4b).4 Figure 4c illustrates the {344} model along the [100] axis; this concave geometry is speculated to be the result of the considerably changed growth rates along the [111] and [100] directions. The ratio (R) given in eq 1 can be used to describe the relationship between the growth rate and the crystal morphology.19,22

\[
R = \frac{\text{growth rate along the [100] direction}}{\text{growth rate along the [111] direction}}
\]
Figure 5. Schematic with SEM images showing the feasibility of tuning the shape of Cu$_2$O microcrystals using SO$_4^{2-}$, CH$_3$COO$^-$, NO$_2^-$, and NO$_3^-$.

The yellow, green, and blue colors represent (111), (100), and (344) facets, respectively.

For example, the $R$ value of a cube is 0.58 and the $R$ value of an octahedron is 1.73$^{10,20}$. The detailed calculation of the $R$ value for a (344) concave octahedron is presented according to Figure 4d, where $\alpha$ is 35.26$^\circ$ and $\beta$ is 54.74$^\circ$. In this case, the $\gamma$ is 46.69$^\circ$ and the $R$ value is 2.16, indicating that the morphology of Cu$_2$O microcrystals is attributable to the changing growth rate along different low-index facets, which results in fast branching growth along the [100] direction.\textsuperscript{23} Figure 4d illustrates a mathematical model viewed along the [110] axis for a general concave structure, which is enclosed by \{khh\} high-index facets in an octagonal symmetric geometry. The relationship between the $R$ values for this type of morphology can be derived as follows:

\[
\tan \gamma = \frac{\sqrt{2} k}{h} \tag{2}
\]

\[
a = \frac{1}{2 \cos \alpha} \tag{3}
\]

\[
b = \frac{1}{2} (\tan \alpha - \tan(\beta - \gamma)) \tag{4}
\]

\[
b = \frac{V_{(100)}}{V_{(111)}} = \frac{1}{\cos \alpha(\tan \alpha - \tan(\beta - \gamma))} \tag{5}
\]

where $\gamma$ is the projection angle between the \{khh\} and \{100\} facets along the [110] direction. In future studies, this model can be used to identify \{khh\} high-index facets by comparing them to the TEM image in an appropriate crystallographic axis.\textsuperscript{3}

Role of Each Ion in the Shape Evolution of Cu$_2$O Microcrystals.\textsuperscript{21} The preferential growth is easy to occur in the concave facets at a more negative potential of 0.75 V (Figure 5). Herein, the binding affinities and preferential adsorption of different ions were investigated to provide a design rule on tuning the morphologies of Cu$_2$O microcrystals through CSE, as illustrated in Figure 5. SO$_4^{2-}$ and CH$_3$COO$^-$ were the two illustrative types of anions in our electrolyte. In 0.1 M Na$_2$SO$_4$ electrolyte (in the absence of CH$_3$COO$^-$), the Cu$_2$O microcrystal was enclosed by eight hexagonal \{111\} facets and six square \{100\} facets were formed when applying CSE in the absence of CH$_3$COO$^-$ ions, indicating the importance of CH$_3$COO$^-$ ions in the formation of the concave shape.

Anions are typically used for selective adsorption on certain crystal planes, blocking or slowing their etching or growth rate to produce high-aspect-ratio structures.\textsuperscript{22} Herein, the binding affinities and preferential adsorption of different ions were investigated to provide a design rule on tuning the morphologies of Cu$_2$O microcrystals through CSE, as illustrated in Figure 5. SO$_4^{2-}$ and CH$_3$COO$^-$ were the two illustrative types of anions in our electrolyte. In 0.1 M Na$_2$SO$_4$ electrolyte (in the absence of CH$_3$COO$^-$), the Cu$_2$O microcrystal was enclosed by eight hexagonal \{111\} facets and six square \{100\} facets were formed when applying CSE in the absence of CH$_3$COO$^-$ ions, indicating the importance of CH$_3$COO$^-$ ions in the formation of the concave shape.
growth rate of [100]/[111], resulting in an increase in the R value from <1.73 to 2.16. The branch growth along the [100] direction was promoted, whereas the growth rate along the [111] direction was inhibited, indicating the preferential adsorption of CH₃COO⁻ ions on Cu₂O {111} planes. Because of the synergistic effect of SO₄²⁻ and CH₃COO⁻ ions, octahedrons were initially formed through the thermodynamic growth, and the crystal growth was then inhibited on {111}, causing preferential kinetic growth along the [100] direction, which in turn resulted in concave octahedrons (Figure S5). The formation of the complex CH₃COO⁻–Cu increased the electroplating energy barrier and also changed the growth mode from being thermodynamic-controlled to kinetics-controlled during CSE. In this study, an optimum ratio of 1.75 in [CH₃COO⁻]/[SO₄²⁻] was found to effectively produce Cu₂O concave octahedrons bounded by 24 high-index (344) facets. When CSE was conducted in a NaN₂(NO₃)₂ electrolyte (pH = 9), NO₂⁻ ions selectively adsorbed on {111} facets and the formation of Cu(OH)₂ in the alkaline electrolyte enhanced the nucleation and electrocrystallization, which caused rapid anisotropic kinetic growth, resulting in a network structure of intercrossed Cu₂O nanocrystals.31 Cubic {100} Cu₂O microcrystals were formed in 0.02 M Cu(NO₃)₂ electrolyte owing to the preferential adsorption of NO₃⁻ on {100} facets.21 By using the CSE technique with different scan rates, the growth mechanism was studied. In a typical electrolyte consisting of SO₄²⁻ and CH₃COO⁻ anions, the spherical polycrystalline Cu₂O particles were formed at a high scan rate of 500 mV/s in the reversed scan. A large overpotential causes a rapid formation of spherical Cu₂O particles in a short period of time (Figure S7a,b). At a low scan rate of 5 mV/s, Cu⁺ ions at the interface were consumed during the diffusion process into the bulk electrolyte. Thus, the anisotropic growth prevailed under a nonequilibrium condition. The extended Cu₂O hexapods were produced (Figure S7c,d), where several small branches grew on the trunk as typical diffusion-limited products.15,22 Therefore, the CSE has a great potential to provide flexibility in tuning the shape of Cu₂O microcrystals by using different combinations of ions and potential waveforms, especially Cu₂O can be tailored into various morphologies via CSE at room temperature and the process can be completed within 7.5 min. Besides, the CSE can be readily extended to other metal or metal oxides. For example, Ag₂O hexapods can be effectively produced on Ag-coated MPS-grafted FTO by using a square waveform (E_{on} = 20 Hz, E_{off} = 40 Hz, and E_{on} = 40 Hz) in the electrolyte comprising 0.1 M Na₂SO₄ and 0.312 M CH₃COONa (Figure S6).

**Photoelectrochemical Activity of High-Index-Faceted Cu₂O Concave Octahedrons.** Cu₂O is a p-type semiconductor with a direct band gap of 2 eV and a conduction band that is 0.7 eV more negative than that of the hydrogen evolution reaction, making it an attractive catalyst for PEC hydrogen production.32–33 At the semiconductor and liquid junction, an electrical field is generated because of band bending, and the photogenerated electrons of Cu₂O are driven into the solution, resulting in the reduction of H⁺ to H₂.27,34 Cyclic voltammetry shows a prominent photoreduction peak for Cu₂O concave octahedrons under illumination (Figure S8). To evaluate the photocatalytic activity of Cu₂O, the concave octahedral (344) Cu₂O and typical cubic {100} Cu₂O were prepared on a stainless steel as the photocathodes in a three-electrode PEC cell, where the Ag/AgCl electrode and Pt wire were used as the reference and counter electrodes, respectively. Figure 6a,b illustrates the current response of linear sweep voltammetry (LSV) measured in 0.5 M Na₂SO₄ solution in a PEC cell under chopped light illumination. The cubic Cu₂O photocathode exhibited an enhanced photocurrent density of 0.75 mA cm⁻² at −0.61 V (0 V vs reversible hydrogen electrode), which is comparable to the reported PEC performance of bare Cu₂O (without the use of co-catalysts).27 The concave octahedral Cu₂O photocathode exhibited an enhanced photocurrent density of −0.75 mA cm⁻². The current densities were calibrated according to the real active surface areas (Figures S9 and S10). The high-indexed facets with active surface atomic structures facilitated electron excitation, which caused the accumulated electrons in the conduction band to enhance the photocatalytic activity.35,36 To evaluate the cyclability of photocathodes, the photocurrent was collected at a fixed

![Figure 6](image-url)
potential of $-0.61\ V$ ($0\ V$ vs reversible hydrogen electrode) under chopped light (light on/off cycle 20 s). As presented in Figure 6c,d, both the cubic Cu$_2$O and concave octahedral Cu$_2$O photocathodes exhibited high stability in aqueous solution, with more than 60% photocurrent density remaining after 15 min of illumination.\ The concave octahedral Cu$_2$O microcrystals were examined by using X-ray photoelectron spectroscopy (XPS). Prior to the PEC test, the primary peak is located at a binding energy of 932.4 eV, which can be assigned to Cu(I) in Cu$_2$O (Figure S11a).\ After the PEC test, a small shoulder peak is observed (Figure S11b), where Cu 2p$_{3/2}$ spectra can be fitted into three peaks at positions of 932.4, 933.6, and 935.2 eV corresponding to Cu(I) in Cu$_2$O, Cu(II) in CuO, and Cu(II) in Cu(OH)$_2$, respectively.\ It is believed that the formation of a stable Cu(OH)$_2$ and CuO layer protects Cu$_2$O against photocorrosion.\  

**CONCLUSIONS**

Synthesis of high-indexed metal or metal oxide microcrystals is challenging. In this study, we developed a CSE technique to electrochemically convert a Cu film into Cu$_2$O concave octahedrons bound by 24 \{344\} high-index facets. A general formula was presented to identify and quantify the structure of individual crystals enclosed by \{khh\} high-index facets. This electroplating technique has advantages, such as low cost, low temperature, high throughput, and a wide process window, and is thus potentially suitable for industrial production. A systematic study of the role of each ion in an electrolyte enables the design of metal/metal oxide microcrystals with various shapes and facets through CSE. MPS serves as an electroplating nucleation promoter, Ni$_2$O$_5$ is an oxidative etchant, and the ratio of [CH$_3$COO$^-$]/[SO$_4^{2-}$] determines the anisotropic growth for the formation of the concave Cu$_2$O structure. NO$_3^-$ and NO$_2^-$ can also be added into the electrolyte for tuning the shapes of the microcrystal. A high-index-faceted Cu$_2$O concave octahedron was used as the photocathode to demonstrate an enhanced catalytic activity and robust cyclic performance during PEC hydrogen production. Further development of the CSE method (e.g., different ion combinations and potential waveforms) could provide a universal electrochemical approach with the flexibility to control the shapes and facets of metal/metal oxide microcrystals, which has a great potential in numerous emerging technologies, including the photoconversion of CO$_2$ to hydrocarbon fuels, hydrogen production from formic acid, fuel cells, and biosensors.  

**EXPERIMENTAL SECTION**

**MATERIALS**

Copper(II) sulfate pentahydrate (CuSO$_4$·5H$_2$O), copper(II) nitrate hydrate (Cu(NO$_3$)$_2$·4H$_2$O), sulfuric acid (H$_2$SO$_4$), and hydrochloric acid (HCl) were purchased from Sigma-Aldrich. Sodium sulfate (Na$_2$SO$_4$), nickel(II) sulfate hexahydrate (NiSO$_4$·6H$_2$O), and sodium acetate trihydrate (CH$_3$COONa·3H$_2$O) were purchased from Showa. Sodium dodecyl sulfate (SDS) and MPS were purchased from Fluka and TCI America, respectively. Copper plating additive and leveler were obtained from Atotech Asia Pacific Ltd. All chemicals were used as received without further purification. The solutions used in this study were prepared with deionized water and further purified by using a Millipore Direct Q3-5 purification system.

**Electrochemical Synthesis of Cu$_2$O Microcrystals.** The electrochemical synthesis was performed by using a CHI 660E in a standard three-electrode system with a Pt mesh as the counter electrode and saturated Ag/AgCl as the reference electrode. The substrates, including FTO glass (1 cm x 1.5 cm; 8 \Omega/ ) and stainless steel sheet, were immersed in 1 v/v % MPS in ethanol for 3 min. Subsequently, a Cu layer was electroplated on the MPS-grafted substrate in an electrolyte comprising 0.3 M Cu$_2$SO$_4$, 10 v/v % H$_2$SO$_4$, 60 ppm HCl, 0.5 mL/L copper plating additive, and 20 mL/L copper plating leveling at room temperature. To produce concave octahedral Cu$_2$O microcrystals, Cu-coated FTO or a Cu-coated stainless steel sheet was subjected to CSE at a scan rate of 10 mV/s with an anodic scan from $-0.75$ to 1.45 V followed by a cathodic scan from 1.45 to $-0.75\ \text{V}$ in a neutral electrolyte consisting of 0.312 M CH$_3$COONa, 0.078 M NiSO$_4$, and 0.1 M Na$_2$SO$_4$ at room temperature. The reaction was completed within 7.5 min for one scan cycle. To synthesize truncated octahedral Cu$_2$O microcrystals, a Cu-coated substrate was preformed through CSE (cyclic scan from $-0.75$ to 1.45 V at 10 mV/s) in 0.1 M Na$_2$SO$_4$. Cu$_2$O nanoflakes were produced through CSE (cyclic scan from $-0.75$ to 1.45 V at 10 mV/s) in an alkaline electrolyte comprising 0.412 M NaNO$_3$ (pH = 9). For the synthesis of a cubic Cu$_2$O photoanode, the sample was prepared galvanostatically by cathodic deposition (0.7 A m$^{-2}$) in a solution of 0.02 M Cu(NO$_3$)$_2$ and 5 wt % SDS at 60 °C for 20 min.\  

**Structure Characterizations.** The morphologies and crystal structures of Cu microcrystals were characterized by FE-SEM (Hitachi S-4800) and high-resolution TEM (Tecnai, G200S-Twin). The composition and phase of the as-prepared products were determined by XRD (Bruker D8 ADVANCE diffractometer, using Cu Kα radiation) and electron backscatter diffraction (Leo 1530). The binding energies of Cu 2p$_{3/2}$ states were characterized by using XPS (PHI VersaProbe II Scanning XPS Microprobe).

**Photocurrent Measurements.** The PEC performance was evaluated by using a three-electrode configuration in 0.5 M Na$_2$SO$_4$ electrolyte. The photoresponse current was measured under chopped light (light on/off cycle of 10 s) by using a standard solar simulator (Pecell PEC-L01, Japan) equipped with a UV (425 nm) filter and an IR (800 nm) filter, where the intensity of the light source was calibrated to simulate AM 1.5 illumination (100 mW cm$^{-2}$) at the top side of the PEC cell. Prior to measurements, the electrolyte was continuously bubbled with N$_2$ for 15 min. For LSV, the potential was scanned from $-0.3$ to $-0.95\ \text{V}$ at 5 mV/s. To evaluate the stability, the photocurrent density was measured versus time at a fixed potential of $-0.61\ \text{V}$ (Ag/AgCl) for $>900 \text{s}$ under chopped light (light on/off cycle of 20 s).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b12076. Additional XRD patterns, EBSD maps, SEM images, XPS analysis, and electrochemical analysis (PDF)

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**Notes**

The authors declare no competing financial interest.

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REFERENCES


