



# Facile synthesis of cuprous oxide nanooctahedra using electrodeless deposition



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## ABSTRACT

A facile electrodeless deposition method was developed for the preparation of cuprous oxide ( $\text{Cu}_2\text{O}$ ) nanooctahedra by immersing different metal substrates with patterns or scratches on surface into a solution consisting of cupric sulphate ( $\text{CuSO}_4$ ) and lactic acid (LA). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) examinations show that the formation of  $\text{Cu}_2\text{O}$  nanooctahedra is attributed to the reducibility of metal substrates.  $\text{Cu}_2\text{O}$  nanooctahedra can form only when the reducibility of metal substrates is more active than that of Cu. The optical properties and photocatalytic activity of  $\text{Cu}_2\text{O}$  nanooctahedra were also investigated.

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## 1. Introduction

Cuprous oxide ( $\text{Cu}_2\text{O}$ ), as a typical *p*-type semiconductor with a direct band gap of  $\sim 2.17$  eV, is one of the few semiconductors that can be excited by visible light. Recently, visible-light photocatalysts have attracted increasing attention because they are widely used in the development and utilization of solar energy [1–4]. In addition,  $\text{Cu}_2\text{O}$  nanoparticles can also be used for photodegradation of water, photoelectric conversion materials, and negative electrode materials for lithium ion batteries [5,6]. Unique properties of nanostructured crystals are associated with both the size and the shape because they dictate the interfacial atomic arrangement of the nanomaterials [7,8]. Typically, the photocatalytic ability is dependent on the shape of  $\text{Cu}_2\text{O}$  nanocrystals [9,10]. It has been reported that  $\text{Cu}_2\text{O}$  nanooctahedra show better photocatalytic activity than  $\text{Cu}_2\text{O}$  nanocubes because {111} facets are more active than {100} facets [9]. As a result, novel and facile methods to fabricate  $\text{Cu}_2\text{O}$  nanocrystals with different morphologies have been of great research interest. To date, some progress has been made in the synthesis of  $\text{Cu}_2\text{O}$  nanocrystals with different shapes such as nanowires [11], multipods [12], nanobelts [13], nanocubes [14] and nanooctahedra [15,16]. Particularly, extensive studies have focused on the fabrication of  $\text{Cu}_2\text{O}$  nanooctahedra. For example, electrochemical deposition method [15] and surfactant aqueous phase method [17] have been used to fabricate  $\text{Cu}_2\text{O}$  nanooctahedra. Although different methods have been developed for the preparation of  $\text{Cu}_2\text{O}$  nanooctahedra, most of them are complicated and difficult because multiple additives are required. Currently, few reports can be found concerning a convenient way to prepare well-defined  $\text{Cu}_2\text{O}$  nanooctahedra with high uniformity.

In addition, no detailed investigation has been carried out to clarify the formation mechanism of  $\text{Cu}_2\text{O}$  nanooctahedra.

In this Letter, electrodeless deposition was presented to prepare  $\text{Cu}_2\text{O}$  nanooctahedra. Electrodeless deposition is a type of redox reaction, which does not require a direct current voltage injection and any kind of additives. Uniform  $\text{Cu}_2\text{O}$  nanooctahedra with an average edge length of  $150 \pm 30$  nm have been successfully fabricated. Based on the experimental results, a possible formation mechanism has been proposed. Furthermore, the optical properties and photocatalytic activity of  $\text{Cu}_2\text{O}$  nanooctahedra were studied.

## 2. Experimental details

First, we prepare a solution composed of 0.4 M cupric sulfate ( $\text{CuSO}_4$ ) and 3 M LA. LA complexes with  $\text{Cu}^{2+}$  ions to stabilize them in alkaline solution and also subtly determines the morphology of final products as a face selective adsorption additive. Sodium hydroxide (NaOH) solution (4 M) is dropped into the solution under constant stirring. In this way, the pH of the solution is adjusted to 9, and the color will change from sky-blue to dark blue. The temperature of the solution is kept at 60 °C by immersing the beaker in a water bath. The Al foil with patterns or scratches on its surfaces was rinsed several times with acetone and deionized water. Subsequently the Al foils were immersed into the reaction mixture solution for 30 min and  $\text{Cu}_2\text{O}$  nanooctahedra were produced on the surface of Al foils. Three different metals (Fe, Cu and Pt) were also used as substrates to study the growth rate of  $\text{Cu}_2\text{O}$  nanooctahedra on different metal substrates. Finally,  $\text{Cu}_2\text{O}$  nanooctahedra were washed with deionized water several times to remove the reaction mixture. The as-deposited  $\text{Cu}_2\text{O}$  nanooctahedra were characterized using JEOL JEM2100F transmission electron microscope (TEM) operating at 200 kV and Hitachi S4800 scanning electron microscope (SEM).

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For measuring the optical properties of  $\text{Cu}_2\text{O}$  nanooctahedra, they were scraped off the Al substrates and dispersed into a mixture of ethanediol and water (volume ratio 1:1) to form a homogeneous suspension. The UV–vis absorption spectra were recorded on a TU 1909 UV–vis spectrophotometer.

Methyl orange (MO) was used as a pollutant to investigate the photocatalytic efficiency of  $\text{Cu}_2\text{O}$  nanooctahedra. Considering that  $\text{Cu}_2\text{O}$  nanooctahedra are deposited on Al foils, we immerse the Al foils with dimensions of  $1 \times 2 \text{ cm}^2$  into 5 mL MO solution with a concentration of 15 mg/L. Solutions were constantly stirred in the dark for 5 h before being irradiated by a 500 W xenon lamp equipped with a UV cutoff filter ( $\lambda \geq 400 \text{ nm}$ ) for 3 h at room temperature. The orange color of the MO solution gradually diminishes under the visible light irradiation in the presence of  $\text{Cu}_2\text{O}$  nanooctahedra indicating the degradation of MO. The MO concentration was analyzed by UV–vis absorption spectra.

### 3. Results and discussion

Figure 1a shows the full view of regular pattern on the surface of Al substrate. The pattern of QDU provides a template for the nucleation and growth of nanocrystals. Figure 1b shows the SEM image of the region enclosed by a square in Figure 1a. In Figure 1b, it can be found that most aggregations and particles gather together inside the kerfs of the patterns with only a few outside. A low-magnification SEM image of as-deposited nanoparticles is shown in Figure 1c, from which it can be seen that the shape of all particles is a regular octahedron. Analysis of more than 100 nanoparticles shows that the edge length of the octahedra ranges from 130 to 180 nm. Interestingly, the  $\text{Cu}_2\text{O}$  nanoparticles grew predominantly where the Al was scratched just prior to exposure to NaOH. In addition, their growth orientations are slightly tilted in random directions. Closer examination of the SEM image shows that the scratched areas of the Al substrate surface are covered with pores which might be due to the corrosive effects of the alkaline solution. Enlarged SEM images of  $\text{Cu}_2\text{O}$  nanooctahedron viewed from the top and side are shown in Figure 1d. They all look like a pyramid viewed from the top and a rhombus from the side, proving that these particles are perfect octahedron enclosed by eight  $\{111\}$  planes.

The morphology and microstructure of  $\text{Cu}_2\text{O}$  nanooctahedra were further characterized using TEM. Figure 2a shows a typical

TEM image taken from an individual octahedron. Figure 2b shows a typical HRTEM image of the region enclosed by a square in Figure 2a. The interplanar spacing is measured to be 2.21 Å, which corresponds to the  $\{002\}$  crystal plane of  $\text{Cu}_2\text{O}$ . The corresponding SAED pattern viewed from  $[011]$  zone-axis shown in the inset indicates that it is single crystalline. The diffraction spots can be indexed using the lattice parameters of  $\text{Cu}_2\text{O}$  ( $a = 4.2696 \text{ Å}$ ).

To disclose the formation mechanism of  $\text{Cu}_2\text{O}$  nanooctahedra, the microstructure of the products deposited on different substrates was investigated. Four different metals, Al, iron (Fe), copper (Cu) and platinum (Pt), were used as substrates and the other conditions (pH, temperature, and solution concentrations) were kept the same during the experiments.

Figure 3a–d show SEM images of  $\text{Cu}_2\text{O}$  nanocrystals fabricated on different substrates by electrodeless deposition. Figure 3a shows a typical SEM image of  $\text{Cu}_2\text{O}$  nanocrystals on Al substrate, from which monodispersed  $\text{Cu}_2\text{O}$  nanooctahedra with an average edge length of  $150 \pm 30 \text{ nm}$  can be seen. When Al is replaced with Fe, a solid and continuous film composed of many nanooctahedra on the surface of Fe substrate, as shown in Figure 3b. The dimensions are determined to be  $111 \pm 37 \text{ nm}$  from statistical analysis of more than 100 nanooctahedra in the SEM images. Therefore,  $\text{Cu}_2\text{O}$  nanooctahedra grow faster on Fe than Al.  $\text{Cu}_2\text{O}$  nanooctahedra can also be obtained on the Cu substrate (Figure 3c). However, compared with Al substrate, fewer and smaller nanoparticles can be found on Cu surface without pores or netted texture. By analyzing more than 100 nanooctahedra, the average edge length of the nanooctahedra on Cu substrate is  $130 \pm 16 \text{ nm}$ . This indicates that  $\text{Cu}_2\text{O}$  nanooctahedra grow faster on Al than Cu. If Pt was used as the substrate (Figure 3d), no  $\text{Cu}_2\text{O}$  nanocrystals formed. As we all know that the work function is the minimum amount of energy required to remove an electron from the surface of a metal. The higher the work function is, the weaker the reducibility of the metal is. The work functions for the different metal substrates are  $\varphi_{\text{Al}} = 4.28 \text{ eV}$ ,  $\varphi_{\text{Fe}} = 4.5 \text{ eV}$ ,  $\varphi_{\text{Cu}} = 4.65 \text{ eV}$  and  $\varphi_{\text{Pt}} = 5.65 \text{ eV}$  [18], therefore the reducibility of different metal substrates can be determined to be  $\text{Al} > \text{Fe} > \text{Cu} > \text{Pt}$ . From the above experimental results, it can be concluded that the growth rate of  $\text{Cu}_2\text{O}$  nanooctahedra depends on the reducibility of the metal substrate. The higher reducibility metal substrate has, the faster  $\text{Cu}_2\text{O}$  nanooctahedra growth rate (except for Al substrate) is. This is due to the dense and compact Al oxide film covered on the regions of Al surface without scratch, which can not be dissolved by NaOH. In order to certify

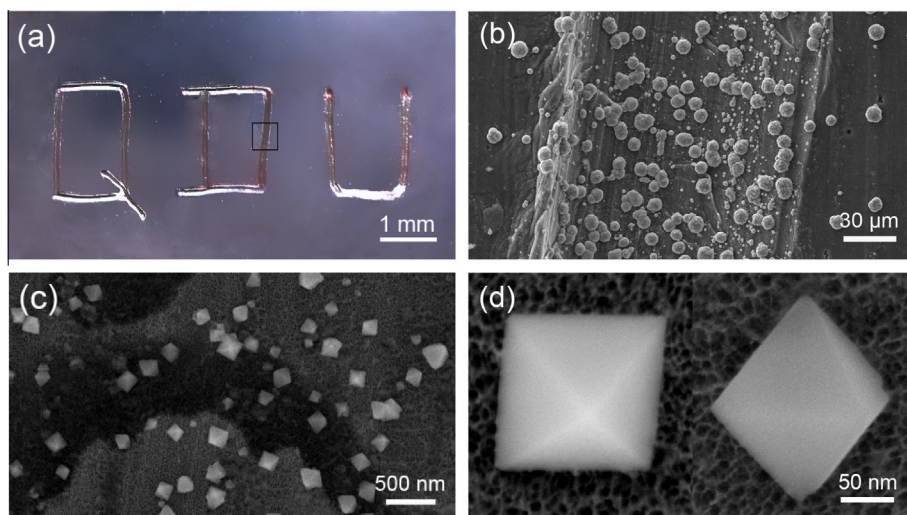


Figure 1. (a) Al foil with regular pattern after deposition; (b) SEM image of the region enclosed by a square in (a); (c) low-magnification SEM image of a part of (b); (d) enlarged SEM image of single  $\text{Cu}_2\text{O}$  nanooctahedra.

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