



# Copper oxide nanomaterials synthesized from simple copper salts as active catalysts for electrocatalytic water oxidation



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## ABSTRACT

Copper oxide (CuO) is a quite cheap and abundant material but there are very few reports of using it as water oxidation catalyst (WOC). In this present study, we report for the first time that CuO nanomaterials synthesized from simple copper salts can be used as WOCs with good activity. CuO materials with different morphologies (microspheres, nanosheets, nanowires) were facilely synthesized without using any template or surfactants. The influence of different morphologies and sizes on the catalytic activity toward oxygen evolution was investigated. Among the four kinds of samples tested, CuO nanowire material exhibited the lowest overpotential for water oxidation and CuO microsphere material had the best catalytic current densities from 1.10–1.40 V. Based on the CV scans, in optimal conditions for these nanomaterials, water oxidation can be achieved under an onset potential of  $\sim 0.90$  V at pH 9.2. The slope of the Tafel plot is 54.5 mV/dec. The Tafel plot also shows appreciable catalytic current at  $\eta = 340$  mV (onset) and that a current density of  $\sim 0.1$  mA/cm<sup>2</sup> required an overpotential at  $\eta = 430$  mV. The Faradaic efficiency was measured to be  $>95\%$ . The CuO samples were further characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS).

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## 1. Introduction

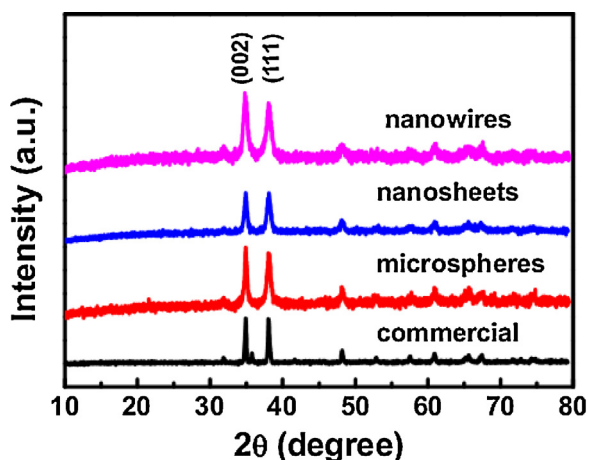
Hydrogen production via water splitting by using solar energy has attracted great attention because it provides an ideal renewable, carbon-neutral, and abundant energy resource [1,2]. A highly efficient water-splitting system requires catalysts with high activity, excellent stability, and low overpotential for catalyzing both water oxidation and hydrogen evolution reactions. It is especially desirable to develop robust and highly active catalysts made of earth-abundant elements for the former reaction, as has been well discussed in previous reports [3–7]. Recently, much progress has been made to explore catalysts based on first-row transition metals such as manganese [4,5,8], cobalt [3,7,9–14], nickel [15–20], and iron [21,22].

As the second cheapest metal among the above-mentioned elements, copper provides wide prospects for practical catalysis but it has seldom been studied for catalytic water oxidation.

Recently, a few copper-based homogeneous systems have been reported for this purpose [23–27]. In addition, our group was the first to report that a nanostructured CuO electrodeposited from both a copper salt and molecular copper(II) 2-pyridylmethylamine complexes could also catalyze water oxidation in aqueous solutions (pH 7–11) [28]. Unfortunately, the organic precursors for electrodeposition of nanostructured CuO were not cost-effective, compared with a simple copper salt.

In this present study, we report on the use of CuO nanomaterials directly synthesized from simple and cheap copper divalent salts as effective catalysts for water oxidation. These nanostructured CuO materials with varying morphologies (microspheres, nanosheets, and nanowires) were synthesized by three facile methods without using any template or surfactants. The CuO nanomaterials were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS). All three different-shaped CuO materials showed catalytic activity for water oxidation. The influence of different shapes and sizes on the catalytic activity was studied.

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**Fig. 1.** XRD patterns CuO materials: nanowires (pink), nanosheets (blue), microspheres (red), commercial CuO (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental Section

### 2.1. Materials

All chemicals, including  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99.0%),  $\text{CuCl}_2$  (99.0%),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (98.0%), commercial CuO (99.0%), sodium dodecyl benzene sulfonate (SDBS, 95.0%), NaOH (96.0%), potassium acetate (KOAc, 92.0%), boric acid (HBI, 99.99%), potassium phosphate (99.0%), and  $\text{K}_2\text{CO}_3$  (99.0%) were commercially purchased (Aldrich or Acros) and used without further purification unless otherwise noted. All electrolyte solutions were prepared with millipore water (resistivity: 18  $\text{M}\Omega \text{ cm}$ ).

### 2.2. Preparation of CuO microspheres

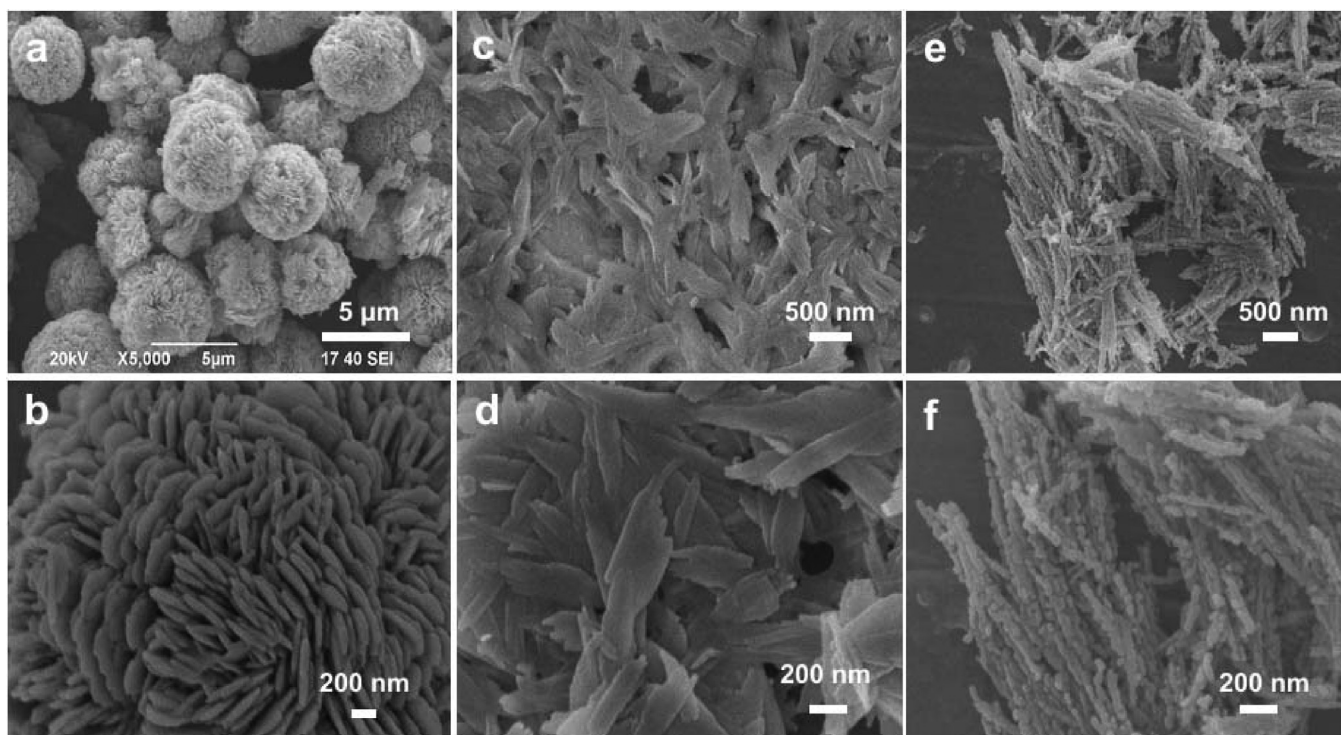
The synthesis was performed using a method modified from a previous report [29]: Initially, 25 mL  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (1.0 M) ethanol solution was mixed with 25 mL of ammonia solution (32%). Then, 5 mL NaOH (1.0 M) was added. The solution was transferred to a Teflon-lined stainless autoclave and heated at 100 °C in a regular oven for 24 h. Thereafter, the autoclave was cooled and the CuO products were washed three times each by deionized water and ethanol and finally dried at 90 °C in air.

### 2.3. Preparation of CuO nanosheets

The CuO nanosheets were prepared as follows [30]: 4.0 g  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  was dissolved in 50 mL water. Then, 40 mL NaOH (1.0 M) was slowly added to the solution with stirring. The as-prepared solution was transferred into a Teflon-lined stainless autoclave which was then heated at 110 °C in a regular oven for 2 h. The autoclave was taken out of the furnace and cooled to room temperature. The black product was washed three times each by deionized water and ethanol and finally dried at 90 °C in air.

### 2.4. Preparation of CuO nanowires

The CuO nanowires were synthesized according to a previously reported method [31]: 0.02 g of sodium dodecyl benzene sulfonate (SDBS) was added into 50 mL  $\text{CuCl}_2$  (0.0125 M) aqueous solution under constant stirring. After stirring for 10 min, 50 mL of  $\text{K}_2\text{CO}_3$  solution (0.0125 M) was added into the above solution dropwise and the solution was stirred for 30 min. Then, 2.0 g NaOH was added into above mixed solution under vigorous stirring, which was continuously stirred for another 10 min and then ultrasonicated for 20 min. Subsequently, the mixture was centrifuged and the blue precipitate was washed three times each by distilled



**Fig. 2.** SEM images of CuO microspheres (a and b), nanosheets (c and d), and nanowires (e and f).

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