

## Synthesis of CuO nanoflower and its application as a H<sub>2</sub>O<sub>2</sub> sensor

AIXIA GU<sup>1,3</sup>, GUANGFENG WANG<sup>1,3</sup>, XIAOJUN ZHANG<sup>1,2,\*</sup> and BIN FANG<sup>1,3</sup>

<sup>1</sup>College of Chemistry and Materials Science, <sup>2</sup>Anhui Key Laboratory of Functional Molecular Solids,

<sup>3</sup>Anhui Key Laboratory of Chem-Biosensing, Anhui Normal University, Wuhu 241000, P.R. China

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**Abstract.** CuO three-dimensional (3D) flower-like nanostructures were successfully synthesized by a simple method at 100°C with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and NH<sub>3</sub>·H<sub>2</sub>O for 6 h in the absence of any additives. We found that NH<sub>3</sub>·H<sub>2</sub>O amount was critical for CuO morphology evolution. The phase analysis was carried out using X-ray diffraction (XRD) and the result confirmed that the CuO nanoflowers were single-phase. The morphological investigations by field emission scanning electron microscope (FESEM) revealed that the CuO nanoflowers were mono-dispersed in a large quantity and consisted of nanosheets. And then, CuO nanoflowers were successfully used to modify a gold electrode to detect H<sub>2</sub>O<sub>2</sub> with cyclic voltammetry (CV) and amperometric (AC). It was found that CuO nanoflowers may be of great potential for H<sub>2</sub>O<sub>2</sub> electrochemical sensing.

**Keywords.** CuO; nanoflowers; electrochemical; H<sub>2</sub>O<sub>2</sub>.

### 1. Introduction

Cupric oxide (CuO) is an important transition metal oxide with a narrow bandgap ( $E_g$  1.2 eV) and forms the basis of several high temperature superconductors and giant magnetoresistance materials (Musa *et al* 1998; Zheng *et al* 2000). Furthermore, because of the complex magnetic phases (Prabhakaran *et al* 1999), CuO has been used for the preparation of a wide range of organic–inorganic nanostructure composites that possess unique characteristics such as high thermal and electrical conductivities as well as high mechanical strength and high-temperature durability (Kumar *et al* 2001). Therefore, on the basis of the fundamental and practical importance of CuO nano-materials, well-defined CuO nanostructures with various morphologies have been fabricated, and many synthesis techniques have been developed to prepare different assemblies of CuO building blocks. Among these, hydrothermal treatment (Liu and Zeng 2004; Lu *et al* 2004; Xu *et al* 2005; Yao *et al* 2005; Liu *et al* 2006), chemical vapour deposition (CVD) (Pan *et al* 2001) and electrochemical techniques (Zhu *et al* 2000) have been documented. Fan's group reported that CuO nanowire arrays were prepared through directly annealing the sputter-deposited Cu<sub>3</sub>N film at 300°C (Fan *et al* 2008). Liu and co-workers studied the effect of additives (NaOH, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Na<sub>2</sub>WO<sub>4</sub> or Na<sub>2</sub>MoO<sub>4</sub> and SDS) on the growth of CuO crystals (Liu *et al* 2007). However, it can be observed from the previous reports that to obtain CuO

nanostructures, generally high temperature, elevated pH of the solution and complex apparatus and reagents are needed. Therefore, it is required to develop a simple and effective method to synthesize complex CuO nanostructures in large quantity at low temperature.

In this paper, we report a successful synthesis of monodispersed CuO nanoflowers using Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and NH<sub>3</sub>·H<sub>2</sub>O at 100°C for 6 h without use of any complex apparatus and reagents. The gold electrode modified with CuO nanoflowers was prepared and used to detect H<sub>2</sub>O<sub>2</sub>. The results showed that the CuO nanoflowers give a very high activity for detecting H<sub>2</sub>O<sub>2</sub>.

### 2. Experimental

All of the chemical reagents were used as received without further purification. In a typical procedure, 6 mL NH<sub>3</sub>·H<sub>2</sub>O (1 M) was added to 10 mL Cu(NO<sub>3</sub>)<sub>2</sub> (0.01 M) solution. The mixture was stirred vigorously to homogeneity and then transferred into a 60 mL steel autoclave. The clave was sealed, maintained at 100°C for 6 h, and then cooled naturally to room temperature. The black precipitate was washed with ethanol and distilled water for several times to remove the impurities before characterizations.

CuO nanoflowers (10 mg) were dissolved into a mixture of 0.1 mL of Nafion perfluorosulfonated ion-exchange resin and 0.9 mL of distilled water. Approximately 60 min of ultrasonication was necessary to obtain uniformly dispersed CuO nanoflowers. After dropping 10 μL of the mixture onto the prepared electrode surface, the electrode was dried in air. The resultant electrode was denominated

\*Author for correspondence (zhangxj@mail.ustc.edu.cn)

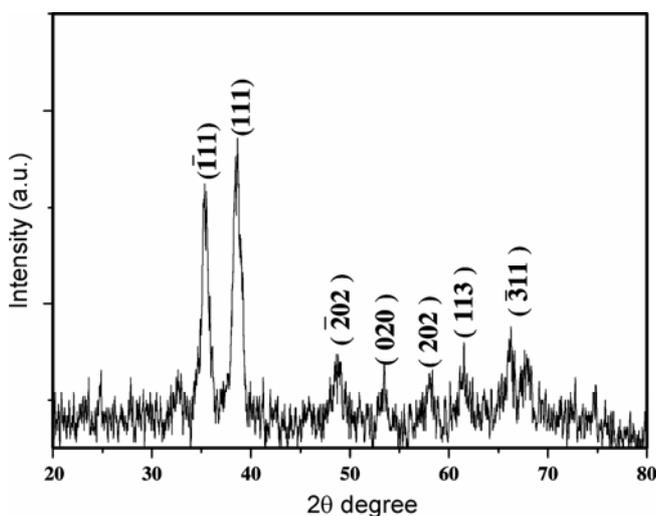
as CuO NFS/Nafion-Au. Electrochemical measurements were performed on a model CHI 660B electrochemical analyser (ChenHua Instruments Co. Ltd., Shanghai, China) controlled by a personal computer using the modified gold electrode as working electrode, an Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. The cyclic voltammetry (CV) and amperometric (AC) data were measured in a 50 mM phosphate buffer solution (PBS, pH 7.2).

X-ray powder diffraction (XRD) patterns of the products were recorded on a Shimadzu XRD-6000 X-ray diffractometer at a scanning rate of  $0.05^\circ/\text{s}$  with  $2\theta$  range from  $20$  to  $80^\circ$ , with high-intensity  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154178 \text{ nm}$ ). Field-emission scanning electron microscopes (FESEM) were obtained using Hitachi S-4800 SEM (operated at 10 kV).

### 3. Results and discussion

Figure 1 shows the XRD profiles taken from the as-prepared CuO nanoflowers. All of the major reflections can be indexed to the monoclinic-phase CuO (space group  $C2/c$ ), which is very close to the reported data (JCPDS 80-1268). At the same time no characteristic peaks of impurities can be detected. This indicates that pure CuO products were obtained under current synthetic conditions.

The general morphologies of as-synthesized CuO nanoflowers were observed by FESEM and shown in figure 2. A large number of CuO nanoflowers agglomerates with a uniform size of about  $1 \mu\text{m}$  are shown in figure 2a. An individual flower-like nanostructure with a diameter approaching  $1 \mu\text{m}$  is shown in figure 2b, which demonstrates that the CuO nanostructures with flower-like shapes are composed of many interconnected sheet-like crystallites with thicknesses in the range of  $3\text{--}5 \text{ nm}$ .



**Figure 1.** XRD pattern of CuO product prepared by the present route.

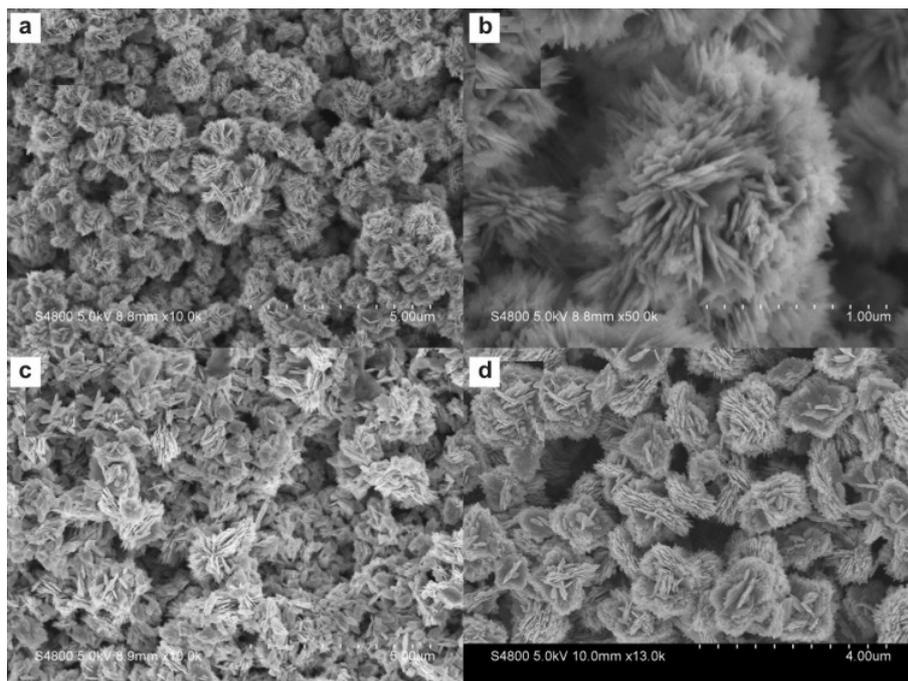
We studied the influence of ratio of  $C_{\text{NH}_3}$  to  $C_{\text{Cu}(\text{NO}_3)_2}$  ( $R_{\text{ac}}$ ) on the formation of the nanoflowers. When  $2 \text{ mL}$   $\text{NH}_3\cdot\text{H}_2\text{O}$  was utilized and  $R_{\text{ac}}$  was 20, only CuO nanosheets but not nanoflowers were obtained when the reaction was carried out at  $100^\circ\text{C}$  for 6 h (figure 2c). As  $R_{\text{ac}}$  increased to 40, CuO nanoclusters can be seen with disappearing of the nanosheets (figure 2d). Further increasing  $R_{\text{ac}}$  to 60, the well-defined nanoflowers would be precipitated, in which the CuO petals appeared (figure 2a). These results indicate that the dosage of  $\text{NH}_3\cdot\text{H}_2\text{O}$  would greatly affect the morphology, aggregation and shape of the building blocks. We estimated that  $\text{NH}_3\cdot\text{H}_2\text{O}$  plays a role as additives which can connect nanosheets to nanoflowers, here.

Figure 3a exhibits the CV response of  $\text{H}_2\text{O}_2$  at different electrodes with a scanning rate of  $50 \text{ mV s}^{-1}$  in pH 7.2 PBS. As curve 2 shows, with  $1 \text{ mM}$   $\text{H}_2\text{O}_2$ , there was almost no redox peaks of  $\text{H}_2\text{O}_2$  which can be seen at the bare gold electrode. However, for CuO NFS/Nafion-Au, the reduction peak current of  $\text{H}_2\text{O}_2$  was obvious in the presence of  $1 \text{ mM}$   $\text{H}_2\text{O}_2$  (figure 3a, curve 3). As curve 4 displays, with addition of  $\text{H}_2\text{O}_2$ , there was an enhancement in the cathodal current demonstrating that CuO nanoflowers possess effective electrocatalytic activity on the reduction of  $\text{H}_2\text{O}_2$ . This suggests that the electrocatalytic activity of the modified electrode could be applied to the determination of  $\text{H}_2\text{O}_2$ .

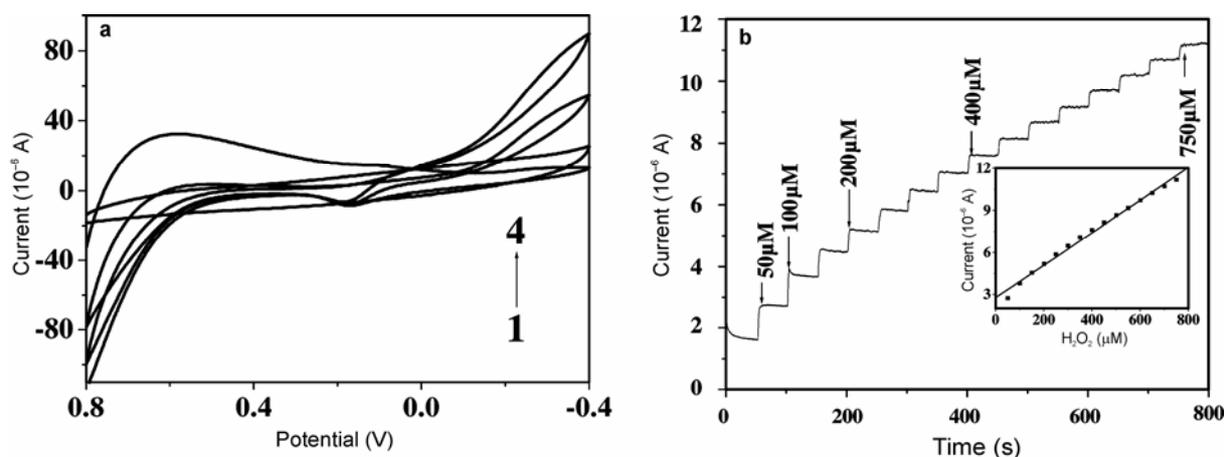
Figure 3b displays the amperometric response of the CuO NFS/Nafion-Au upon the addition of  $\text{H}_2\text{O}_2$  at an applied potential of  $0.35 \text{ V}$ . A subsequent addition of  $\text{H}_2\text{O}_2$  to stirred PBS produces a remarkable increase in the current. The response time is  $< 3 \text{ s}$ , revealing the faster response of the sensor to  $\text{H}_2\text{O}_2$  detection than that of other  $\text{H}_2\text{O}_2$  sensors based on CuO (Jia *et al* 2008; Miao *et al* 2008). The calibration plot of the sensor under the optimized experimental conditions is shown as the inset of figure 3b. The linear amperometric response is in the  $\text{H}_2\text{O}_2$  concentration range between  $50$  and  $750 \mu\text{M}$  corresponding with a sensitivity of  $116.1 \mu\text{A mM}^{-1}$ , which shows that the CuO NFS/Nafion-Au is quite sensitive towards the  $\text{H}_2\text{O}_2$  sensing. And the detection limit ( $S/N = 3$ ) was determined to be  $5 \mu\text{M}$ . The repeated use of the electrode did not affect its long-term stability as long as the measurement was not performed at a high concentration of  $\text{H}_2\text{O}_2$  ( $> 20 \text{ mM}$ ).

### 4. Conclusions

In summary, we have successfully synthesized CuO nanoflowers by using  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  and  $\text{NH}_3\cdot\text{H}_2\text{O}$  for 6 h at low temperature. No additives, surfactants and templates were used in our synthetic route. The ratio of  $C_{\text{NH}_3}$  to  $C_{\text{Cu}^{2+}}$  was found to affect the morphology of CuO nanoflowers greatly. In addition, a gold electrode modified with CuO nanoflowers was used to detect  $\text{H}_2\text{O}_2$  in PBS. The results show that the CuO nanoflowers held a



**Figure 2.** a. Low-magnification and b. high-magnification view of CuO nanoflowers prepared with 4 mL ammonia at 100°C for 6 h. SEM images of CuO nanoflowers obtained with different NH<sub>3</sub>·H<sub>2</sub>O amounts: c. 2 mL and d. 4 mL.



**Figure 3.** a. CV images of H<sub>2</sub>O<sub>2</sub> at different electrodes in pH 7.2 PBS with a scan rate of 50 mV s<sup>-1</sup> (curves 1, 3 and 4 mean 0, 1, and 5 mM H<sub>2</sub>O<sub>2</sub> for the modified electrode in PBS, respectively; curve 2 means CV images of 1 mM H<sub>2</sub>O<sub>2</sub> at the bare gold electrode) and b. AC response of CuO NFS/Nafion-Au upon subsequent addition of H<sub>2</sub>O<sub>2</sub> into pH 7.2 PBS with stirring, the working potential was 0.35 V; calibration curve and linear plot of response current vs H<sub>2</sub>O<sub>2</sub> concentration are shown as the inset of figure 3b.

very high activity for detecting H<sub>2</sub>O<sub>2</sub>, and we think that CuO nanoflowers may be of great potential for H<sub>2</sub>O<sub>2</sub> determination.

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