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Synthesis of CuO nanoflower and its application as a H_2O_2 sensor

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Abstract. **CuO three-dimensional (3D) flower-like nanostructures were successfully synthesized by a simple method at 100°C with $Cu(NO_3)_2{\cdot}3H_2O$ and $NH_3{\cdot}H_2O$ for 6 h in the absence of any additives. We found that $NH_3{\cdot}H_2O$ 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_2O_2 with cyclic voltammetry (CV) and amperometric (AC). It was found that CuO nanoflowers may be of great potential for H_2O_2 electrochemical sensing.**

Keywords. **CuO; nanoflowers; electrochemical; H_2O_2.**

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 nanomaterials, 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_3N film at 300°C (Fan *et al* 2008). Liu and co-workers studied the effect of additives (NaOH, $(NH_4)_2S_2O_8$, Na_2WO_4 or Na_2MoO_4 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 $Cu(NO_3)_2{\cdot}3H_2O$ and $NH_3{\cdot}H_2O$ 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_2O_2. The results showed that the CuO nanoflowers give a very high activity for detecting H_2O_2.

2. Experimental

All of the chemical reagents were used as received without further purification. In a typical procedure, 6 mL $NH_3{\cdot}H_2O$ (1 M) was added to 10 mL $Cu(NO_3)_2$ (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

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*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°/s with 2θ range from 20 to 80°, with high-intensity CuKα radiation ($\lambda = 0{\cdot}154178$ 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 *C*2/*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 μm are shown in figure 2a. An individual flower-like nanostructure with a diameter approaching 1 μm 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 3–5 nm.

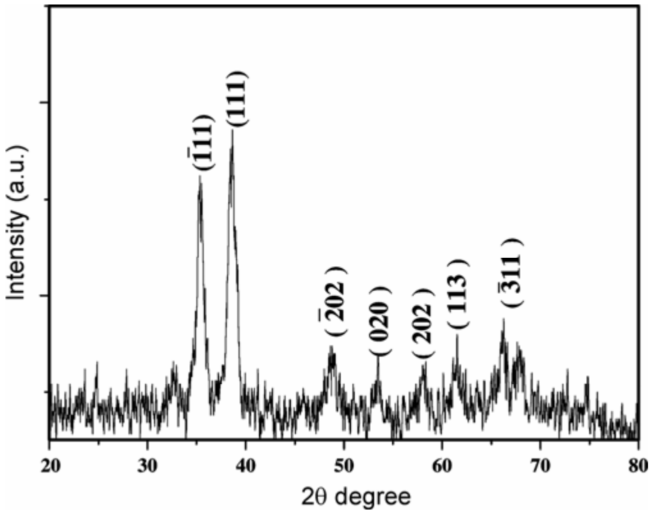

Figure 1. XRD pattern of CuO product prepared by the present route.

We studied the influence of ratio of C_{NH_3} to $C_{Cu(NO_3)_2}$ (R_{ac}) on the formation of the nanoflowers. When 2 mL $NH_3{\cdot}H_2O$ was utilized and R_{ac} was 20, only CuO nanosheets but not nanoflowers were obtained when the reaction was carried out at 100°C for 6 h (figure 2c). As R_{ac} increased to 40, CuO nanoclusters can be seen with disappearing of the nanosheets (figure 2d). Further increasing R_{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 $NH_3{\cdot}H_2O$ would greatly affect the morphology, aggregation and shape of the building blocks. We estimated that $NH_3{\cdot}H_2O$ plays a role as additives which can connect nanosheets to nanoflowers, here.

Figure 3a exhibits the CV response of H_2O_2 at different electrodes with a scanning rate of 50 mV s^{-1} in pH 7·2 PBS. As curve 2 shows, with 1 mM H_2O_2, there was almost no redox peaks of H_2O_2 which can be seen at the bare gold electrode. However, for CuO NFS/Nafion-Au, the reduction peak current of H_2O_2 was obvious in the presence of 1 mM H_2O_2 (figure 3a, curve 3). As curve 4 displays, with addition of H_2O_2, there was an enhancement in the cathodal current demonstrating that CuO nanoflowers possess effective electrocatalytic activity on the reduction of H_2O_2. This suggests that the electrocatalytic activity of the modified electrode could be applied to the determination of H_2O_2.

Figure 3b displays the amperometric response of the CuO NFS/Nafion-Au upon the addition of H_2O_2 at an applied potential of 0·35 V. A subsequent addition of H_2O_2 to stirred PBS produces a remarkable increase in the current. The response time is < 3 s, revealing the faster response of the sensor to H_2O_2 detection than that of other H_2O_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 H_2O_2 concentration range between 50 and 750 μM corresponding with a sensitivity of 116·1 μA mM^{-1}, which shows that the CuO NFS/Nafion-Au is quite sensitive towards the H_2O_2 sensing. And the detection limit ($S/N = 3$) was determined to be 5 μM. 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 H_2O_2 (>20 mM).

4. Conclusions

In summary, we have successfully synthesized CuO nanoflowers by using $Cu(NO_3)_2{\cdot}3H_2O$ and $NH_3{\cdot}H_2O$ for 6 h at low temperature. No additives, surfactants and templates were used in our synthetic route. The ratio of C_{NH_3} to $C_{Cu}{}^{2+}$ was found to affect the morphology of CuO nanoflowers greatly. In addition, a gold electrode modified with CuO nanoflowers was used to detect H_2O_2 in PBS. The results show that the CuO nanoflowers held a

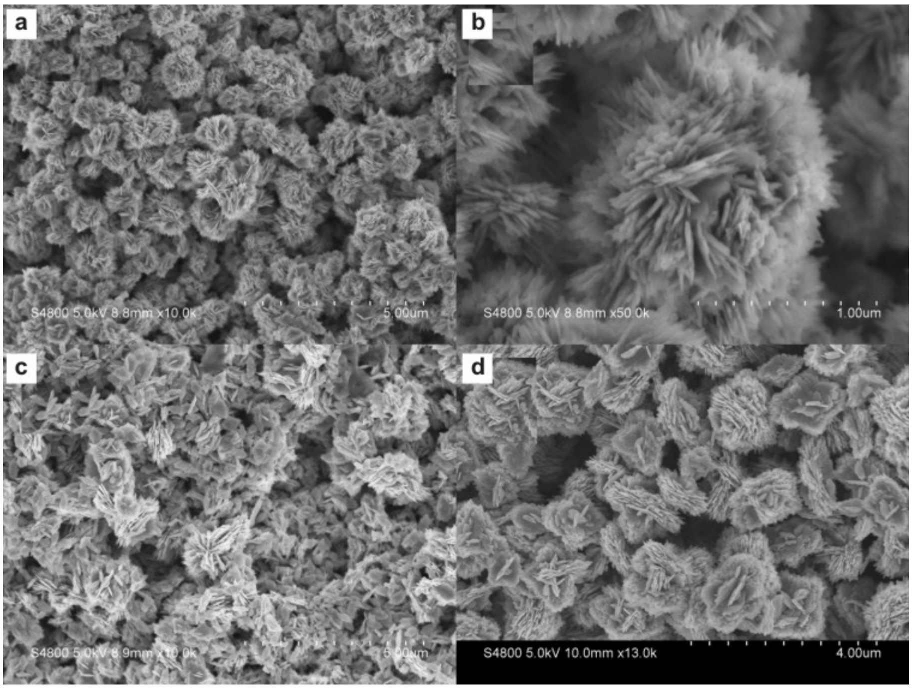

Figure 2. **a**. Low-magnification and **b**. high-magnification view of CuO nanoflowers prepared with 4 mL ammonia at 100°C for 6 h. SEM images of CuO nanoflowers obtained with different $NH_3{\cdot}H_2O$ amounts: **c**. 2 mL and **d**. 4 mL.

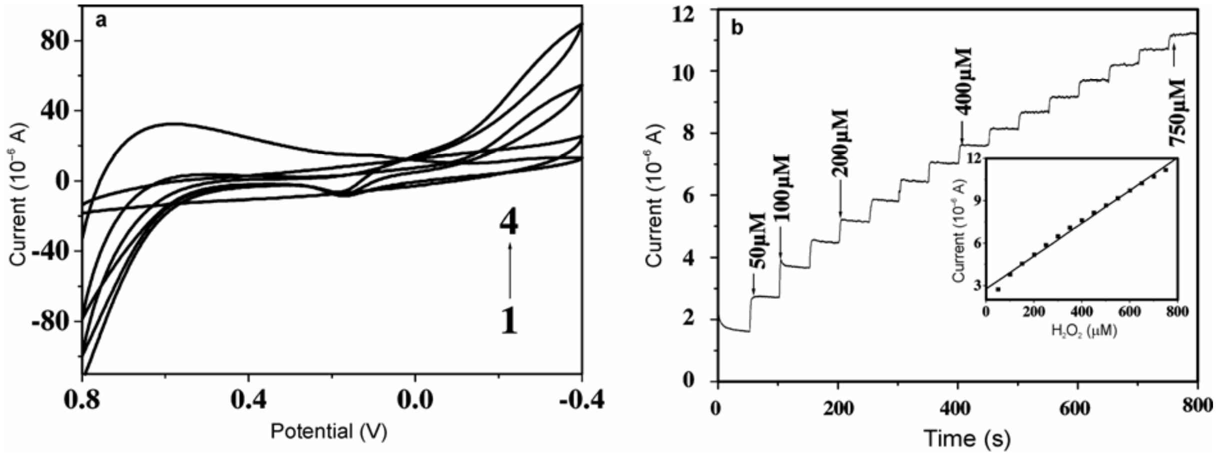

Figure 3. **a**. CV images of H_2O_2 at different electrodes in pH 7·2 PBS with a scan rate of 50 mV s^{-1} (curves 1, 3 and 4 mean 0, 1, and 5 mM H_2O_2 for the modified electrode in PBS, respectively; curve 2 means CV images of 1 mM H_2O_2 at the bare gold electrode) and **b**. AC response of CuO NFS/Nafion-Au upon subsequent addition of H_2O_2 into pH 7·2 PBS with stirring, the working potential was 0·35 V; calibration curve and linear plot of response current vs H_2O_2 concentration are shown as the inset of figure 3b.

very high activity for detecting H_2O_2, and we think that CuO nanoflowers may be of great potential for H_2O_2 determination.

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