

# Synthesis of three-dimensional porous Cu<sub>2</sub>O microspheres by template-free solvothermal method

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Three-dimensional (3D) porous Cu<sub>2</sub>O microspheres were successfully synthesised by a simple template-free solvothermal method. Systematic studies showed that solvent, precipitator and temperature reaction parameters played a key role in controlling the morphology and structure of Cu<sub>2</sub>O. The crystallisation, morphology and composition of the as-prepared Cu<sub>2</sub>O was characterised by X-ray diffraction, a scanning electron microscope and energy-dispersive spectroscopy, respectively. It revealed that the 3D porous Cu<sub>2</sub>O microspheres were built from small 2D nanosheets with a thickness of 50–80 nm. Cyclic voltammetry was applied to investigate the electrochemical performance of the products. It was found that the 3D porous Cu<sub>2</sub>O microspheres possessed high electrocatalytic activity. The growth mechanism of the 3D porous Cu<sub>2</sub>O microspheres was proposed with a 3D molecule model.

**1. Introduction:** Functional nanocrystals, that are hierarchically assembled into hollow microstructures, can provide more space for mass transportation-related applications [1], which is of great scientific and practical value. Cu<sub>2</sub>O, one of the few naturally exhibited p-type conductivity oxides, has been explored as a photon absorber in solar cells [2, 3], photocatalyst [4], NO<sub>2</sub> gas sensor [5] and coherent propagation of excitons [6]. Although various synthesis methods of nanostructured Cu<sub>2</sub>O with different sizes and shapes have been reported, they may involve a sol-gel preparation at high-temperature [7, 8] or with multi-step preparation methods [9]. To date, it remains a great challenge to assemble higher-order hierarchical hollow microspheres with nanosized Cu<sub>2</sub>O. To the best of our knowledge, the hard template approach [10, 11] is an effective synthesis method for hollow microspheres. However, the method often involves the coating of the nanoparticles in the template, followed by the removal of the template using calcination or etching, leading to imperfect patterns in the structure of the final product.

In this Letter, a simple template-free solvothermal method was developed to synthesise three-dimensional (3D) porous Cu<sub>2</sub>O microspheres without toxicants and complex operations. The effects of the reaction parameters on the morphology of the Cu<sub>2</sub>O products was investigated. The growth mechanism of 3D porous Cu<sub>2</sub>O microspheres is also proposed.

**2. Experimental procedure:** 1.4 mmol of cupric acetate and 5.6 mmol of citric acid were dissolved in 15 ml of absolute ethanol, respectively. Subsequently, a 5 ml citric acid solution and a 5 ml ethanol–ammonia mixture was added dropwise into the cupric acetate solution under constant vigorous stirring. Then the mixture was transferred into a stainless Teflon-lined autoclave and heated at 160°C for 24 h. After cooling to room temperature, black products were collected by ultra-pure water cleaning.

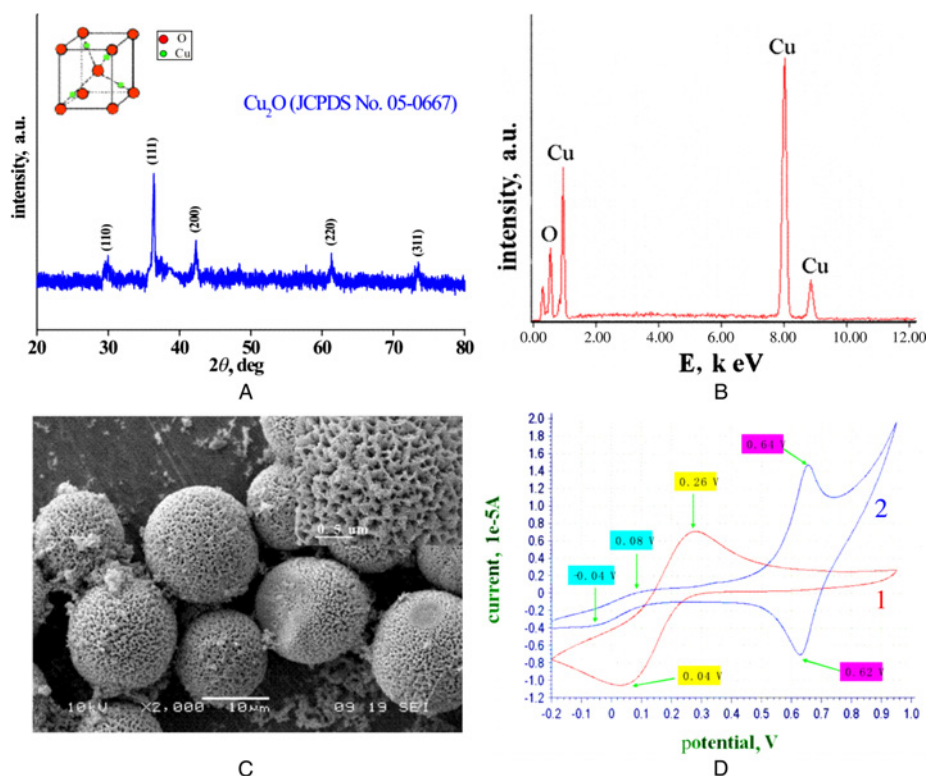
The obtained products were analysed by X-ray diffraction (XRD) (XD-5A Shimadzu, Japan), a scanning electron microscope (SEM) (JSM-5510LVA, Japan) and energy-dispersive spectroscopy (EDS) (EDAX-FALCON60, USA). Cyclic voltammetry (CV) was carried out using an electrochemical workstation (CHI-660C, China) in a standard three-electrode configuration.

**3. Results and discussion:** Fig. 1a shows the XRD pattern of the 3D porous Cu<sub>2</sub>O microspheres with absolute ethanol as the solvent and

NH<sub>3</sub>·H<sub>2</sub>O as the precipitant. The corresponding pattern shows that all the diffraction peaks can be exclusively indexed to the cubic phase Cu<sub>2</sub>O (JCPDS file No. 05-0667) with a lattice constant  $a = 4.27 \text{ \AA}$ . No other impurities were detected. As shown in the inset of Fig. 1a, each O atom is surrounded by a tetrahedron of copper ions, and each Cu cation has two oxygen neighbours in the cubic structure of the Cu<sub>2</sub>O crystals. The observation also revealed that the preferential orientation of the growth direction of Cu<sub>2</sub>O was along the (111) plane, in accordance with other reports [5]. The molar ratio of the Cu and O elements is about 2:1 (Fig. 1b), suggesting that pure Cu<sub>2</sub>O was fabricated. The SEM image (Fig. 1c) shows that the Cu<sub>2</sub>O products display monodisperse porous microspheres with an average diameter of 15  $\mu\text{m}$ . The high-power SEM image reveals that the 3D porous Cu<sub>2</sub>O microspheres were built from small 2D nanosheets with a thickness of 50–80 nm (inset of Fig. 1c). Meanwhile, CV was applied to investigate the electrochemical behaviour of the 3D porous Cu<sub>2</sub>O microspheres modified electrode in a  $\text{Fe}(\text{CN})_6^{3-/4-}$  solution. From Fig. 1d (2), two pairs of redox peaks were observed at the 3D porous Cu<sub>2</sub>O–chitosan (CS)–glassy carbon electrode (Cu<sub>2</sub>O–CS–GCE). A pair of redox peaks were seen at 0.08 and –0.04 V, where the oxidation peak potential of  $\text{Fe}(\text{CN})_6^{3-/4-}$  was found to have a negative shift of 0.18 V and  $\Delta E_p$  was decreased relative to the bare electrode [Fig. 1d (1)]. The other pair of strong redox peaks was at 0.62 and 0.64 V. We ascribe this peak pair to the redox conversion of  $\text{Cu}^+/\text{Cu}$ . The above results indicate that the 3D porous Cu<sub>2</sub>O microspheres were modified to the surface of the GCE and the reversibility of  $\text{Fe}(\text{CN})_6^{3-/4-}$  was improved greatly, which also implied that the 3D porous Cu<sub>2</sub>O microspheres possessed high electrocatalytic activity.

The effects of the solvent, precipitant, concentration of precipitant, reaction time and temperature on the morphology of the Cu<sub>2</sub>O were investigated. Figs. 2a–c show the SEM images of the Cu<sub>2</sub>O products synthesised in different solvents. The chrysanthemum flower-like (Fig. 2a), loose microspheres (Fig. 2b) and irregular nanoparticle agglomerations (Fig. 2c) were obtained with CH<sub>3</sub>CH<sub>2</sub>OH (95%), H<sub>2</sub>O and (CH<sub>2</sub>OH)<sub>2</sub> as solvents, respectively. The results indicated that the polarity of the solvent had a great influence on the morphology of the Cu<sub>2</sub>O and the absolute ethanol solvent was favourable for the formation of monodisperse porous Cu<sub>2</sub>O microspheres.

Figs. 2d–f show the SEM images of the Cu<sub>2</sub>O products synthesised with different precipitants. The self-assembled Cu<sub>2</sub>O



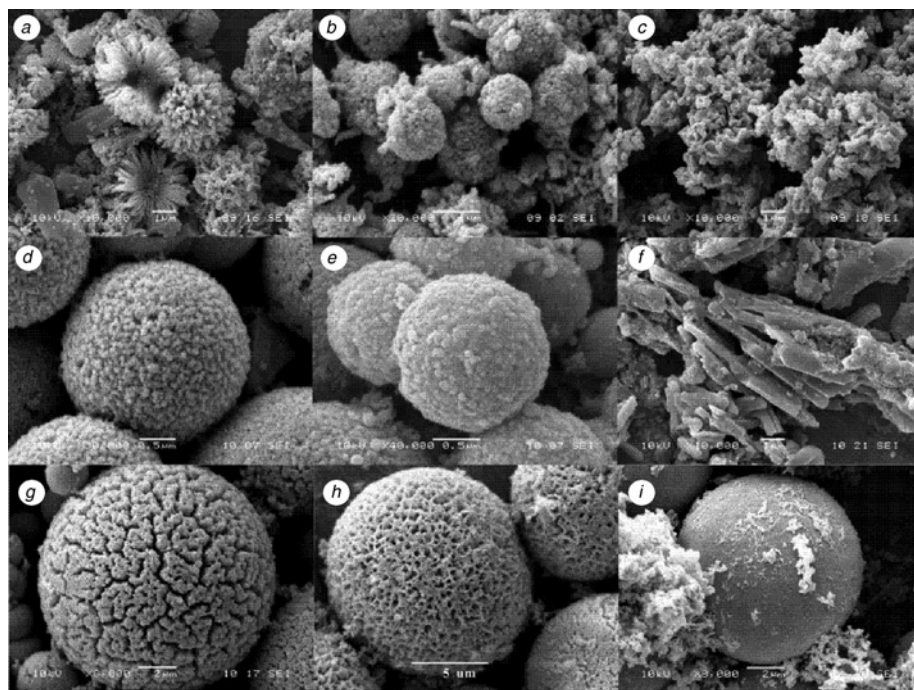
**Figure 1** XRD pattern, EDS spectrum, SEM image and CV measurement

A XRD pattern

B EDS spectrum

C SEM image

D CV of 1 mmol/l  $\text{Fe}(\text{CN})_6^{3-/4-}$  at a bare GCE (1) and a porous  $\text{Cu}_2\text{O}$ -CS-GCE (2) as the working electrode  
Inset of Fig. 1a and 1c show the crystal structure and a high-power image of 3D porous  $\text{Cu}_2\text{O}$  microspheres



**Figure 2** SEM images of  $\text{Cu}_2\text{O}$  products synthesised in different solvents

a  $\text{CH}_3\text{CH}_2\text{OH}$  (95%)

b  $\text{H}_2\text{O}$

c  $(\text{CH}_2\text{OH})_2$  and with different precipitators

d  $\text{CO}(\text{NH}_2)_2$

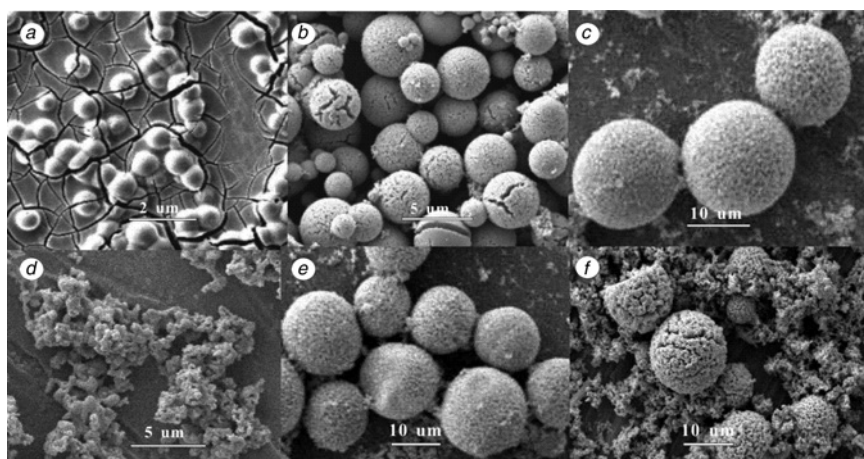
e  $\text{C}_5\text{H}_5\text{N}$

f  $\text{NaOH}$  and different concentrations of  $\text{NH}_3 \cdot \text{H}_2\text{O}$

g 0.15 mol/l

h 0.3 mol/l

i 0.38 mol/l



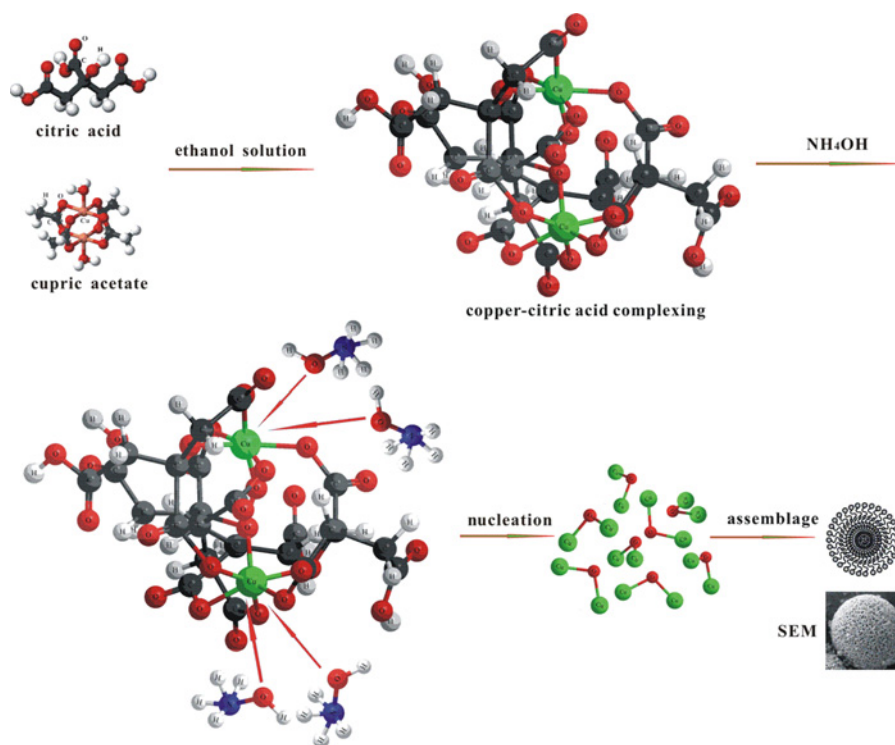
**Figure 3** SEM images of  $\text{Cu}_2\text{O}$  products synthesised for different reaction times (a–c) and at different temperatures (d–f)

a 8 h  
b 16 h  
c 24 h  
d 120°C  
e 160°C  
f 190°C

microspheres from the nanoparticles were formed with  $\text{CO}(\text{NH}_2)_2$  precipitant (Fig. 2d), however, non-porous microspheres (Fig. 2e) and irregular agglomerations (Fig. 2f) were obtained with  $\text{C}_5\text{H}_5\text{N}$  or NaOH as the precipitants, respectively. Compared with  $\text{NH}_3\cdot\text{H}_2\text{O}$  as the precipitant (Fig. 1c), it indicated that the  $\text{NH}_3\cdot\text{H}_2\text{O}$  precipitant with complexing action was beneficial for the formation of the  $\text{Cu}_2\text{O}$  microspheres with larger open holes. Meanwhile, the effect of the concentration of  $\text{NH}_3\cdot\text{H}_2\text{O}$  on the  $\text{Cu}_2\text{O}$  products was investigated. Along with the varying of concentrations of  $\text{NH}_3\cdot\text{H}_2\text{O}$  in the range of 0.15 to 0.3 mol/l, the morphologies of  $\text{Cu}_2\text{O}$  were changed from a crack-like microsphere (Fig. 2g)

to a flower-like microsphere (Fig. 2h). When the concentration of  $\text{NH}_3\cdot\text{H}_2\text{O}$  was increased to 0.38 mol/l, non-monodisperse microspheres with a smooth, non-porous surface were formed (Fig. 2i). This result implied that the concentration of  $\text{NH}_3\cdot\text{H}_2\text{O}$  was a great factor in the formation of monodisperse porous  $\text{Cu}_2\text{O}$  microspheres.

The influence of the reaction time and temperature on the morphology of the  $\text{Cu}_2\text{O}$  products is shown in Fig. 3. When the reaction proceeded for 8 h, some microspheres in gel states (Fig. 3a) were formed. Some opening cracks on the surface of the  $\text{Cu}_2\text{O}$  microspheres were observed for 16 h (Fig. 3b). By continuously increasing the reaction time for 24 h, monodisperse porous microspheres were



**Figure 4** Growth mechanism of 3D porous  $\text{Cu}_2\text{O}$  microspheres



fabricated (Fig. 3e). Meanwhile, when the temperature was kept at 120°C or 190°C, only nanoparticle agglomerations (Fig. 3d) or non-monodisperse microspheres (Fig. 3f) were formed. However, monodisperse porous microspheres were obtained at 160°C (Fig. 3e). These results suggest that monodisperse Cu<sub>2</sub>O microspheres can not be formed under 160°C or above 190°C.

On the basis of the experimental results, the growth mechanism of the 3D porous Cu<sub>2</sub>O microspheres is illustrated in Fig. 4. At the initial stage, cupric acetate is combined with citric acid in an ethanol solution to form six-coordinated copper complexes. When the NH<sub>4</sub>OH was added, Cu<sub>2</sub>O crystal nuclei were formed along with the decomposition of copper complex. During the solvothermal reaction process, the crystal nuclei grew up through extending edges and spheres accumulated in the horizontal and vertical directions for producing small hole microspheres. Finally, the 3D porous Cu<sub>2</sub>O microspheres with larger open holes were obtained along with the Ostwald process.

**4. Conclusion:** 3D porous Cu<sub>2</sub>O microspheres with a cubic phase were fabricated through a template-free solvothermal method and the growth process was illustrated by the molecule model. We discovered that the morphologies of Cu<sub>2</sub>O were sensitive to important reaction parameters such as solvent, precipitator and temperature, and the reversibility of Fe(CN)<sub>6</sub><sup>3-/4-</sup> at Cu<sub>2</sub>O-CS-GCE was improved greatly. The obtained Cu<sub>2</sub>O possesses potential electrocatalytic application.

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