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Ultrasound assisted quick synthesis of square-brick-like porous CuO and optical properties

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1. Introduction

Cupric oxides have been extensively investigated due to their various applications in solar energy materials, gas sensors, electronics, heterogeneous catalysts, optical switches and magnetic storage media [1–3]. Since the morphology of nanostructure materials was found to influence their properties significantly, effectively controlling their morphologies has attracted much attention and become a hot issue in recent years. The common morphologies of monoclinic CuO nanostructures include nanoparticles, one-dimensional nanowires, nanorods and nanobelts [4-7], two-dimensional nanosheets, nanoleaves and nanowiskers [8-10], three-dimensional peach stonelike, boat-like and ellipsoid-like nanostructures [11,12]. However, a porous square-brick-like hierarchical CuO has been hardly seen in literature [13]. Recently, Aimable et al. have synthesized a similar structure using copper acetate and sodium oxalate as raw materials and hydroxypropylmethylcellulose as an organic additive. Lei et al. [14,15] have prepared CuO nanostructures with novel morphologies by calcining the intermediate products of Cu(OH)₂ from Cu₂(OH)₃Cl and Cu₄SO₄(OH)₆ precursors, respectively. Malachite Cu₂(OH)₂CO₃ has also been applied as a precursor to prepare CuO with the preserved morphologies through a thermal conversion [16–18].

Although many raw materials and synthetic methods were tried to prepare CuO with various morphologies, a quick facile synthesis route using cheap raw materials is still a challenging task for synthesis

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ABSTRACT

Square-brick-like CuC_2O_4 intermediate was synthesized quickly by an ultrasound and microwave assisted solution route in the presence of sodium dodecyl benzene sulfonate (SDBS) surfactant using $CuCl_2$ and $K_2C_2O_4$ as raw materials. The CuC_2O_4 was transformed into CuO with a preserved morphology by heating at 300 °C for 2 h. The products were characterized by XRD, TG-DTA, XPS, SEM, TEM, HRTEM and N_2 adsorption–desorption measurement. The light harvesting capability, photoluminescence and surface photovoltage properties of the CuO were investigated. The width and thickness of the obtained porous CuO square bricks are ca. 0.5–1 μ m and 200 nm, respectively. Its average primary particle size is 12 nm. The formation mechanism of this square-brick-like CuO was investigated on the basis of series of controlling experiments. The results show that SDBS, $C_2O_4^{2-}$ and ultrasonic processing play important roles in the formation of this square-brick-like morphology.

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of CuO with a desirable morphology. In the present article, porous hierarchical CuO square bricks were fabricated quickly via CuC₂O₄ intermediate, assisted by ultrasound and microwave processing, and its formation mechanism was discussed. Compared to the work in literature [13,19], where a thermal conversion of CuC₂O₄ was also included, our work has the following characteristics: (1) the synthesis route is facile and fast where ultrasound and microwave were used to assist the quick synthesis of CuC₂O₄ intermediate. Moreover, the temperature for thermal conversion of CuC_2O_4 into CuO is low); (2) a cheap and water soluble surfactant, sodium dodecyl benzene sulfonate (SDBS), was applied as a directing agent, which could be easily removed by rinsing after reactions; (3) the size of the obtained CuO square bricks is much smaller than the reported one [13]. Especially it possesses hierarchical porous structure; (4) the CuO product can emit purple-blue light and has rich surface states, which makes it to be potential optics and catalyst materials.

2. Experimental

In a typical procedure, 50 mL of $K_2C_2O_4$ aqueous solution with a concentration of 0.0125 mol L⁻¹ was dropped into 50 mL of CuCl₂ aqueous solution (0.0125 mol L⁻¹) under vigorous stirring and kept stirring for 10 min to obtain an azury suspension. Then 0.02 g of SDBS was added into the above suspension and continuously stirred for another 10 min. The molecular structure of SDBS is shown in the Scheme 1. After an ultrasonic processing for 30 min, the suspension was transferred into an 800 W domestic microwave oven and intermittently (5 min interval) heated with 20% power for 30 min. The precipitate was separated by centrifugation,

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Scheme 1. Molecular structure of sodium dodecyl benzene sulfonate (SDBS) molecule.

followed by washing and drying processes. Finally the azury powder was calcined in a muffle furnace at 300 °C for 2 h with a heating rate of 1 °C min⁻¹ and a dark CuO powder was obtained. The series of controlling experiments were performed in a similar procedure under various reaction conditions.

X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/max-2500 diffractometer with Cu Kα radiation $(\lambda = 0.154056 \text{ nm})$ at 40 kV and 100 mA. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) measurements were performed on a TG-DTA 6300 (Japan Seiko) thermoanalyzer using Al₂O₃ as a reference and heating at a rate of 5 K min⁻¹ under a dynamic Ar atmosphere. Scanning electron microscope (SEM) images were taken by a JSM 6700F fieldemission scanning electron microscope. Transmission electron microscope (TEM) and HRTEM images were obtained with a JEM-2100 field emission electron microscope operating at 200 kV. The UV-vis absorption spectra were recorded on a Hitachi/U-3900 UVvisible spectrophotometer. The X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI-5300 ESCA system. N₂ adsorption-desorption isotherm was obtained with a V-Sorb 2800P surface area and pore size analyzer. The photoluminescence (PL) emission spectrum was obtained from a FL3-2-IHR221-NIR-TCSPC steady and time resolved spectrometer excited at 350 nm. Surface photovoltage spectrum (SPS) was measured by a homemade sandwich-type solid junction cell ITO/Sample/ITO with light monochromator-lock-in detection technique. Details on this setup have been described elsewhere [20]. The SPS was normalized to make the light intensity of the lamp the same at each wavelength.

3. Results and discussion

The crystal structures of the two products before and after calcination were examined by XRD, as shown in Fig. 1. In the inset of Fig. 1, the diffraction peaks except the weak peak at 31° are indexed to orthorhombic CuC₂O₄·xH₂O (space group: Pnnm 58, JCPDS No. 21-0297), which indicates that the intermediate product before calcination are mostly CuC₂O₄·xH₂O. Thermal conversion of the CuC₂O₄·xH₂O at 300 °C led to the formation of monoclinic CuO (JCPDS No. 48-1548, space group: C₂/c15) with lattice constants a = 0.468, b = 0.342 and c = 0.513 nm (Fig. 1). The strong and sharp diffraction peaks indicate a high purity and crystallinity of the CuO square bricks. The average primary particle size of the CuO was calculated by using Debye–Scherrer formula based on the 200 diffraction peak, which is 12 nm.

The TG-DTA results (see Fig. 2) demonstrate that the phase transition from CuC_2O_4 ·xH₂O to CuO occurs at around 294 °C



Fig. 1. XRD patterns of the as-prepared porous CuO square bricks and the intermediate product CuC₂O₄ (the inset).



Fig. 2. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves for the as-prepared CuC_2O_4 square bricks.

where a sharp exothermal peak appears and the corresponding weight loss is 45%. This result implies that heating at 300 °C is appropriate for full conversion of the intermediate to CuO without bringing any impurity. According to the calculation based on the decomposition reaction of the CuC₂O₄, the total theoretical weight loss should be 47.4 wt.%. Therefore, we presume that the water content in the intermediate product CuC₂O₄·xH₂O is almost zero. In that case, the measurement error is a reasonable value, ca. 5%. Thus the accurate expression for the intermediate product would be CuC₂O₄. The possible reactions are as follows:

$$CuCl_2 + K_2C_2O_4 \rightarrow CuC_2O_4 \downarrow + 2KCl \tag{1}$$

$$CuC_2O_4 \xrightarrow{\Delta} CuO + CO_2 + CO$$
⁽²⁾

The purity of the CuO square bricks was further confirmed by XPS results, as shown in Fig. 3. The peaks sitting at 933.2 eV and



Fig. 3. XPS spectra of the CuO square bricks for Cu2p region (left) and O1s region (right).



Fig. 4. SEM images of (a) CuC₂O₄, (b) panorama (c) front view (d) side view of the CuO square bricks; TEM (e) and HRTEM (f) images of the CuO square bricks.

953.4 eV for Cu2p region are attributed to $Cu2p_{3/2}$ and $Cu2p_{1/2}$, respectively. The existence of strong satellite features at 942.1 eV and 961.8 eV for Cu2p rules out the possibility of the presence of Cu₂O phase [19]. The peaks observed at 529.4 eV and 531.4 eV for O1s region are identified as lattice binding of O²⁻ with Cu and oxygen adsorbed onto the surface of CuO square bricks, respectively. The high peak intensity at 531.4 eV suggests rich adsorbed oxygen on the CuO surface, which may result in rich surface states and a high catalytic activity.

Morphologies and microstructures of the as-prepared CuO and CuC_2O_4 square bricks were examined by SEM, as shown in Fig. 4ad. Obviously the square brick-like morphology of the CuC_2O_4 (Fig. 4a and the inset) was well reserved after heating at 300 °C for 2 h although the surface roughness and aperture of the CuO became larger. The CuO square bricks are about 0.5–1 μ m in width and 200 nm in thickness with slightly convex surface in the middle



Fig. 5. N_2 adsorption-desorption isotherm and pore size distribution of CuO square bricks (inset).

of the square. The inset of Fig. 4a shows that the square brick composes of numerous self-assembled nanoparticles in the middle and surrounded by thin nano-sheet layers at outer side surfaces. This structural difference at the surrounding part of the square bricks is also observed in Fig. 4c-e although the nanosheets also become porous structures due to release of gases after thermal decomposition of CuC₂O₄. One observes in Fig. 4c and e that the primary particle sizes of the CuO micro-nanometer composite structure are about 10-20 nm, which is consistent with the XRD result. The porous nature of the CuO is clearly observed in Fig. 3e. Apart from small pores, there exist some big pores due to collapse of some CuO nanoparticles in the calcination process. This could be confirmed by the N₂ adsorption-desorption measurement in the following text. Based on the HRTEM image, lattice spacings of the CuO were measured to be 0.23 and 0.28 nm, corresponding to the (1 1 1) and (1 1 0) planes, respectively, of monoclinic CuO.

The adsorption–desorption isotherm and pore size distribution results, see Fig. 5, show that the BET specific surface area of the CuO square bricks is 29.8 m² g⁻¹, and the main pore sizes are in the range of 2–50 nm. There is also a little macropores larger than 50 nm. The unclosed loop in Fig. 5 may be due to partial pore structure collapse of the CuO, leading to irreversible adsorption of N₂ on the material surface. It is known that porous solids have excellent adsorptive properties and the catalytic process would occur more efficiently in materials with hierarchical pore size distribution on the nanoscale [21,22]. Therefore, a good catalytic activity could be expected for this hierarchical porous CuO.

In order to understand the formation mechanism of the squarebrick-like CuO nanostructures series of controlling experiments were performed. The morphologies of these series of CuO products are shown in Fig. S1 in the supporting information. The corresponding reaction conditions and properties of these products are summarized in Table 1. When CuCl₂ and K₂C₂O₄ were used as the raw materials, CuO nanoparticles, nanosheets, large irregular particles or conglomeration (sample a–e) were obtained at the absence of SDBS. At the presence of SDBS, however, CuO square bricks were hardly formed either without an ultrasound processing

Series of CuO produ	cts prepared in var	ious conditions ^a .

Samples	Raw materials	Directing agents	Preparation methods	Morphologies of CuO products
a	$CuCl_2 + K_2C_2O_4$	None	Ultrasound + microwave	Nanoparticles
b	$CuCl_2 + K_2C_2O_4$	Triethylamine	Microwave	Nanosheets
с	$CuCl_2 + K_2C_2O_4$	PEG (2000)	Microwave	Irregular particles
d	$CuCl_2 + K_2C_2O_4$	Poly(acrylic acid)	Ultrasound	Irregular particles
e	$CuCl_2 + K_2C_2O_4$	Oleyl amine	Ultrasound	Agglomeration
f	$CuCl_2 + K_2C_2O_4$	SDBS	-	Irregular particles
g	$CuCl_2 + K_2C_2O_4$	SDBS	Ultrasound	SB ^b + little particles
h	$Cu(NO_3)_2 + K_2C_2O_4$	None	Ultrasound + microwave	Particles + little SB ^b
i	$CuCl_2 + K_2CO_3$	None	Microwave	Nanorod clusters

^a Note: All products above were calcined at 300 °C for 2 h.

^b Square bricks.

(sample f). When Cu(NO₃)₂ was used instead of CuCl₂ in the absence of SDBS, only little amount of square bricks was produced (sample h). Completely different morphology, nanorod clusters and flowers (sample i), was obtained when K₂CO₃ instead of K₂C₂O₄ was used as the raw material. The above results reveal that the morphology of the CuC₂O₄ intermediate is significantly influenced by the structure of a guiding agent and the ultrasound or microwave processing. The ultrasonic processing is necessary to form the square-brick-like CuC₂O₄, whereas the microwave heating can improve the uniformity of the product morphology. The existence of C₂O₄^{2–} is also a key factor to formation of the square-brick-like morphology.

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As we know, when a liquid is subjected to ultrasound bubbles are formed, which grow and implode. This leads locally to extremely high instantaneous temperatures and pressures, being accompanied by shock wave and micro-jet flow [23]. The cavitation effect induced by ultrasound could on the one hand crumble object and increase its dispersivity. Thus, well-dispersed CuC₂O₄ nanoparticles were possibly formed firstly under ultrasound. On the other hand, the cavitation effect could speed up the diffusion of the CuC₂O₄ nanoparticles, which benefits the oriented self-assembly of the CuC₂O₄ nanoparticles in the later reaction stage after the adsorption of SDBS molecules on the CuC₂O₄ surfaces. The adsorption of the polar SDBS molecule may reduce the surface energy of the CuC₂O₄ nanoparticle in certain crystal face, which would result in epitaxial growth of CuC₂O₄. Combining with the XRD result in Fig. 1, we found that the relative growth speed along the $(1 \ 1 \ -1)$ plane is slow. Thus the crystal facet along the thickness direction of the square-brick-like product is the $(1 \ 1 \ -1)$ plane. In the orthorhombic crystal system of the precursor phase, the adsorption of SDBS molecules decreases the growth speed of the $(1 \ 1 \ -1)$ plane, which leads to the formation of the square-brick-like morphology. The adsorption of the polar SDBS molecules on the CuC_2O_4 surfaces could also change the intermolecular forces in the reaction system under ultrasound radiation.

The formation of the square-brick-like CuO possibly consists of three steps: (i) formation of CuC₂O₄ nanoparticle seeds in terms of chemical reaction described in Eq. (1); (ii) SDBS adsorbed on the surface of CuC₂O₄ nanoparticles, followed by quick oriented selfassembly of these nanoparticles under ultrasound and microwave radiation to form square-brick-like structures. The nanoparticles are interconnected with each other and the pores are the interparticle voids. Then a few layers of nanosheet-like CuC₂O₄ aggregated around the square bricks via oriented attachment. Since CuC_2O_4 is a nonpolar molecule, the aggregation of the nanoparticles (without SDBS) may be driven by dispersive force, and the orientation is random, which results in the formation of irregular shape. After adsorption of the polar molecule SDBS on the CuC₂O₄, the nanoparticles assemble along certain direction under ultrasound induction. Here the driving forces could include induction force, orientation force and dispersive force. Moreover, the adsorption of SDBS could also change the surface energy of CuC₂O₄ in certain crystal face. Consequently a square-brick-like morphology was formed; (iii) thermal conversion from CuC_2O_4 to CuO with preserved morphology, being accompanied by release of gases to form more and larger pores.

The optical properties were investigated by UV–vis diffuse reflection absorption spectrum and PL emission spectrum. As shown in Fig. 6a, there is an abroad absorption band from 280 nm to 800 nm. The band gap energy of the as-prepared CuO square bricks was estimated by making a tangent line at the band edge, referring to the method in the reference [24]. It is 1.5 eV, which is much larger than the reported value for the bulk CuO (1.2 eV). This blue shift in absorption could be attributed to the quantum size effect since the primary particle size of the CuO square brick is as small as 12 nm. The PL spectrum (Fig. 6b) demonstrates there is a



Fig. 6. UV-vis diffuse reflectance absorption spectrum (changing light source at 370 nm) and photoluminescence emission spectrum of the as-prepared CuO square bricks.



Fig. 7. Surface photovoltage spectrum (SPS) of the as-prepared CuO square bricks.

single abroad emission band centered at 400 nm, which indicates that the CuO square bricks can emit purple-blue light. This is different from the result by Aslani and Oroojpour where greenyellow emission was observed [25]. This PL emission band could be attributed to the near-band-edge emission of the absorption band at low wavelength.

The surface photovoltage method is a well-established contactless and nondestructive technique for semiconductor characterization based on analyzing illumination-induced changes in the surface voltage [20,26,27]. It has a very high sensitivity (ca. $10^8 a$ / cm^2) which exceeds that of conventional spectroscopies such as XPS and Auger spectroscopies by many orders of magnitude. SPS can provide information about the properties of the sample surface layer (several atomic layers). SPS method has been proven to be one of the most effective methods to reflect the separation and recombination situation of photogenerated electrons and holes [28]. The SPS response of the as-prepared CuO square bricks (Fig. 7) includes two bands centered at 331 nm and 463 nm, respectively. The band from 300 nm to 360 nm is attributed to band-to-band transition (from valence band to conduction band of CuO). The other response band between 360 nm and 800 nm could be caused by surface states. Comparing with the SPS response at 360 nm, the stronger signal at 463 nm suggests the existence of rich surface states for this CuO sample. The photogenerated electrons could transfer to the surface state, which would enhance the separation of the photogenerated carriers and consequently the photocatalytic activity of CuO.

4. Conclusions

Porous square-brick-like CuO nanostructures were quickly prepared via CuC_2O_4 intermediate by assistance of ultrasound and microwave processing, combining with thermal conversion reaction. The pure monoclinic CuO has high crystallinity with an average primary particle size of 12 nm. The CuO square bricks are about 0.5–1 µm in width and 200 nm in thickness with slightly convex surface in the middle of the square. The as-prepared CuO possesses hierarchical pores with sizes mainly in the range of 2-50 nm and its BET surface area is 29.8 $m^2 g^{-1}$. The surfactant SDBS, C₂O₄^{2–}, and ultrasonic processing are found playing crucial roles on the formation of the square-brick-like CuC₂O₄. This morphology was well preserved after heating at 300 °C for 2 h except that the surface roughness and aperture of the CuO became larger due to release of gaseous CO₂ and CO. This square-brick-like CuC_2O_4 nanostructure may be produced through an oriented selfassembly mechanism driven by induction force, orientation force and dispersive force under ultrasound radiation in the case of adsorption of the polar molecules SDBS on the CuC₂O₄ surfaces. The as-prepared CuO has good light harvesting capability in UVvisible region and can emit purple-blue light. The SPS result demonstrates that it has rich surface state, which could enhance the separation of the photogenerated electrons and holes. Consequently it could increase the photocatalytic activity of CuO. This porous square-brick-like CuO could be potential catalyst, optics and gas sensor materials.

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