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3D hierarchical walnut-like CuO nanostructures: Preparation, characterization and their efficient catalytic activity for CO oxidation

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ABSTRACT

In this work, 3D hierarchical walnut-shaped, 2D nanosheet and 3D microspheres single phase CuO nanostructures are functioning as catalysts and supporting materials, differing from the conventional ways. The novel nanostructures were synthesized via hydrothermal method under a stainless steel autoclave. The as-prepared materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and H_2 temperature-programmed reduction (H_2-TPR). The walnut-shaped structures with high O/Cu atomic ratio (1.22) exhibit high oxygen adsorption capacity and greatly enhanced catalytic activity. These results will be enrich the techniques for tuning the morphologies of metal oxide micro/nanostructures and open a new field in catalytic applications.

1. Introduction

The metal oxide semiconductor materials (MOSMs) can find applications in the area of such as electronics, chemical reactivity, energy conversion, and optics [1–6]. Electrochemical process [7], template method [8], microwave-activated approaches [9], nanosphere lithography [10,11] and electrospinning process [12] are widely used to synthesize MOSMs. With the development of nanotechnologies and synthesis routes, by tuning the materials with micro/nanostructures, the properties of MOSMs as well as their applications can be greatly expanded. Nevertheless, the conventional micro/nano-scale fabrication technologies are time-consuming and expensive (for example, require special equipments, extreme conditions, and multiple complex steps). An efficient, low-cost and time-saving technique to fabricate novel structures with controllable properties is therefore highly desired.

As a well-known p-type MOSM with a narrow band gap (E_g = 1.2 eV), copper oxide (CuO) has gained considerable attention in a wide range of fields [13–18,19]. 1D, 2D and 3D CuO micro/nanostructure have been intensively synthesized [20–29,30,31]. Most applications of CuO are focused on the catalytic activity for CO oxidation. Qin et al. fabricated porous CuO–CeO_2 nanospheres products to obtain higher catalytic activity [32]. Ma et al. reported an improved sol–gel method with incorporation of thermal treatment under N_2 to $Cu_1Ce_8Fe_x$–O catalysts for low temperature CO oxidation [33]. Although these MOSMs have efficiently improved catalytic activity, they are still restricted by the poor monodispersity and poor size uniformity of these nanostructures. To meet practical needs and expand the applications of CuO micro/nanostructures, a facile and controllable synthetic strategy in aqueous solution is therefore of great interest and significance.

In this study, CuO nanostructures are directly grown onto stainless steel substrates via a simple hydrothermal method without surfactants. Compared with other methods, the approaches are additive-free, facile and easy to control. The morphology of the CuO nanostructures can be easily tuned by changing the pH value of the reaction mixture in air. Highly catalytic activities are obtained by this method. This would enrich the techniques for tuning the morphologies of MOSMs, and may open a new way for catalytic applications with CuO.

2. Experimental section

2.1. Samples synthesis

All chemical reagents were of analyst grade and used without further purification. All the water used was deionized water (18.2 $\Omega\,cm^{-1}$). The typical synthesis of 3D hierarchical CuO micro-nanostructure is as follows. Briefly, $CuSO_4\cdot 5H_2O$ (0.187 g) was dissolved in a beaker containing 30 mL of water. Afterwards, ammonia solution (0.2 ml, 28 wt%) was added into copper sulfate

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solution dropwisely at room temperature for several minutes to form a blue solution.

The mixture was placed in a stainless steel autoclave with a Teflon liner of 50 mL capacity, and heated at 130 °C for 4 h. After the reaction, the resulting dark brown product and a colorless supernatant were obtained. The product was filtered and washed with water, and finally dried in air at 60 °C for 8 h.

2.2. Characterization

The X-ray diffraction (XRD) analysis was performed using a Netherlands X'Pert PRO X-ray diffractometer equipped with Ceramic Cu Kα radiation in the diffraction angle range of $2\theta=20$–70°. The morphologies of the as-prepared samples were examined by field emission scanning electron microscopy (FESEM) on a German Zeiss ULtra 55 scanning electron microscopy. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were performed on a Libra 200FE. Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer FTIR spectrum 100) was used to determine the molecular structure in the range of 400–4000 cm^{-1}. The X-ray photoelectron spectroscopy (XPS, XSAM800) was determined with an Al Kα monochromator X-ray source operating at a power of 12 KV × 15 mA. The XPS binding energies were internally referenced to the no pollution C 1s peak at 284.8 eV. The nitrogen adsorption and desorption isotherm, pore size distribution and specific surface area were measured using an AUTOSORB-1 surface area and pore size analyzer at 77 K.

2.3. Catalytic evaluation

The CO oxidation reaction with 51.4 mg CuO catalysts was performed in a glass tubular reactor under an atmosphere pressure. CuO samples prepared at different pH values were picked to compare their catalytic performance. A feed gas consists of 1% CO and 1% O_2 in N_2 with a total flow rate of 60 mL/min^{-1}. The catalyst was directly exposed to reaction gas without any pretreatment. The CO concentration in the reactor effluent was analyzed using an on-line gas chromatograph (GC-9790, Zhejiang Fuli Analysis Equipment Company) equipped with a TCD detector (thermal conductivity detector). H_2-TPR experiments were analyzed with a quartz tube reactor packed 10 mg samples. Before testing, the catalyst was pre-treated at 100 °C for 60 min in 20% (volume) hydrogen and 80% (volume) argon gas mixture and then cooled down to room temperature, and swept at a heating rate of 10 °C min^{-1} form room temperature to 900 °C.

3. Results and discussion

Fig. 1 shows that the XRD patterns of the products obtained after reactions at 130 °C for 4 h with different pH values. The XRD pattern of the products obtained at pH values over 5 (Fig. 1a) was properly indexed according to the crystallographic database, and assigned to $Cu_2(OH)_3Cl$ (JCPDS no. 85-1713). All the diffraction peaks of other products obtained which pH values from 8 to 11 can be indexed to monoclinic CuO crystal structure (JCPDS File no. 48-1548, $a=4.688$ Å, $b=3.423$ Å, $c=5.132$ Å) [34], the major peaks located at 2θ values of 20–80° clearly indicated that the CuO product was a pure phase, and the lattice constants were calculated to be $a=4.68$ Å, $b=3.43$ Å and $c=5.14$ Å, respectively.

The morphology and size of the products were examined by FESEM and TEM. We obtained CuO samples under different pH values of ammonia solutions (pH=8–11) via hydrothermal synthetic strategies. Fig. 2a showed that the product consists of relatively uniform walnut-like CuO nanostructures with an average size of about 350 nm and the surfaces are relatively rough (pH=8). It was interesting that each nano-walnut was made up of many CuO nanosheets (Fig. 2b) (see also the Supporting information, Fig. S1). Increasing the pH value in this reaction system can change the morphology gradually. CuO nanosheets final formed with an average size of about 300 nm when the pH value reached 9 (Fig. 2c and d). Interestingly, CuO microspheres consisted of relatively uniform hierarchical nanosheets formed when the pH value reached 11 (Fig. 2e and f). Fig. 2f showed a typical CuO microsphere made of CuO nanosheets. The influence of other pH values on the formation of CuO nanostructures was investigated (see the Supporting information, Fig. S2). These morphologies evolution was presumably as a result of OH^- in the selective adsorption of CuO crystal plane. Since when the OH^- ions concentrations were high, there would have higher adsorption on (001)-Cu planes, followed by the (100) and then (010) plane [35]. The priority of OH^- adsorption on the (001)-Cu surfaces could stabilize these planes, and then facilitate to generate nanosheet structures (also can be confirmed with XRD analysis). In our work, careful control of pH value of ammonia solution was a necessary condition to get uniform and highly dispersive nanowalnut structures, as indicated in Fig. 2a for the samples with a low-magnification.

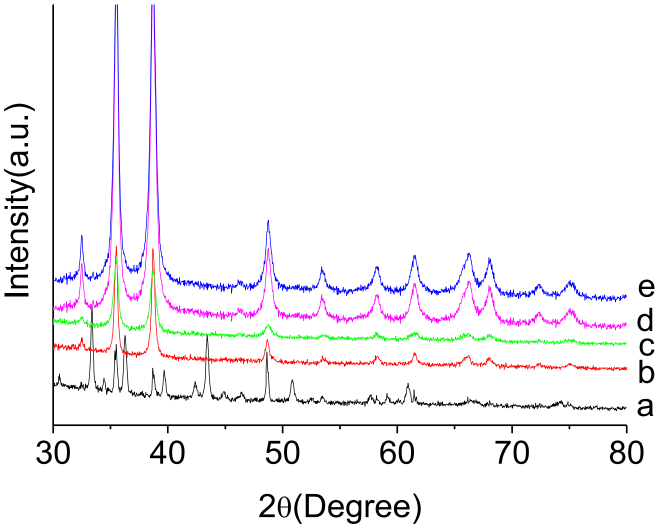

Fig. 1. XRD patterns of the products obtained after reaction at 130 °C for 4 h with different pH values: (a) 5, (b) 8, (c) 9, (d) 10 and (e) 11.

To further analyze the nanostructure, TEM analysis was performed to get insights into the nanowalnut structures. Fig. 3a showed that the CuO nanowalnut particle is hierarchical, and consists of nanowalnut building blocks with rough surfaces. The corresponding selected area electron diffraction (SAED) pattern (Fig. 3a inset) displayed that the CuO nanowalnut exhibited several concentric diffraction rings and some orderly diffraction spots, suggesting that a polycrystalline structure was successfully synthesized. Fig. 3b shows the detailed microstructure of the nanowalnut building blocks. The spacing between two neighboring fringes was about 0.27 and 0.23 nm, corresponding to the distance of the (110) and (002) lattice fringes of monoclinic CuO, respectively. The (020) planes of the growth direction for the nanowalnut CuO can also be seen. Moreover, from the FFT image, one can see that the lattice orientations of (110) and (002) were parallel. The uniform and continuous lattice structure implied that the spontaneous oriented assembly of adjacent nanosheet with each other via crystal fused at the planar interface [36]. The above observations evidently supported that shape-controlled nanowalnut CuO were successfully obtained via hydrothermal method without any surfactants.