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Synthesis of polyhedron hollow structure Cu_2O and their gas-sensing properties

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ABSTRACT

Well-defined polyhedral hollow structures (PHSs) Cu_2O with hollow interior and high geometrical symmetry are successfully prepared via a novel in situ oxidative etching method at room temperature. X-ray power diffraction (XRD), field-emission scanning electron microscope (FESEM), and high-resolution transmission electron microscopy (HRTEM) techniques were employed to elaborately characterize the structure and morphology of the as-prepared samples. These PHSs Cu_2O with hollow interiors and open "window" show effective-applied and good-diffusion structure for the gas-sensing application, which will exhibit short good response, response/recovery times and good reproducibility to ethanol. It is found that type-I nanocages Cu_2O have a response of 8.6–50 ppm ethanol at the optimal operating temperature of 210 °C and the response time is within 23.7 s.

1. Introduction

Usually, different facets of a single crystal exhibit distinctive chemical and physical properties, for example, gas-sensing ability, chemical reactivity, and adsorption capacity. In principle, gas-sensing by metal-oxide semiconductors is based on the oxidation–reduction reaction of the detected gases occurring on the semiconductor surface, which leads to an abrupt change in conductance of the sensor. For this reason, the gas-sensing ability of metal oxide semiconductors is in theory very sensitive to the crystal facets of the sensing materials [1–3]. In addition, the gas response and recovery kinetics are closely related to the diffusion of gases onto the sensing surface and the charge transfer interactions on the surface including the adsorption of negatively charged oxygen and the oxidative/reductive interaction between analytic gases and adsorbed oxygen. Gas diffusion in a sensing layer can be facilitated by employing porous or hollow structures [4–6]. Thus, it is desirable to design feasible approaches to organize primary polyhedron into hollow structures with perfect desired facets, novel geometrical shapes.

Polyhedral hollow structures (PHSs) exhibit inherent high symmetry and beauty, and both naturally occurring and synthetic molecular-scale cages have been discovered. Their characteristic high surface area and voids have led to them to be used as catalysts and catalyst supports, filtration media, gas-sensor and gas storage materials [7–9]. Cu_2O, as an important P-type semiconductor material, also exhibits high response to H_2S, NO_2, humidity, ethanol, gasoline, etc. [10–13]. Recently, besides traditional spherical hollow architectures, nonspherical hollow Cu_2O nanostructures with well-defined geometrical shape have attracted more attention. Qi and co-workers have prepared octahedral Cu_2O nanocages by Pd-catalytic reduction of an alkaline copper tartrate complex with glucose followed by a catalytic oxidation process [14]. Truncated rhombic dodecahedral Cu_2O nanoframes and nanocages have been synthesized by particle aggregation and acidic etching [15]. Compared with solid polyhedron as sensing materials, PHSs have the following two advantages: (i) their characteristic high surface area and void could provide much on the surface active sites, (ii) special "window" facilitates the adsorption of analytic molecular and the diffusion of gas onto the interior surface. Here, we establish a new strategy for PHSs Cu_2O via a simple and environmentally friendly oxidative etching method at room temperature. Especially, the PHSs Cu_2O exhibit high response to ethanol vapor due to their particular architectures and high specific surface area, which is significant for exploiting new gas-sensing materials in the future.

2. Experimental

2.1. Synthesis and characterization of PHSs Cu_2O

Here, the nanoframes Cu_2O were synthesized by a facile and green synthetic wet chemical process [16]. Briefly, an aqueous solution was first prepared by mixing 17 mL of water, 1 mL of 0.68 M copper sulfate, and PVP (0.9 g, K-30, Mw = 30,000) in a round-bottomed glass flask. The mixture was stirred with a magnetic stirrer for about 15–20 min, and then 1 mL of 0.74 M sodium citrate and 1.2 M anhydrous sodium carbonate mixed solution was

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added in dropwise manner. After about 10 min, 1 mL of 1.4 M glucose solution was slowly dropped into this solution. The solution was kept in a water bath at 80 °C for 2 h, and then allowed to cool to room temperature. The resulting solution was then exposed to air and allowed to age for up to 16 days at room temperature (ca. 20 °C). The orange precipitate was collected by filtration, washed several times with distilled water and absolute alcohol, and finally dried in vacuum at 60 °C for 8 h. Further experiments were also conducted under different conditions, using procedures similar to those presented above (The detailed experimental conditions are shown in Supplementary Materials). Subsequently, the as-prepared products were characterized by X-ray powder diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Field-emission scanning electron microscopic (FESEM) images were performed on a JEOL JEM-6700F microscope operating at 5 kV. Transmission electron microscopic (TEM) images, selected area electron diffraction (SAED) patterns, and high-resolution transmission electron microscopic (HRTEM) images were obtained on a JEOL JEM-2000EX microscope with accelerating voltage of 200 kV and a JEOL JEM-3010 microscopy operated at 200 kV, respectively.

2.2. Fabrication and measurement of gas sensor

The gas-sensing properties of Cu_2O were measured using a gas-sensing characterization system (Supplementary Materials), and the detailed fabrication of the gas sensor has been described in the literatures [17,18]. The desired concentrations of the testing gases were obtained by the static liquid gas distribution method, which was calculated by the following formula [19].

$$Q = \frac{V \times \varphi \times M}{22.4 \times d \times \rho} \times 10^{-9} \times \frac{273 + T_R}{273 + T_B} \quad (1)$$

where Q (mL) is the liquid volume of the volatile compound, V (mL) is the volume of the testing chamber, φ is the required gas volume fraction, M (g mol^{-1}) is the molecular weight, d (g cm^{-3}) is the specific gravity, and ρ is the purity of the volatile testing liquid, and T_R and T_B (°C) are the temperatures at ambient and test chamber, respectively. The response (R) of sensor was defined as the ratio of the resistance of the sensor in testing gases (R_g) to that in dry air (R_a), that is, $S = R_g/R_a$. The response and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively.

3. Results and discussion

3.1. Structural and morphological characteristics

As shown in Fig. 1A, the nanoframes Cu_2O are achieved, and are relatively uniform in size. A single nanoframe Cu_2O is shown in the enlarged FESEM image in Fig. 1B. It is found that the nanoframe Cu_2O with hollow interior and high geometrical symmetry is a regular truncated octahedra with mean edge length of ~300 nm. An important feature of the as-synthesized products is that most of the surface of the six {1 0 0} faces of the truncated octahedral structure is absent. It is known that each truncated octahedral particle contains eight hexagonal {1 1 1} faces and six quadrangular {1 0 0} faces. Thus the nanoframes Cu_2O are constructed of hexagonal {1 1 1} skeletons. The thickness of the nanoframe is ~60 nm. Consistent with FESEM observation, Fig. 1C shows a TEM image of nanoframes Cu_2O with hollow hexagonal shape; the average outer diameter of the nanoframes Cu_2O is about 700 nm. HRTEM images confirm the single-crystal structure of the nanoframes Cu_2O. The fringes in a typical HRTEM image (Fig. 1D) are separated by ~0.24 nm, in good agreement with the (1 1 1) lattice spacing of Cu_2O. The single-crystalline structure is also mirrored in the fast-Fourier-transform (FFT) pattern (Fig. 1D, inset). Furthermore, the phase purity of the products was examined by X-ray diffraction (Fig. 2). All the peaks can be well-indexed to a pure cubic phase Cu_2O (space group: *Pn3m*, a = 0.4294 nm).

Type-I nanocages are shown in Fig. 3A–D. Fig. 3A shows a typical FESEM image of the type-I nanocages, which suggests that

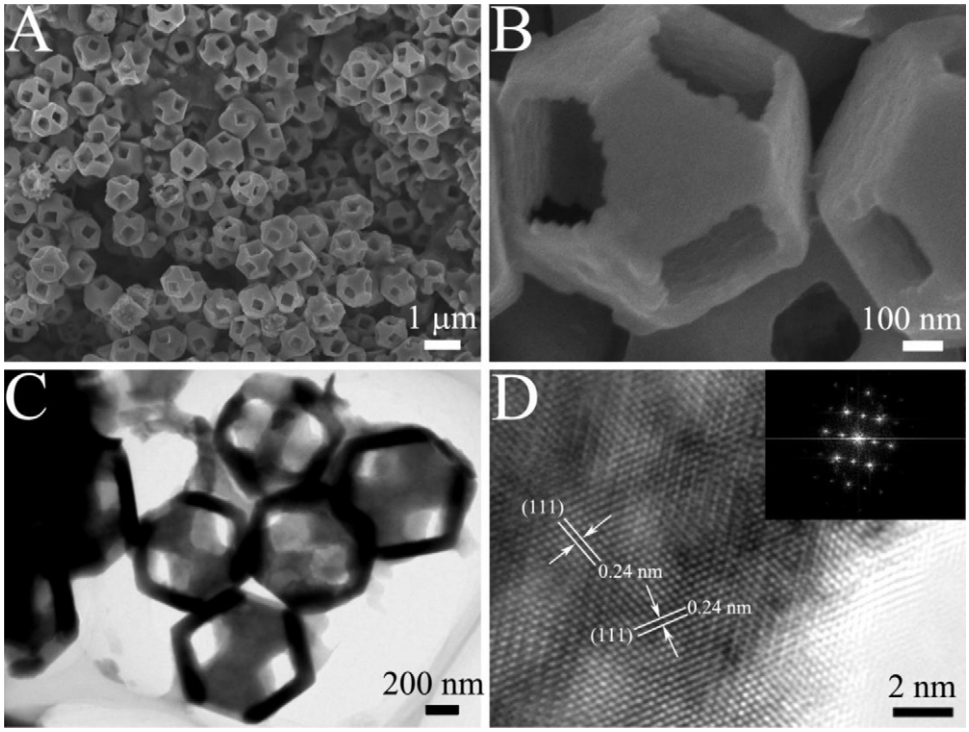

Fig. 1. (A) Low-magnification FESEM image of the nanoframes Cu_2O. (B) High-magnification FESEM image of the nanoframe Cu_2O. (C) TEM image of the nanoframes Cu_2O. (D) Typical HRTEM image taken from a nanoframe Cu_2O (the inset of D shows corresponding FFT pattern).