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# Multi-shelled copper oxide hollow spheres and their gas sensing properties

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ABSTRACT

In this work, multi-shelled copper oxide hollow composite microspheres with tunable shell number and composition were successfully synthesized by means of hard template method. The source for the carbonaceous microspheres templates affects the compositions of the final copper oxides spheres critically. When changing the sucrose to glucose, the composite hollow spheres of cupric oxide (CuO) and cuprous oxide ($Cu_2O$) were synthesized instead of the pure CuO hollow spheres. The structure of products can be tuned from single-, double- to triple-shelled hollow spheres by precisely increasing the calcination rate. The pure CuO hollow-shell spheres had uniform diameters of about 900 nm and an average shell thickness of 45 nm. While the diameters and thicknesses of $Cu_2O$/CuO composite hollow-shell spheres are 90–500 nm and 15–35 nm, respectively. Both of these two kinds of hollow-shell spheres showed much improved response to ethanol gas as gas sensors, the triple-shelled CuO/$Cu_2O$ hollow spheres exhibited the highest response at 140 °C, 1000 ppm.



## 1. Introduction

Reliable sensors for detecting ethanol gas are very important in food industry, medicine and biotechnology, especially in wine quality monitoring and breathing analysis [1]. Nowadays, metal oxide semiconductors have been widely employed for sensing ethanol gas [2]. Copper oxide, as the important p-type transition metal oxide with narrow band gap, has been extensively investigated owing to its promising applications in various fields, such as gas sensors, photo cathodes for $CO_2$ reduction, super capacitors, photo detectors and catalysis [3–7]. Since their physical and chemical properties are strongly dependent on their sizes, shapes, compositions and structures [8], considerable research efforts have been paid to the shape- and structure-controlled synthesis of copper oxide [9–13]. To date, copper oxide with different morphologies like nanorods [9], microflowers [10], nanowires [11], nanobundles [12] and hollow microspheres [13] have been successfully obtained. Among these morphologies, nanomaterials with hollow spherical morphology represent promising applications in gas sensing due to their low density, large specific surface area and superior mass transfer properties. For instance, $\alpha$-$Fe_2O_3$ multi-shelled hollow microspheres were prepared using hard templates method showing both improved gas sensing property and enhanced performance as anodes for lithium ion battery [14,15], hollow $SnO_2$ nanospheres were fabricated as flexible photo detector with excellent light selectivity, stability, and high signal-to-noise ratio [16]. However the multi-shelled hollow spheres are rarely reported for copper oxides.

Besides the morphology, it is also observed that the formation of the composite materials may further improve their properties. For example, the CuO/$Cu_2O$ hollow microspheres [17] exhibited a higher photocatalytic activity than the single-phase CuO or $Cu_2O$ samples. CuO/$Cu_2O$ hollow polyhedrons [18] revealed excellent cycle performance and enhanced lithium storage capacity. However, these composite materials have never been achieved in multi-shelled structures so far.

Herein, we report a successful synthesis of the multi-shelled copper oxide hollow microspheres. By adjusting the kinds of the carbonaceous spheres using different sources, hollow spheres of CuO and CuO/$Cu_2O$ could be synthesized selectively. Moreover, the composite CuO/$Cu_2O$ hollow spheres show much better gas sensing performance for ethanol compared with the pure CuO hollow spheres.

*Abbreviations:* CuO, cupric oxide; $Cu_2O$, cuprous oxide; CS1, carbonaceous microspheres; CS2, carbonaceous spheres; TEM, transmission electron microscopy; SEM, scanning electron microscope; −OH, hydroxyl.

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## 2. Experimental

### 2.1. Materials and reagents

$Cu(NO_3)_2{\cdot}3H_2O$(99%), sucrose (98.5%), ethanol (98%), urea (99%), glucose (99%), were purchased from Beijing Chemical Reagents Company and used without further purification.

### 2.2. The preparation of the carbonaceous microspheres templates

Carbonaceous microspheres (CS1) were synthesized by the hydrothermal emulsion polymerization of sucrose as previously described in literature [19]. In brief, 130 g of sucrose was dissolved in 250 mL of deionized water and heated to 200 °C for 120 min in a sealed Teflon reactor. After that the brown product was washed times alternatively with deionized water and ethanol until clean and dried at 80 °C for 12 h.

Carbonaceous spheres (CS2) were synthesized as follows: 80 g of glucose was dissolved in 80 mL of deionized water and heated to 180 °C for 24 h in a sealed Teflon reactor. After that, the brown product was washed alternatively with deionized water and ethanol, followed by dried at 80 °C for 12 h.

### 2.3. Synthesis of the pure CuO hollow spheres

The prototypical synthesis of CuO hollow microspheres is as follows: 200 mg of prepared CS1 were dispersed by sonication in 5 mL ethanol for 20 min, 1.8018 g urea was added to 50 mL of a 0.06 M copper nitrate solution by stirring, then the mixed solution was added to carbon spheres suspension, stirred for 8 h at 60 °C, followed with three cycles of centrifugation wash/re-dispersion in water and dried at 80 °C for 12 h. The infused precursors were heated to 400 °C with different heating rates in a furnace in air and then naturally cooled to room temperature. While the calcination rates were 2 °C/min, 3 °C/min and 5 °C/min, the morphologies of the products were single-, double- and triple-shelled hollow spheres, separately.

### 2.4. Synthesis of the CuO/$Cu_2O$ composite hollow spheres

For synthesizing the CuO/$Cu_2O$ composite hollow spheres, 50 mg of prepared CS2 was dispersed in 20 mL of 0.035 M copper nitrate solution for 20 min. Then above mixtures were sealed into a 30 mL Teflon-lined autoclave and maintained at 150 °C for 8 h. As-prepared precursors were heated to 400 °C with controlling the calcination rates at 2 °C/min, 3 °C/min and 5 °C/min, followed by maintaining the temperature for 4 h. In this way, the final products were single-, double- and triple-shelled hollow spheres of CuO/$Cu_2O$ composites.

### 2.5. Characterization

The structure and morphology of products were characterized by X-ray diffraction patterns (XRD, Rigaku D/Max 2200PC diffractometer; Rigaku Corp., Tokyo, Japan), a scanning electron microscope (Supra 55; Zeiss, Oberkochen, Germany), and high-resolution transmission electron microscope (HRTEM, JEM-2010; JEOL, Ltd., Tokyo, Japan). The Fourier transform infrared (FT-IR) spectra of the samples were collected using a NEXUS 670 infrared spectrometer (Nicolet Company, USA). In order to determine the composition of the precursors and the calcination temperature of the obtained precursors, differential scanning calorimetry (DSC) data of the precursor were recorded on a thermal analysis instrument (model Q50 V20.6 Build 31) with a heating rate of 5 °C $min^{-1}$ under an air flow.

### 2.6. Measurement of ethanol sensing properties

A gas sensor was fabricated as follows: the as-prepared products were mixed with water, and then coated on an $Al_2O_3$ tube on which two gold electrodes had been installed at each end, and each electrode was connected with a Pt wire. The $Al_2O_3$ tube was about 8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter, a heater of Ni–Cr wire was inserted into the $Al_2O_3$ tube to supply the operating temperature. The electrical resistance of a sensor was measured in air and in sample gases. The gas response S was defined as the ratio $R_g/R_a$, where $R_a$ and $R_g$ are the resistances measured in air and the tested gas atmosphere.

## 3. Results and discussion

After adsorbing $Cu^{2+}$ ions from the solution, Cu-CS1 and Cu-CS2 precursors were obtained. To determine the calcination temperature for the precursors, the thermogravimetric (TG)/differential scanning calorimetric (DSC) curves of the obtained precipitates were measured (Fig. S1). The hollow spheres could be obtained when the Cu-CS1 and Cu-CS2 precursors were calcined from room temperature to 400 °C. The TG measurement results indicated the CS1 precursor exhibited a total weight loss of 90% from 23 to 400 °C, while the CS2 was 83%, which are attributed to the dehydration and decomposition of carbonate and hydroxide, corresponding to the endothermic peaks of the DSC curves.

Upon calcination the hollow-shell products were obtained, and the TEM and SEM were employed to reveal the morphologies of hollow spheres prepared under various synthesis conditions (Fig. 1). As we have known, as water is to fish, ideal morphology is to excellent performance of material. CS1, using sucrose as the source of carbonaceous spheres, was served as template because of its mature technology of synthesis, large particles size and good dispersion, which is to the advantage to forming multi-shells hollow spheres. Upon $Cu^{2+}$ absorbing, the CS1-Cu precursors were heated to 400 °C in air to remove the carbonaceous template and produce the copper oxide multi-shells hollow spheres. Concentric internal multi-shells are controlled by adjusting the calcination conditions, and single-, double- and triple-shelled spheres were produced at heating rate of 2 °C/min, 3 °C/min and 5 °C/min, respectively (Fig. 1a–c). But the yield of triple-shelled hollow spheres is really low, due to the lower adsorbing amount of the $Cu^{2+}$ ions (Fig. 1c). Fig. S2 shows the XRD pattern of products obtained by using CS1 as templates. All diffraction peaks can be perfectly indexed to monoclinic phase CuO (JCPDS 48-1548) without other impurities, indicating the purity of all the single-, double- and triple-shelled spheres obtained from CS1 were formed as pure CuO. These CuO hollow spheres had uniform diameters of about 900 nm (Fig. 1d) and an average shell thickness of ~45 nm (Fig. 1a–c).

Owing to the better performance of the composite material comparing to the single phase, we expected the formation of CuO/$Cu_2O$ composite hollow spheres in similar systems. As another source for carbonaceous template, glucose is different from sucrose not only in molecular weight but also in its aldehyde group, which can reduce $Cu^{2+}$ to $Cu^{+}$ [20]. So if the templates made from the glucose are chose, some $Cu_2O$ phase may be formed. To accomplish this, the CS2 templates were prepared by using the glucose. It is observed that the diameters of CS2s are smaller than that of CS1s (Fig. S3). As we expected, when using glucose as the carbon source, partially reduction of the $Cu^{2+}$ was achieved, and the CuO/$Cu_2O$ composite hollow spheres were synthesized (Figs. 1e–h and 2 ). By increasing the calcination rate from 2 °C/min to 3 °C/min and 5 °C/min, hollow spheres of CuO/$Cu_2O$ composite with single-, double- and triple-shells were obtained. The corresponding diameters of these composite hollow spheres are