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UV-assisted, template-free synthesis of ultrathin nanosheet-assembled hollow indium oxide microstructures for effective gaseous formaldehyde detection

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ABSTRACT

Hollow micro-/nanostructures, especially those with well-defined nanoscale subunits, have been widely used in a variety of areas including catalysis, sensing, energy storage, drug delivery, etc. Herein, we report a novel, UV-assisted, template-free synthesis of hollow indium oxide microstructures that are composed of ultrathin nanosheets (~2.5 nm). The two key steps for the synthesis of the materials being successful are: (i) the UV-induced conversion of a photoactive solid indium alkoxide precursor into hollow indium hydroxide microspheres composed of ultrathin nanosheets, and (ii) the thermal treatment of the resulting hollow hydroxide microspheres into the hollow In_2O_3 material with a morphological preservation. Moreover, we show that the as-obtained hollow nanomaterials exhibit excellent sensing performance (e.g., high response value, good stability, as well as fast response speed) for the detection of ppm-level gaseous formaldehyde. The efficient sensing performance of the material is attributed to their overall conducive structural features, including their hollow architecture and ultrathin nanoscale building blocks. These structural features can offer a large amount of active sites on the surface, facilitate the diffusion and adsorption of the target gas, and thus enhance the material's sensing performance.

1. Introduction

Owing to their unique properties including low density, high specific surface area and remarkable permeability, hollow micro-/nanomaterials with various compositions have attracted great attention, and they have been widely used in a variety of areas including catalysis, sensing, energy storage, drug delivery, etc. [1–12]. Up to now, many efforts have been devoted to exploring the methods for the preparation of micro-/nanomaterials with designed hollow structures. One of the popular synthetic strategies is template-assisted one. The commonly used templates involve hard ones (e.g., silica, polymer, and carbon particles) [13,6,14], and soft ones (e.g., vesicles and emulsion droplets/micelles) [15–17]. However, templating methods for constructing hollow structures usually have some disadvantages such as high cost, multi-step tedious synthesis, long reaction time and strict reaction conditions. In contrast to the templating method, template-free synthesis might be a more attractive strategy. With the rapid development of the template-free synthesis, some mechanisms, such as Kirkendall effect and Ostwald ripening, have recently appeared to explain such synthesis [18–20]. These positive results prompted us to explore further new template-free synthetic routes for the preparation of hollow structures with unique composition and nanoscale subunits as well as improved properties.

On the other hand, two-dimensional (2D) ultrathin nanomaterials with a thickness of <5 nm, such as graphene, have garnered increasing interest because the ultrathin nanostructures may lead to the increase in the number of surface active sites, as well as the exposure of some preferable crystallographic facets [21–23]. However, in contrast to the ease of making layered compounds into ultrathin 2D nanomaterials, it still maintains challenging to prepare such nanomaterials based on non-layered compounds, such as cubic Co_3O_4 [24–26]. This is mainly because these non-layered compounds generally have no spontaneous driving force for 2D anisotropic growth. Moreover, owing to their high surface energy, the ultrathin 2D nanomaterials have a very strong tendency to stack with each other during the material synthesis or application process. To resolve this problem, a feasible method is to assemble the ultrathin nanosheets into a three dimensional (3D)

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structure. This will effectively avoid the nanosheets stacking, and thus retain the structural advantages of ultrathin morphology.

Herein, we report the synthesis of hollow In_2O_3 microspheres composed of ultrathin (~2.5 nm) nanosheets, for the first time. The synthesis of this material is achieved via a two-step method: (i) the UV-induced conversion of a photoactive solid indium alkoxide precursor into hollow indium hydroxide microspheres composed of ultrathin nanosheets, and (ii) the thermal treatment of the resulting hollow hydroxide microspheres into the hollow In_2O_3 material with a morphological preservation. The resulting hollow material combines the advantages of hollow structure and ultrathin nanosheets in a single material system, and thus exhibits excellent sensing properties, such as high response value and fast response speed, for low-concentration gaseous formaldehyde detection. Although hollow In_2O_3 materials were previously reported, their syntheses were always assisted by various templates [27–33]. Additionally, the nanoscale subunits in those hollow In_2O_3 materials were usually the nanoparticles, and ultrathin nanosheets as the subunits were never reported before. Furthermore, our hollow In_2O_3 nanomaterial's sensing performance is also found to be better than that of most of the semiconductor materials reported recently for formaldehyde detection (Table S1).

2. Experimental

2.1. Chemicals and reagents

Indium (III) nitrate hydrate and glycerol were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Isopropanol, ethanol and formaldehyde aqueous solution (37 wt%) were purchased from Beijing Chemical Works (Beijing, China). All the chemicals were used as received without further purification and distilled water was used throughout all experiments.

2.2. Synthesis of solid indium alkoxide microspheres (s-In-Alk)

The solid indium alkoxide microspheres were synthesized according to our previous work [34]. In details, 0.30 g $In(NO_3)_3{\cdot}4.5H_2O$ was firstly dissolved in 30 mL isopropanol under vigorous magnetic stirring, followed by adding 10 g glycerol. Subsequently, this resulting transparent mixture was transferred into a 50 mL Teflon-Lined autoclave and then treated at 180 °C for 1 h in an oven. After naturally cooled to the room temperature, the white precipitate (i.e., s-In-Alk precursor) was washed three times with ethanol to remove the residual inorganic ions and organic species. Finally, the s-In-Alk was dried in an oven at 80 °C for 12 h in air.

2.3. Preparation of hollow In_2O_3 microspheres from the s-In-Alk precursor

1 g of the s-In-Alk sample was dispersed in 100 mL deionized water and then irradiated with UV light for 2 h at room temperature. The UV-light source was a 125 W high-pressure mercury lamp (see the emission spectrum of this light source in Fig. S1), and the irradiation intensity of the UV-light was about 8.0×10^3 μW/cm^2. After irradiation, a fluffy sample was generated, and then this sold sample was washed twice with ethanol and dried in an oven at 80 °C for 12 h. This resulting powdered sample was denoted as UV-In-OH.

In order to obtain In_2O_3 materials, the In-OH was calcined at different temperatures (300, 400, 500, 600, or 700 °C) for 2 h in a muffle furnace in air with a heating rate of 2 °C/min. The as-prepared material was labelled as UV-In_2O_3-T, where T was the calcination temperature. For comparison, an In_2O_3 material (dubbed p-In_2O_3-400) was prepared by directly thermal treatment of s-In-Alk at 400 °C in air for 2 h.

2.4. Instrumentations and characterizations

The powder X-ray diffraction (XRD) patterns were performed with a Rigaku D/Max 2550 X-ray diffractometer using CuKα radiation (λ = 1.5418 Å) operated at 200 mA and 50 kV. The particle size and morphology were determined by transmission electron microscope (TEM, Philips-FEI Tecnai G2S-Twin), equipped with a field emission gun operating at 200 kV, and scanning electron microscope (SEM, JEOL JSM 6700F). The nitrogen adsorption and desorption isotherms were measured by a Micromeritics ASAP 2020M system. The infrared spectra (IR) were acquired with a Bruker IFS 66V/S FTIR spectrometer by placing the samples on predried KBr pellets, from 4000 to 400 cm^{-1} wavenumbers. UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 20 UV/vis spectrometer.

2.5. Sensor fabrication and testing

The In_2O_3 material was firstly mixed with a small amount of ethanol to make viscous slurry, followed by smoothly pasted using a small brush onto a designed ceramic tube (1 mm in diameter and 4 mm in length), which was attached with a pair of Au electrodes and four Pt wires on both ends of the tube. A Ni–Cr alloy coil passing through the ceramic tube was employed as a heater to adjust the operation temperature by tuning the heating current, and the operating temperature was measured on the surface of the sensor. The fabricated gas sensor was then aged at 200 °C for 12 h in air to enhance the stability and repeatability. The gas sensor was welded on a socket and gas sensing measurements were recorded on a commercial CGS-8 Gas Sensing Measurement System (Beijing Elite Tech Company Limited) using environmental air with a relative humidity of ~30% as both reference and diluting gas. Gas sensing properties were evaluated using a static test system which included a 1 L test chamber. In order to prepare the sample gases, a certain amount of formaldehyde aqueous solution (37 wt%) was transferred into the test chamber using a microsyringe and maintained for >120 min to give a homogenous atmosphere. To check the effect of water vapor on the formaldehyde response properties, pure water, in lieu of formaldehyde aqueous solution, was used in the preparation of sample gases. For measurement, the sensor was put into the test chamber to get a stable reading of resistance R_g. When the response reached a constant value, the sensor was taken out to recover in fresh air to get a stable reading of resistance of R_a. The sensor was tested at the temperature range of 80–260 °C and the formaldehyde concentration was in the variation of 1–100 ppm. The working principle of the sensor is shown in Scheme S1 in ESI. A load resistance (R_L) is connected in series to the sensor. The resistance of a sensor in air or a target gas was measured by the output signal voltage (V_{out}), i.e., the voltage at both ends of the load resistance, at a test circuit voltage of 5 V (V_s). The sensor response was defined as $S = R_a/R_g$, where R_a and R_g were the sensor resistance in environmental air and target gas, respectively.

3. Results and discussion

3.1. UV-induced synthesis of hollow indium hydroxide microspheres from the solid indium alkoxide precursor

The solid indium alkoxide microspheres were synthesized according to our previous work (for detailed characterization results of the precursor material, please see our previous report) [34]. This indium alkoxide precursor is denoted as s-In-Alk. SEM and