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Hierarchically porous indium oxide nanolamellas with ten-parts-per-billion-level formaldehyde-sensing performance

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ABSTRACT

Hierarchically porous indium oxide nanolamellas with two levels of nanopores have been designed and synthesized by low-temperature dehydration. Each nanolamella consists of nanoparticles, where nanogaps of 5–50 nm are present between the nanoparticles and concave nanopits of 3 nm exist in the surface of each nanoparticle. The nanopits bring negative curvatures to the surfaces of the nanoparticles, leading to a high density of atomic steps and then enhancing the surface activity. Consequently, the indium oxide nanolamellas have exhibited a formaldehyde-detection limit of 80 ppb (parts per billion) with response and recover times as short as 5 s and 1.3 s respectively. The 80-ppb detection limit is lower than the previously reported values from gas-sensing semiconductors and the health standard limitation on the concentration of formaldehyde in indoor air. The detection signal also has an excellent linearity with the formaldehyde concentration. Moreover, the strategy to synthesize the nanolamellas is just two-step heating and easy to scale up. Therefore, the hierarchically porous indium oxide nanolamellas are ready for industrialization and practical applications.

1. Introduction

Formaldehyde (HCHO) is one of the most widespread indoor air pollutants, because it can be easily released from a plenty of construction materials, furnitures and textiles. It is highly toxic to all animals and humans and can irritate eyes at concentrations as low as 0.1 ppm (=100 ppb, namely 100 parts per billion) in air, which is the health standard limitation on the HCHO concentration in air [1]. Therefore, effective methods to detect 100-ppb HCHO are of great importance and in great demand in practical applications. Up to now, gas chromatography is the only popular method capable of detecting HCHO with the concentration down to 100 ppb [2]. But this method requires users to collect some indoor air and then to analyze the air specimen in a stationary and expensive instrument of gas chromatography for the HCHO concentration, and so it is time-consuming and of high cost [2]. In contrast, semiconductor-based gas sensors can give real-time readings of the HCHO concentration when they are placed in an indoor environment, and they are small, portable and of low cost [3–7]. Semiconductor nanoparticles including the In_2O_3 ones are promising for detecting extremely dilute HCHO in air, because their surfaces contain sites active to react with target gas molecules [3–7] and the morphology of their porous assembly is easily diversified for high specific surface area (SSA) by many methods, such as layer-by-layer assembly [3], template method [6], structural replication [8–11], and hydrothermal synthesis [7–12]. SSAs up to 90 $m^2 g^{-1}$ have been reported for In_2O_3 nanoparticles and their porous assemblies [11]. Although significant progresses with the lowest HCHO-detection limits down to 500 ppb have been achieved in the literature [13], the limits are still higher than 100 ppb and do not meet the requirement of practical applications. This should be due to that the active sites on the surfaces of the In_2O_3 nanoparticles were not sufficient, because the SSAs of their assemblies were already very high.

Fortunately, Chen et al. have reported a significant finding that a concave surface with negative curvature of nanoporous gold

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contains a high density of atomic steps, which are active sites for surface reaction and thus catalysis [14–16]. Atomic steps on the surfaces of semiconductor nanomaterials should also be active for gas sensing, because they contain dangling bonds and low-coordination atoms that can react with gas molecules [17–21]. Up to now, no concave surfaces with negative curvatures have been realized on any gas-sensing semiconductors.

In this contribution we have adopted the concept of negative curvature to the surfaces of In_2O_3 semiconductor nanomaterials and thus designed and synthesized hierarchically porous In_2O_3 nanolamellas by dehydrating $In(OH)_3$ nanolamellas at relatively low temperature. Dehydration has been widely used for the conversion from metal hydroxides to metal oxide materials [7,12,22–26], including In_2O_3 nanocages [7], In_2O_3 nanocubes [12], and In_2O_3 hollow microspheres [22], all of which are composed of In_2O_3 nanoparticles. It is rational to consider that the loss of water molecules should produce concave nanopits with negative curvatures in the surfaces of the In_2O_3 nanoparticles. But, in reality, no nanopits were found in the surfaces of the reported In_2O_3 nanoparticles [7,12,22]. This phenomenon is due to that the dehydration temperatures, 400 – 500 °C [7,12,22], were so high that recrystallization inevitably existing on the surfaces of the In_2O_3 nanoparticles during the high-temperature dehydration must be severe, causing that no nanopits persisted. Based on the above reported results, we propose that a low-temperature dehydration could help the nanopits persist, and choose $In(OH)_3$ nanolamellas as precursors for the proposal, because nanolamellas are thin and so easy to be dehydrated uniformly. The low-temperature dehydration would not only break the precursors into In_2O_3 nanoparticles but also produce nanopits that can survive in the surface of each nanoparticle during the low-temperature process, as depicted in Scheme 1. Thus, the resultant porous In_2O_3 nanolamellas composed of the nanoparticles should possess two levels of nanopores, nanogaps between the nanoparticles and nanopits on the nanoparticle surfaces. The nanopits should endow the surfaces of the nanoparticles with negative curvatures and thus atomic steps. The above design was performed experimentally. Each of the In_2O_3 nanolamellas consists of In_2O_3 nanoparticles and contains two levels of nanopores: nanogaps of 5 – 50 nm between the nanoparticles and concave nanopits of 3 nm in the surface of each nanoparticle. The nanopits bring negative curvatures to the nanoparticle surface, leading to a high density of atomic steps. As a result, the lowest HCHO detection limit achieved is 80 ppb, lower than the health standard limitation (100 ppb), and so meets the requirement of practical applications. Moreover, the HCHO detection is repeatable, and its response and recover times are as short as 5 s and 1.3 s, respectively. The excellent HCHO-sensing performance has been confirmed to originate from the existence of the nanopits in the surfaces of the In_2O_3 nanoparticles. Furthermore, the synthesis method of low-temperature dehydration is easy to scale up. Therefore, the hierarchically porous In_2O_3 nanolamellas are ready for industrialization and practical application. It is also anticipated that the design of the hierarchical porosity with low-temperature dehydration can be easily extended to other metal hydroxides for their oxide nanomaterials.

2. Experimental details

2.1. Synthesis of $In(OH)_3$ nanolamellas

$In(NO_3)_3{\cdot}6H_2O$ of 4.2 g was quickly added in de-ionized (DI) water of 20 ml containing 9 g urea to form a clear solution. The solution was heated at 90 °C for 5 h and then cooled to room temperature, resulting in $In(OH)_3$ nanolamella precipitates in the solution. The nanolamellas were separated from the solution by centrifugation at 2000 rpm (revolutions per minute) for 10 min, and were then washed with DI water and ethanol.

2.2. Synthesis of hierarchically porous In_2O_3 nanolamellas

The as-prepared $In(OH)_3$ nanolamellas were heated in air from room temperature to 100 °C by the rate of 1.3 °C/min, then to 300 °C by 2.2 °C/min, kept at 300 °C for 5 h and finally cooled to room temperature. This process converted the $In(OH)_3$ nanolamellas into hierarchically porous In_2O_3 nanolamellas.

2.3. Characterization

The morphologies and structures of the products were characterized by field emission scanning electron microscope (SEM, JEM-5500), conventional transmission electron microscope (TEM, Tecnai $G^2$20 at 200 kV), environmental TEM (H-9500 at 300 kV) and aberration-corrected TEM (Titan 80–300 at 300 kV). The SSAs were measured by the Bruauer–Emmett–Teller (BET) method with nitrogen adsorption–desorption isotherm, and the pore size distribution was analyzed using the Barrett–Joyner–Halenda (BJH) algorithm.

2.4. HCHO-sensing measurement

As-prepared porous In_2O_3 nanolamellas were mixed and ground with glycol in an agate mortar to form a paste. The paste was smeared evenly onto the alumina tube of a standard commercial sensor device purchased from Zhengzhou Winsen Electronics Technology, China (see its schematic and optical images in Fig. S1a and S1b of Supporting Information) [23]. The tube has the length of 0.4 cm, the outer diameter of 0.1 cm and the inner diameter of 0.08 cm. It already has a pair of Au electrodes on its surface and a resistive heater inside it. When it is coated with gas-sensing materials (such as the In_2O_3 nanolamellas), the sensor device becomes a ready gas sensor [22]. After being dried in air for a week, the thickness of the In_2O_3 nanolamella coating was 1.5 μm. Then, the Au electrodes and the heater of the sensor were connected to the sensor holder of a WS-30A measuring system (Zhengzhou Winsen Electronics Technology, China) and the sensor was placed in the test chamber of the measuring system. The chamber can supply an isolated environment to the target gas, HCHO. The measuring system also contains one quickly evaporating heater and two electric fans to make HCHO distributed uniformly in the air confined in the chamber. In the beginning of the HCHO-sensing measurement, the In_2O_3 nanolamella coating was aged for 2 h by heating it at 300 °C. The aging had been checked and found not to change the structures of the samples (see more details in Fig. S2 of Supporting Information). After the aging, some HCHO solution was injected onto the quickly evaporating heater, and the change in the reading of the voltage meter of the measuring system was monitored. The coating was kept at 300 °C during the test. The HCHO concentration was calculated with the dose of the injected HCHO and the volume of the air in the chamber. The desired concentrations of HCHO in ppb can be obtained and calculated by the following equation with the air as a reference gas and a diluting gas:

$$C = \frac{V_{HCHO}\rho_{HCHO}C_{HCHO}V_m}{M_{HCHO}V_{box}} \quad (1)$$

where C is the HCHO concentration in ppb, V_{HCHO} is volume of the detected HCHO solution, ρ_{HCHO} is the density of HCHO solution, C_{HCHO} is concentration of HCHO solution, V_m is molar value of ideal gas, M_{HCHO} is the molar mass, and V_{box} is volume of the detection chamber. By injecting different volume of the detected HCHO solution, the different HCHO concentration in the chamber can be obtained, for example, 80 ppb concentration environment can be created by injecting 0.05 μl HCHO solution (3.5% HCHO diluent).