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Promoting effects of Ag on In_2O_3 nanospheres of sub-ppb NO_2 detection

Bingxin Xiao[a], Shanliang Song[b], Pan Wang[b], Qi Zhao[a], Mingyan Chuai[a], Mingzhe Zhang[a,*]

[a] State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
[b] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Street, Changchun 130012, China

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ABSTRACT

Herein, high performance of sub-ppb NO_2 sensors were fabricated based on Ag nanoparticles (NPs) decorated on hierarchical In_2O_3 nanospheres assembled by several nanocubes subunit via a facile hydrothermal route and the subsequent decoration process. The morphology evolution of the nanospheres is investigated, which revealed that the nanocubes of the nanospheres shared the same surface and self-assembled together according to the oriented attachment mechanism. When performing as sensors, such nanostructures possessed relatively good sensitivity to NO_2. With respect to the decoration of Ag NPs, the sensing performances can be further remarkably promoted on account of the catalyst activation and spill-over effect.

1. Introduction

Nitrogen dioxide (NO_2) has been the main pollutants in the ambient atmosphere and can also irritate to the respiratory tract, even cause the lung lesion and pulmonary edema of human [1]. For this reason, NO_2 sensor is still an increasingly expanding topic and has attracted great interest due to their potential applications in environmental monitoring, exhaled breath detection, chemical and food industries, etc. [2–6]. Up to now, the NO_2 sensing performance is continuously increased. To date, in light of their desirable characteristics of low cost, simplicity of fabrication and reliable solid state, metal oxide semiconductors are being considered to be the most promising material of gas sensors [7,8]. In recent years, various types of metal oxides (for instance ZnO [9,10], SnO_2 [11], α-Fe_2O_3 [12], WO_3 [13], and In_2O_3 [14]) have been studied and various types of gases could be detected, thereby bringing the on-site gas detection of interest closer to a reality. Nevertheless, new sensor strategies towards NO_2 gases to achieve more excellent performance such as sub-ppb detection limit and fast detection speed for practical application are still in a nascent stage [15]. Hence, to expand the application of gas sensors virtually should hinge on the improvement of sensitivity and the reduction of detection time.

Typically, sensing performance is intrinsically associated with morphology of the material [16]. As a result, nanomaterials have been the major components in sensing devices due to their fascinating merits of size and shape dependent characteristics. Optimizing material structures with low dimensional subunit-assembled hierarchical architectures have been demonstrated favourable for application owing to their intrinsic anisotropy and adjustable spatial distribution as well as the improved special surface area [17,18]. Several efforts are attempted to obtain high performance sensors based on the hierarchical nanostructures and these attempts have indeed remarkably improved. For instance, Bai et al. and another group of Wang et al. both reported hierarchical WO_3 microspheres assembled by nanosheet or nanorod with excellent NO_2 sensing [19,20]. Manjulaet et al. have fabricated high performance sensing material based on the porous SnO_2 nanospheres assembled by nanoparticles [21]. Not long ago, our group has synthesized a fast H_2S sensor acted by a nanorod-assembled hierarchical WO_3 architecture [22]. Thus, it plays a critical role in obtaining superior sensors to synthesis the low dimensional subunit-assembled hierarchical architectures [23].

Noble metals have been demonstrated to be effect introduction to the sensing materials to overcome the essential weaknesses these years [24,25]. As reported, the NO_2 sensitivity could be improved by the introduction of AgNPs due to the catalytic activity of Ag to dissociate the NO_2 molecules into ${NO_2}^-$ [20]. For instance, some researchers have reported that NO_2 sensing was enhanced

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* Corresponding author.
E-mail address: zhangmz@jlu.edu.cn (M. Zhang).

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by the decoration of AgNPs into mesoporous WO_3 nanostructures, SnO_2-microrods, MWCNTs and MWCNTs/SnO_2 hybrids and CuO nanostructures, etc. [20,26–28].

Based on the above consideration, Ag decorated hierarchical In_2O_3 nanospheres assembled from nanocubes are designed via a facile hydrothermal route and followed by the facile decoration of Ag NPs. The effect of Ag NPs is investigated. As expected, the as-prepared sample exhibits far better NO_2 sensing performance, especially the detection limit is lowered as sub-ppb level than the primary In_2O_3 nanospheres. For practical application point of view, this work proposes a facile approach to fabricate the well-dispersed hierarchical nanostructures and the highly efficient NO_2 sensors. As best as we known, the sub-ppb detection limit of NO_2 was achieved, this is rarely reported among the metal oxide sensors.

2. Experimental

2.1. Preparation of hierarchical In_2O_3 nanospheres

All the reagents (analytical-grade) were used without further purification. Deionizer water was used throughout the experiments. The pure In_2O_3 nanospheres were synthesized via a facile hydrothermal treatment. Typically, 19.6 mg of $In(NO_3)_3·4.5H_2O$, 30 mg of urea and 14.4 mg of sodium dodecyl sulfate (SDS) were dissolved in 20 mL mixed solution contained 10 ml of distilled water and 10 ml of *N,N*-dimethylformamide (DMF) to form a transparent solution under stirring. Then the solution was transferred to a 20 ml vial, sealed and subsequently heated at 100 °C for 12 h. The resulting white precipitates were centrifuged, washed with distilled water and ethanol for several times, dried at 60 °C for 2 h in air and calcined at 500 °C for 2 h in air to obtain the In_2O_3 nanospheres.

2.2. Preparation of Ag decorated hierarchical In_2O_3 nanospheres

The Ag decoration was conducted with $NaBH_4$ as the strong reducing agent and citric acids as the capping agent. In a typical synthesis, 40 mg of the In_2O_3 nanospheres was added into a solution containing 1 ml citric acids solution (0.02 M) and 100 ml $AgNO_3$ solution (0.2 mM) under vigorous stirring for 30 min at 0 °C. Then 3 ml $NaBH_4$ (7 mM) was dropwised into the mixed solution under ultrasonication for 2 h. The sample decorated with Ag NPs was obtained by the following centrifugation and dring at 60 °C.The weight percentage of Ag in the composites is 5 wt%. For comparison, 2 wt% and 8 wt% of Ag decorated In_2O_3 samples were also fabricated.

2.3. Characterization

The In_2O_3 samples were characterized by the X-ray diffraction (Rigaku D/max-Ra), transmission electron microscope (JEOL JEM-2200FS) and the Scanning electron microscopy using a Magellan 400, FEI microscope operating at 20 kV. The TGA was carried out on a TG 209 F1 Netzsch apparatus under nitrogen with a 10 °C min^{-1} heating rate. The specific surface area was estimated using the Brunauer-Emmett-Teller (BET) equation based on the nitrogen adsorption isotherm. Pore diameter distribution was calculated by Barrett–Joyner–Halenda (BJH) method using the adsorption branch of the isotherms. The valence state of the samples was characterized by X-ray photoelectron spectroscopy (XPS) (ESCALAB MK II).

3. Results and discussion

3.1. Structure and morphology

Fig. 1a of scanning electron microscopy (SEM) image shows the hierarchical $In(OH)_3$ samples obtained before calcination treatment are relatively homogenously and uniformly dispersed. From the inset of which, it can be observed that the nanospheres are conducted by several nanocubes with diameter of ~35 nm in length and ~15 nm in width. XRD pattern of $In(OH)_3$ samples (Fig. 1b) showed that the diffraction peaks matches well with the standard cubic structure of $In(OH)_3$ (JCPDS 16-0161) which indicates the purities of the product.

SEM micrograph of Fig. 2a shows that particles of In_2O_3 adopt a hierarchical sphere-like morphology. As is revealed from the enlarged SEM image in Fig. 2b, the In_2O_3 nanospheres assembled by several nano-cubes inherited the morphology of $In(OH)_3$ precursor without damages after the calcination.

Transmission electron microscopy (TEM) is then employed to gain further insight into the In_2O_3nanostructures. Fig. 2c shows a typical low-magnification TEM image of the synthesized In_2O_3 samples, it can be found that the samples are nearly monodispersed and in which a batch of nano-cubes is integrated together, forming a hierarchical sphere-like morphology. The complete nanosphere of the synthesized In_2O_3 is observed to be in the size of about 150 nm with regular edges and well-defined morphology, as shown in Fig. 2d, an enlarged TEM image.

Fig. 2e is the selected area electron diffraction (SAED) pattern, which suggests that the intrinsic single crystal of nanocubes constitute the multi-crystals nanospheres. The continuous clear diffraction rings at surface as (211), (222), (400), (420), (440), (622), (732) and (822) demonstrate the conformance with XRD analysis results. As can be seen from the high-resolution TEM (HRTEM) image in Fig. 2f, the clear lattices fringes are obviously observed on

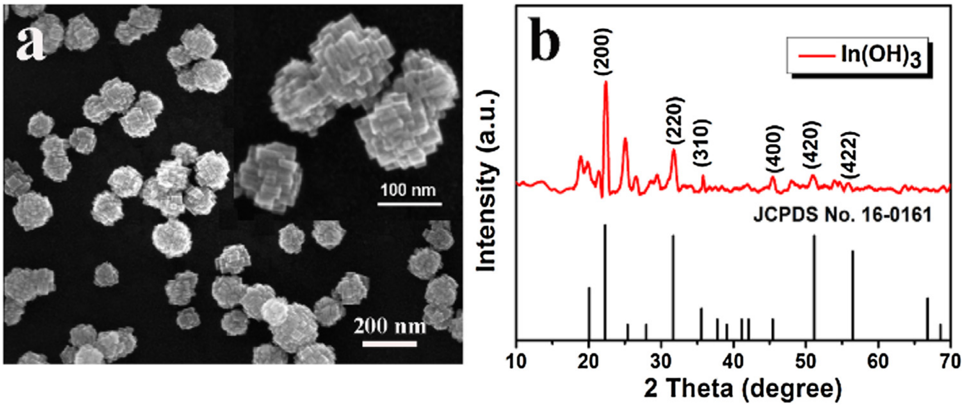

Fig. 1. (a)Typical SEM image of precursor of hierarchical $In(OH)_3$ nanospheres obtained before calcination. (b) Corresponding XRD pattern.