In situ immobilization of tin dioxide nanoparticles by nanoporous polymers scaffold toward monolithic humidity sensing devices

Shu Wei [a], Dong-Dong Han [a], Li Guo [a], Yinyan He [b], Hong Ding [b], Yong-Lai Zhang [a,*], Feng-Shou Xiao [c]

[a] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China
[c] Department of Chemistry, Zhejiang University, Hangzhou 310028, China

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ABSTRACT

Reported here is *in situ* immobilization of tin dioxide (SnO_2) nanoparticles (NPs) within nanoporous polymer scaffolds for the development of monolithic humidity sensing devices. Through solvothermal polymerization of divinylbenzene (DVB) monomers in the interspaces of SnO_2 fine powders, SnO_2 NPs could be homogeneously immobilized in polymer matrices, forming a novel composite material. Immobilization of SnO_2 NPs in nanoporous polymer matrices not only simplifies the fabrication process of NPs-based sensing devices, but also improves their adsorptive properties. The resultant nanoporous polymer/SnO_2 NPs composites with adjustable SnO_2 contents possess high BET surface areas, large pore sizes and pore volumes, thus they exhibit high adsorptive capacities for H_2O vapor. As a general approach to NPs/nanoporous polymer composites, this work may open up a new way to nanomaterial-based sensing devices that features enhanced adsorptive property.

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1. Introduction

Recent years have witnessed a significantly increased research interests in nanomaterials that possess many superior properties as compared with their corresponding bulky materials [1–3]. Thereby, nanomaterials become attractive in various disciplines such as electronics, optics, catalysis and medicine [4–13], and have already revealed a cornucopia of both scientific researches and multifunctional applications. With relatively large surface-to-volume ratio and unique physical/chemical properties derived from the significantly reduced feature sizes, nanomaterials have always been considered as preferred building blocks for device fabrication. However, in most cases, quite a few problems appear in practical manufacturing procedures, especially, in the cases of some fixed-bed or flow-through devices. Moreover, nanomaterials with a feature size smaller than 50 nm also suffer from serious problems in separation and reuse. As a result, the demands for the methods that could be used for nanomaterial immobilization toward the development of functional devices become more and more critical.

To date, a large number of strategies such as spin coating [14], assembly of nanobuilding blocks into bulky materials [15], growth on substrates [16], large-surface-area supporters [17–19], forma-tion of composite materials [20,21], and high temperature agglomeration [22] have been successfully employed to immobilize nanomaterials toward the tractable fabrication of micro-nanodevices. Nonetheless, the immobilization treatments would more or less limit their properties as compared with pristine nanomaterials. Taking gas sensor as a typical example, semiconductor nanoparticles (NPs) with large surface areas hold great promise for the improvement of sensing performance [23–27]. However, in order to assemble semiconductor NPs between testing electrodes, these NPs have to be mixed with adhesive slurries before coating on the electrodes, which significantly lowers the active surface area and limits their interaction with sensing molecules. To overcome this drawback, an ideal way is to post-immobilize these NPs in the matrices of a nanoporous scaffold. In this way, the nanoporous hosts would not only facilitate the device manufacture, but also promote their adsorptive capacities; and thereafter, significantly improved sensing performance would be expected. However, to the best of our knowledge, it is still lack of *in situ* synthetic methods that permit post-immobilization of NPs within the nanoporous structures. Currently, in the field of material and interface science, it is still challenging to develop a generally available route to immobilize NPs through the formation of nanoporous composites toward the development of monolithic sensing devices.

Previously, we have successfully prepared nanoporous polymers that featured high BET surface area, large pore size and pore

* Corresponding author. Fax: +86 431 85168281.
  E-mail address: yonglaizhang@jlu.edu.cn (Y.-L. Zhang).

volume, revealing outstanding adsorptive properties toward a wide range of compounds [28–32]. In this work, as proof-of-concept, SnO_2 NPs have been post-immobilized within the matrices of the nanoporous polymers scaffold through an *in situ* solvothermal polymerization process. The immobilization of SnO_2 NPs in nanoporous polymers leads to the formation of a novel monolithic NPs/nanoporous polymer composite with high BET surface area and large pore size. Therefore, the resultant monolithic composites show improved adsorptive capacity for H_2O, which promotes their humidity sensing property significantly. As a general approach to NPs/nanoporous polymer composites, we anticipate that the present work would open up a facile way to the development of sensing devices with significantly enhanced adsorptive property.

2. Experimental section

2.1. Materials

SnO_2. NPs were purchased from Alfa Aesar company, divinylbenzene (DVB) was purchased from Tianjin-Guangfu Chemical Company, azobisisobutyronitrile (AIBN) and tetrahydrofuran (THF) were purchased from Beijing Chemical Company. All chemicals were used as received without any further purification.

2.2. Synthesis

In a typical preparation of polymer precursors, *a* g divinylbenzene (DVB, and *a* = 0.6, 1.2, 1.8, 2.4 and 3.0) was dissolved in mixed solvent consisting of tetrahydrofuran (THF) and deionized water (volume ratio of $V_{THF}/V_{water} = 20$, and total volume of each polymer precursor was equal to 12 mL), then 0.05 g azobisisobutyronitrile (AIBN) was added. After stirring mild for 4 h, uniform polymer precursors were obtained (Fig. S1).

In a typical synthesis of nanoporous PDVB/SnO_2 NPs composites, 6 g of SnO_2 NPs was added into a Teflon-lined stainless-steel autoclave, and 12 mL of polymer precursors was transferred into the autoclave (mass ratio of $mDVB/mSnO_2 = 0.1, 0.2, 0.3, 0.4, 0.5$) and fully filled in the interspaces formed by the stacking of SnO_2 NPs due to the capillary action. After a solvothermal treatment at 100 °C for 24 h, DVB monomers were polymerized; and a solid monolith was finally obtained after evaporation of the solvents at room temperature. The products were designated as Sn-P-*x*, where *x* = 0.1, 0.2, 0.3, 0.4, 0.5.

2.3. Characterization

Powder X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation (*k* = 1.5418). N_2 isotherms were measured with a Micromeritics Tristar 3000 analyzer at −196 °C. Samples were outgassed for 10 h at 150 °C under vacuum before the measurements. Before the adsorption test of H_2O, the nanoporous polymer/SnO_2 NPs composite samples were treated at 120 °C under vacuum for 5 h to remove any guest molecules. Thermogravimetric (TG) curves were carried out on a NETZSCH STA 449C with a heating rate of 20 °C min^{-1} from room temperature to 800 °C. SEM experiments were performed on a Hitachi S4800 scanning electron microscope equipped with energy dispersive X-ray (EDX) detectors.

2.4. Fabrication and measurement of sensors

The Sn-P-*x* (and pristine SnO_2) sample was coated on a ceramic substrate (6 mm × 3 mm, 0.5 mm thick) with five pairs of Ag–Pd interdigitated electrodes (electrodes width and distance: 0.15 mm) to form a sensing film and then dried in air at about

25 °C for 12 h. Finally, the humidity sensors were obtained after aging at 95% RH with a voltage of 1 V, 1000 Hz for 24 h to improve their stability and durability. Humidity sensitive properties of the sensors were investigated by recording the electrical response of the sensors at 1 V AC under different RH by a ZL-5 intelligent LCR analyzer at about 25 °C. The atmosphere of RH is produced by different saturated salt solutions in their equilibrium states including LiCl for 11% RH, CH_3COOK for 23% RH, $MgCl_2$ for 33% RH, K_2CO_3 for 43% RH, $Mg(NO_3)_2$ for 54% RH, NaBr for 59% RH, NaCl for 75% RH, KCl for 85% RH, and KNO_3 for 95% RH. The uncertainty of the RH values is about ±1%.

3. Results and discussion

3.1. Preparation of nanoporous PDVB/SnO_2 NPs composites

The preparation of nanoporous PDVB/SnO_2 NPs composites was carried out *via* an *in situ* solvothermal polymerization of DVB monomers in the presence of SnO_2 NPs fine powders. As shown in Fig. 1, polymeric precursor containing DVB as monomers, AIBN as initiators and THF/water mixture as porogenic solvent was fully filled in the interspaces formed by the stacking of SnO_2 NPs in an autoclave due to the capillary action. Then a simple solvothermal treatment was performed to prepare nanoporous polydivinylbenzene (PDVB) monolith. Finally, composite materials formed and SnO_2 NPs were immobilized homogeneously in the matrices of nanoporous polymeric scaffold after evaporation of the solvents. The nanoporous structure formed during the solvothermal polymerization due to the presence of porogenic solvent has been reported previously [28–30]. It is noteworthy that the whole procedure was quite simple and facile, and no undesired by-products were present.

3.2. Structure investigation of the nanoporous PDVB/SnO_2 NPs composites

Fig. 2 displays wide-angle XRD patterns of pristine SnO_2 NPs and nanoporous PDVB/SnO_2 NPs composite samples. As a typical character of SnO_2 NPs, a pure phase of rutile could be identified clearly from the patterns. No significant differences could be observed after the solvothermal treatment (100 °C for 24 h), indicating that the solvothermal treatment does not influence the crystalline phase of SnO_2 NPs. With the increase in polymer contents, the peak intensity with respect to rutile SnO_2 decreased slightly; this would be attributed to the presence of amorphous PDVB. To quantificationally investigate the influence of solvothermal treatment on SnO_2 crystal size, the full width at half maximum (FWHM) of the (1 1 0) crystal plane has been compared (Fig. S2). Notably, the FWHM of the (1 1 0) crystal plane of different samples almost
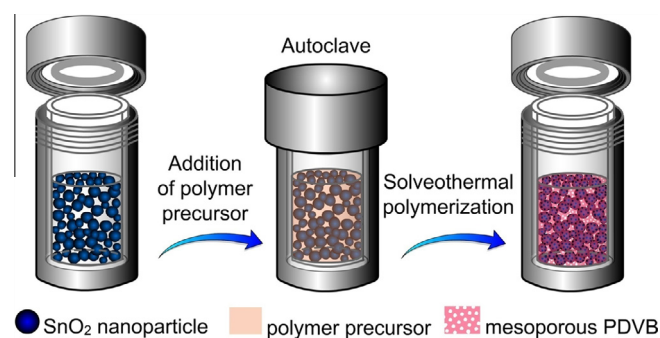

Fig. 1. Synthetic process for nanoporous PDVB/SnO_2 NPs composite samples.