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Composites of Fe_2O_3 nanosheets with polyaniline: Preparation, gas sensing properties and sensing mechanism

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ABSTRACT

Fe_2O_3 nanosheets were in-situ deposited on the interdigitated gold electrodes by hydrothermal treatment of the electrospun nanofibers containing $FeCl_3$ and poly(vinyl butyral). As-prepared electrode was further dip-coated with water-dispersible polyaniline (PANI) to fabricate a resistance gas sensor based on Fe_2O_3/PANI nanocomposite. The structure and morphology of the nanocomposite were investigated by X-ray diffraction pattern, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy. It was found that the nanocomposite sensor exhibited much higher response magnitude towards low concentration of NH_3 (0.5–10.7 ppm) than the sensors based on either PANI or Fe_2O_3 at room temperature (~20 °C), indicating an obvious synergetic effect. The nanocomposite sensor was featured with ultra high response magnitude (relative resistance change of ~3070% towards 10.7 ppm of NH_3) and excellent selectivity towards NH_3. A sensing mechanism has been put forward, which takes into account of the conducting network comprising of bulk PANI and composites of PANI and Fe_2O_3 nanosheets. It was proposed that the p/n heterojunction established between Fe_2O_3 nanosheets and PANI coating played a major role in the highly desirable sensing performance of the composite.

1. Introduction

In modern society, gas sensors have played an increasingly important role in various areas including industrial and agricultural production, environment monitoring and control and anti-terrorism. As a result, great interests have been stimulated towards the development of high performance gas sensitive materials. Among the vast number of materials ever investigated, inorganic semiconductor oxides (typically SnO_2, ZnO, TiO_2, Fe_2O_3) have received most attention and represented a major part of the commercially available gas sensors [1–4]. In spite of the prominent advantages such as relatively high sensitivity, fast response, low cost and versatile applications, these inorganic oxides generally have to work at high temperature. Consequently, the corresponding sensors exhibite increased power consumption which limits their applications in portable instrument. Moreover, the lifetime of the sensors is deteriorated. Additionally, the high working temperature brings about safety concern for use in places where combustible gases might exist [5,6].

Forming nanocomposites with conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) is proved to be an effective approach to realizing the gas detection at room temperature [7–9]. Furthermore, there have been a number of reports on the synergetic effect between the constituents, which endow the composites with much enhanced sensing performances. Meanwhile, the establishment of the nanostructure could increase the surface to volume ratio and provide more active reaction sites, leading to higher sensitivity and fast response [10–12].

Fe_2O_3 is a typical inorganic gas sensing material with the capability of detecting a number of vapors, such as CO, NH_3, NO_2, ethanol, acetone, H_2, liquid petroleum gases (LPG), at high temperatures [4,5,13]. Recently, gas sensors based on the composite of Fe_2O_3 with PANI or PPy have been prepared to realize the room temperature detection of gases with desirable sensing performance. Patil et al. employed the mixture of nanoparticles of α-Fe_2O_3 with chemically polymerized PANI or PPy in m-cresol to fabricate gas sensors [13–16]. It was revealed that the nanocomposite of PANI/α-Fe_2O_3 showed a relative resistance change of 50% towards 100 ppm of NH_3 and moderate selectivity at room temperature [14]. By contrast, the PPy/α-Fe_2O_3 nanocomposite exhibited a response magnitude of 54% towards 100 ppm of NO_2 [13]. Moreover, impedance spectroscopy studies were carried out to elucidate the sensing behaviors of PPy/α-Fe_2O_3 nanocomposite

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and its sensing mechanism [15]. Mishira and coworkers prepared the nanocomposite of γ-Fe_2O_3 with PANI by solution polymerization of aniline in the presence of sonochemically prepared γ-Fe_2O_3 nanoparticles. They found that PANI alone is insensitive to LPG. However, the composite displayed a relative resistance change of 0.5 towards 50 ppm of LPG at room temperature [17]. Despite the progress made in Fe_2O_3/conducting polymer composite gas sensors, much more work is needed to dramatically enhance their sensing behaviors (sensitivity, response and recovery time, selectivity, etc.) by careful design and tuning of the microstructure and morphology of the nanocomposites.

Both electrospinning (ES) and hydrothermal synthesis are well-known methods for the preparation of nanostructured materials, especially inorganic semiconductor oxides [18,19]. Recently, we fabricated nanostructured SnO_2, TiO_2 and ZnO with a new method of hydrothermally treating the electrospun nanofibers containing metal salt precursors [20–22]. The simple method avoids high temperature calcination which is usually a necessity for obtaining nanostructured inorganic semiconductors. Moreover, the nanostructured materials could be in-situ deposited on the substrate for the facile fabrication of functional devices. In this work, we extended this method to the fabrication of Fe_2O_3 nanosheets by hydrothermally treating the electrospun nanofibers containing $FeCl_3$ and poly(vinyl butyral) (PVB) on different substrates. Subsequent coating with water-dispersible PANI resulted in a Fe_2O_3/PANI nanocomposite. Examination of the electrical responses of the nanocomposite sensor towards NH_3 revealed its ultrahigh response magnitude towards low concentration of NH_3 (relative resistance change of 54%–3070% to NH_3 of 0.5–10.7 ppm), and excellent selectivity at room temperature (~20 °C). The sensing mechanism has been explored, and the high sensing performance of the nanocomposites is ascribed to the distinct morphological characteristics of the nanocomposite and the p/n heterojunction between PANI and Fe_2O_3.

2. Experimental

2.1. Materials

Aniline (Sinopharm Chemical Regent Co., Ltd.) was purified by distillation under reduced pressure and stored in a refrigerator prior to use. $FeCl_3$, ethanol (EtOH), ether, hexane, acetone, methanol (MeOH), tetrahydrofuran (THF) and *N*, *N*-dimethyl formamide (DMF) were all purchased from Sinopharm Chemical Regent Co., Ltd. Poly(vinyl butyral) (M_W:170,000–250,000) and ammonium persulfate (APS) were supplied by Aladdin Chemical Reagent Co. Ltd. Poly(styrene sulfonic acid) (PSSA, Mw: 75,000, 30 wt% water solution) was obtained from Alfa Aesar. All the chemicals were of analytical grade and used as received unless noted otherwise.

2.2. In situ preparation of Fe_2O_3/PANI nanocomposite gas sensor

Fe_2O_3 nanosheets were in-situ grown on the substrates (glass or interdigitated gold electrodes) by the hydrothermal treatment of the electrospun nanofibers containing $FeCl_3$ and PVB. In a generic procedure, 0.21 g of PVB was dissolved with 4 mL of ethanol by vigorous stirring to get the solution A. Meanwhile, 0.28 g of $FeCl_3$ was dissolved in 3 mL of DMF to obtain the solution B. The mixture of solutions A and B was used as the precursor solution for ES and loaded into a plastic syringe with a pinhead whose internal diameter was 0.9 mm. The pinhead was connected to a high voltage supply (DW-P303-1ACF0, Tianjin Dongwen High Voltage Power Supply Plant). The operating voltage applied for ES was ~9 kV, and the flow rate of the solution was set at 0.3 mL/h by a syringe pump (WZ-50C6, Smith Medical Instrument (Zhejiang) Co. Ltd.). The time for the collection of the electrospun nanofibers was 3 min.

An aluminum foil was grounded and situated about 15 cm from the tip of the pinhead. The electrospun nanofibers were deposited onto glass or interdigitated gold electrodes placed above the aluminum foil and dried in air. The gold electrodes (size: 6 mm×5 mm×0.5 mm) possessed a ceramic substrate, where an interdigitated array of gold tracks had been previously evaporated and photolithographically defined (both width and gaps of the gold tracks are 40 μm).

The glass or electrodes covered with the electrospun nanofibers were then transferred into a Teflon-lined stainless-steel autoclave containing deionized water, and kept at 135 °C for 8 h. After cooling to room temperature naturally, the resulting substrates with in-situ grown Fe_2O_3nanosheets were taken out and dried in air.

Water-dispersible PANI was obtained by chemical oxidation polymerization with PSSA as the dopant ([PSSA]: 0.068 mol L^{-1}; [APS]: 0.06 mol L^{-1}; molar ratio of aniline to structural unit of PSSA: 1/1) as described in the reference [23]. The electrodes with in-situ grown Fe_2O_3 nanosheets were dipped into the aqueous solution of PANI using an automatic dip-coating machine, followed by drying in air to give gas sensors based on Fe_2O_3/PANI nanocomposites. For comparison, gas sensors based on PANI or Fe_2O_3 alone were prepared on the blank gold electrodes.

2.3. Characterizations

Morphology of the samples was investigated using a field-emission scanning electron microscope (FE-SEM, s-4800, Hitachi, accelerating voltage of 3 kV). Lattice spacing and fast Fourier transform (FFT) images and Energy Dispersive X-ray Spectrum (EDX) were obtained with a high resolution transmission electron microscope (HRTEM, JEM-2100F, JEOL, accelerating voltage of 200 kV). X-ray powder diffraction (XRD) patterns were recorded on a PAN analytical X'Pert PRO using CuKα (λ = 0.15406 nm) radiation with a 2θ scanning range of 20–80°. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Vector 22 infrared spectrometer (KBr pellets). Current-voltage (I–V) characteristics were determined using a CHI660D electrochemical workstation (Chenhua instrument Co. Ltd., Shanghai).

Gas sensing properties of the Fe_2O_3/PANI nanocomposites were evaluated by measuring their real-time electrical responses to NH_3 at room temperature (~20 °C) with an Agilent 34972A LXI Data Acquisition/Switch Unit (Agilent technologies Co. Ltd). Different concentrations (0.5-10.7 ppm) of NH_3 were obtained by diluting standard NH_3 (NH_3 in air, Hangzhou New century Gas Co.) with dry air using computer-driven digital mass flow controllers (MFC CS200A, Beijing Sevenstar electronics Co., Ltd.). The total gas flow rate was maintained at 1 L/min, and the volume of the test chamber was 350 mL. The response magnitude *S* is defined as

$$S = \frac{R_{gas} - R_{air}}{R_{air}} \times 100\% \quad (1)$$

where R_{gas} and R_{air} are the resistance of Fe_2O_3/PANI nanocomposites in the target gas and air, respectively. The response time and recovery time of the nanocomposites are defined as the time to reach 90% of total resistance change. The organic vapors of different concentrations were obtained by injecting a calculated quantity of organic liquid into a testing chamber equipped with an electric fan.