Sensors and Actuators B 224 (2016) 449–457

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Highly sensitive NH_3 gas sensors based on novel polypyrrole-coated SnO_2 nanosheet nanocomposites

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ARTICLE INFO

Article history:
Received 2 July 2015
Received in revised form
28 September 2015
Accepted 23 October 2015
Available online 25 October 2015

Keywords:
Nanocomposite
NH_3 sensor
Tin oxide
Polypyrrole
Electrospinning
Hydrothermal synthesis

ABSTRACT

Nanocomposites of SnO_2 nanosheets and polypyrrole (PPy) were facilely prepared and their gas sensing properties towards low concentration of NH_3 have been investigated at room temperature. Vertically aligned SnO_2 nanosheets were in situ grown on the substrates via hydrothermal treatment of electrospun nanofibers containing $SnCl_2$ precursors at a low temperature (135 °C), and coated with PPy by vapor phase polymerization of pyrrole. The SnO_2 nanosheets and the nanocomposites were characterized by X-ray diffraction patterns, Fourier transform infrared spectroscopy, field emission scanning electron microscopy and high resolution transmission microscopy. The nanocomposite sensors exhibited much higher response magnitude towards NH_3 than the sensors based on PPy alone. The effect of the type of doping acids and polymerization time of pyrrole on the sensing properties of the nanocomposites was examined. The nanocomposite sensors revealed sensitive (sensitivity of ~6.2%/ppm in the range of 1–10.7 ppm of NH_3, detection limit of ~257 ppb), selective and repeatable response to NH_3, and the sensing mechanism has been explored. This work could provide references for the facile preparation of advanced gas sensors based on in situ grown nanostructured metal-oxide semiconductors and their composites.

1. Introduction

In recent years, gas sensors have seen fast development worldwide due to their wide applications in a large variety of fields such as environmental monitoring and protection, modern industrial and agricultural production, national defense, anti-terrorism and even disease diagnosis [1–7]. Among the huge number of gas sensing materials investigated, SnO_2, which is a typical metal-oxide semiconductor, has received much attention owing to its fascinating gas sensing properties including highly sensitive and fast detection of a broad spectrum of species, such as H_2S, H_2, C_2H_5OH, CO, NH_3, volatile organic compounds, etc. [8–13].

Despite the great success of SnO_2 based gas sensors in both scientific research and practical applications, they generally have to work at high temperatures, which bring about the problems such as high power consumption and reduced working life. Additionally, their sensitivity and selectivity need further improvement. There have been reports on decreasing the working temperature and even realizing room temperature sensing of SnO_2 based gas sensors by preparing nanocomposites of SnO_2 (or doping SnO_2) with inorganic materials or metals, such as carbon nanotubes, reduced graphene oxide, In_2O_3, Te, Cu, Pd, Pt, SiC, CuO [14–25]. Moreover, greater efforts have been devoted to the nanocomposites of SnO_2 with conducting polymers, including polyaniline (PANI) and polypyrrole (PPy), since the nanocomposites are easy to prepare and could show much improved gas sensing characteristics than the constituent components at room temperature [26–37].

Electrospinning (ES) is a versatile method for the preparation of one-dimensional (1D) nanomaterials such as polymers, inorganic materials, or the composites. The preparation of nanostructured SnO_2 by ES generally involves high temperature calcination of electrospun nanofibers containing the precursor of tin salt for the removal of the polymer template and the conversion of the precursor to SnO_2. Hydrothermal treatment is also frequently employed for the preparation of nanostructured SnO_2. However, high temperature annealing is often a necessity. Moreover, the sensors based on nanocomposites of SnO_2 with conducting polymers are generally prepared by depositing nanostructured SnO_2 or the nanocomposite dispersions onto the substrates by dropping, dip coating or screen printing [28,38–40]. The uniform dispersion of the

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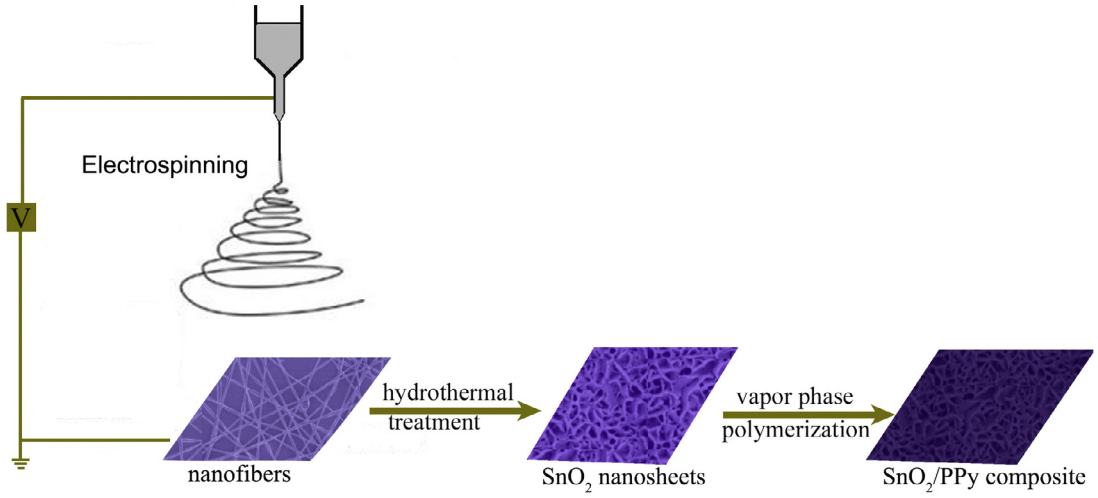
http://dx.doi.org/10.1016/j.snb.2015.10.078
0925-4005/



Scheme 1. The preparation procedure of SnO_2/PPy nanocomposite.

nanomaterials could be a problem. Furthermore, good adhesion between the sensing material and the underlying substrate, which greatly affects the contact resistance and the sensing behaviors [41], is not guaranteed.

Herein we report a novel method for in situ growth of SnO_2 nanosheets on the substrate by hydrothermal treatment of electrospun nanofibers of poly(vinyl butyral) (PVB) containing $SnCl_2$ precursors at a low temperature (135 °C), and subsequent coverage of PPy layer on the nanosheets by vapor phase polymerization to fabricate gas sensors based on nanocomposites of SnO_2/PPy. The synthetic route is outlined in Scheme 1. Apparently, the method circumvents high temperature annealing or calcination which is frequently required for the synthesis of nanostructured SnO_2. Moreover, the hydrothermal treatment is carried out at a low temperature in the absence of any additives but water, which is an environmentally friendly process. The resulting SnO_2 nanosheets are in situ grown on the substrates, avoiding the dispersion of the nanomaterials in the solvents and ensuring good adhesions between the sensing materials and underlying substrates. Gas sensors based on the nanocomposite are featured with high response magnitude, good sensing repeatability and excellent selectivity to low concentration of NH_3 (1–10.7 ppm) at room temperature. Both the nature of dopants and polymerization time of pyrrole could significantly affect the sensing properties of the nanocomposite. It is proposed that much improved sensing properties of the nanocomposite as compared to the separate component is related to the nanostructure of the sensing materials, and more importantly, the p/n junction established between p-type PPy and n-type SnO_2.

2. Experimental

2.1. Materials

Poly(vinyl butyral) (Mw: 170,000–250,000) was supplied by Aladdin Chemical Reagent Co. Ethanol, ether, hexane, acetone, methanol, tetrahydrofuran (THF), *N*,*N*-dimethyl formamide (DMF), hydrochloric acid (HCl), (±)-10-camphorsulfonic acid (CSA), *p*-toulenesulfonic acid (TSA), and $SnCl_2{\cdot}2H_2O$ were all purchased from Sinopharm Chemical Regent Co., Ltd. Pyrrole was obtained from Taizhou Qingquan Chemical Co., Ltd., and distilled under reduced pressure prior to use. Poly(styrene sulfonic acid) (PSSA, Mw: 75,000, 30 wt% water solution) was supplied by Alfa Aesar. Ammonium persulfate (APS) was purchased from Shantou Xilong Chem. Co. All the chemicals were of analytical grade and used as received unless noted otherwise.

2.2. In situ growth of SnO_2 nanosheets and SnO_2/PPy nanocomposites on the substrate

SnO_2 nanosheets were in situ grown on the substrate via hydrothermal treatment of electrospun nanofibers composed of PVB and $SnCl_2$. In a typical procedure [36], 0.6 g of $SnCl_2{\cdot}2H_2O$ was dissolved in 4 mL of ethanol by vigorous magnetic stirring for 30 min. Subsequently, 0.28 g of PVB and 3 mL of DMF were added to the solution, followed by vigorous magnetic stirring for 12 h. The resulting mixture was loaded into a plastic syringe with a pinhead with an internal diameter of 0.7 mm. The pinhead was connected to a high voltage supply (DW-P303-1ACF0, Tianjin Dongwen High Voltage Power Supply Plant). An operating voltage of ~8 kV was applied for electrospinning, and the flow rate of the solution was set at 0.2 mL h^{-1} by a syringe pump (WZ-50C6, Smith Medical Instrument (Zhejiang) Co. Ltd.), and 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 electrode (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 were 40 μm).

The glass or electrodes covered with the electrospun nanofibers were then transferred into a Teflon-lined stainless-steel autoclave containing distilled water, and kept at 135 °C for 8 h. After cooling to room temperature naturally, the resulting substrates with in situ grown SnO_2 nanosheets were taken out and dried in air.

The SnO_2/PPy nanocomposite was prepared by vapor phase polymerization of pyrrole on the substrate bearing SnO_2 nanosheets. The concentration of both the dopants (HCl, TSA, CSA and PSSA) and the oxidizing agent (APS) was 0.02 M, and the injected pyrrole was 0.5 mL. In a generic procedure [37], the interdigitated gold electrode with SnO_2 nanosheets was immersed into the aqueous solution of the mixture of PSSA (0.02 M) and APS (0.02 M) with a home-made automatic dip-coating machine, followed by drying in air. Afterwards, the electrode was put into a vacuum desiccator and kept in reduced pressure. 0.5 mL of pyrrole was then injected, and vapor phase polymerization was carried out at room temperature (~20 °C) for 60 min, giving a gas sensor based