Materials Research Bulletin 107 (2018) 46–53

Contents lists available at ScienceDirect

Materials Research Bulletin

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

In-situ packaging ultra-uniform 3D hematite nanotubes by polyaniline and their improved gas sensing properties

Liwei Wang[a,b,c], Hao Fu[a,b,c], Hongjie Liu[d], Kefu Yu[a,b,c,**], Yinghui Wang[a,b,c,**], Jianmin Ma[d,*]

[a] School of Marine Sciences, Guangxi University, Nanning, 530004, China
[b] Coral Reef Research Center of China, Guangxi University, Nanning, 530004, China
[c] Guangxi Laboratory on the Study of Coral Reefs in the South China Sea, Nanning, 530003, China
[d] School of Physics and Electronics, Hunan University, Changsha 410082, China

ARTICLE INFO

Keywords:
Hematite nanotube
Polyaniline
Nanocomposite
Heterojunction
Gas sensing

ABSTRACT

This paper reports the PANI (polyaniline)-packaged three-dimensional (3D) α-Fe_2O_3 nanotubes P/N heterojunction, which was constructed successfully though a facile hydrothermal reaction without adding any surfactant followed by *in-situ* chemical polymerization in the liquid phase. The structure and morphology of the products were characterized by means of FESEM, XRD, TEM & HRTEM, TGA and FT-IR. Gas sensing test results found that, the PANI/α-Fe_2O_3 nanocomposite sensor exhibited obviously higher response, lower working temperature (180 °C), fast response and recovery speeds, good selectivity and excellent stability to acetone gas, indicating its promising application for high-performance acetone sensors. The enhanced gas sensing performances can be attributed to the factors like ultra-uniform 3D nanotube-like structure for α-Fe_2O_3, the noticeable advantages of PANI, as well as the construction of heterojunction barrier at their interface. The as-prepared PANI/α-Fe_2O_3 nanocomposite may be also applied in other areas like photocatalysis, water purification, ion batteries, optical devices, and so on.

1. Introduction

Exploiting high-performance gas sensors has been attracting researchers' attentions, as the rapid progress of modern industry and serious environment pollutants make it urgent to develop portable electronic devices for the detection of trace concentration of pollution molecules in environment [1–4]. The traditional sensing materials are mainly based on metal oxide semiconductors (MOSs), including ZnO [1], α-Fe_2O_3 [2,3], SnO_2 [3], CuO [5], and so on. But some inevitable drawbacks for the application of pure MOS, such as high working temperature and poor selectivity, have caused serious power consumption and safety concern in some places, then limitied its practical usage [6,7].

Combining the inorganic MOS nanomaterials with conducting polymers to form polymer/MOS nanocomposite can provide an effective way to lower the working temperature [8]. Besides, the synergetic effect between each constituent has been reported to much improve the gas sensing performances. Meanwhile, designing nanostructure with multiple dimensions and various morphologies can increase the surface/volume ratio, thus providing more active reaction sites to increase sensitivity and response speeds [9].

Thereinto, hematite (α-Fe_2O_3, Eg = 2.2 eV, n type), an environmentally friendly semiconductor, has been used as a good gas sensitive material for detecting toxic and explosive gases in both home and industrial areas [10–12], such as CO, formaldehyde, NO_2, acetone, LPG (liquid petroleum gases) at higher temperatures. Whereas, polyaniline (PANI), one of the conducting polymers, has been found to be sensitive to some of the VOC vapors even at room temperature but still kept its good environmental stability [13–16]. Thus, various gas sensors have been widely studied based on the nanocomposites of PANI/α-Fe_2O_3 nanomaterials. For example, Patil et al. applied the mixture of α-Fe_2O_3 nanoparticles with polymerized PANI as gas sensors [2,17,18], and the result was that the PANI/α-Fe_2O_3 nanocomposite showed a relative resistance change of 50%–100 ppm of NH_3, as well as a moderate selectivity under room temperature. While Mishira et al. employed the method of solution polymerization of aniline to prepare the nanocomposite of PANI/α-Fe_2O_3 [19]. And it was amazing that even at room temperature, the pure PANI was nearly insensitive to LPG, but the composite-based sensor exhibited a relative resistance change of 0.5–50 ppm of LPG. Though great progresses have made for the studies

* Corresponding author.
** Corresponding authors at: School of Marine Sciences, Guangxi University, Nanning, 530004, China.
E-mail addresses: kefuyu@gxu.edu.cn (K. Yu), wyh@gxu.edu.cn (Y. Wang), nanoelechem@hnu.edu.cn (J. Ma).

https://doi.org/10.1016/j.materresbull.2018.06.034
Received 2 April 2018; Received in revised form 29 May 2018; Accepted 27 June 2018
Available online 09 July 2018

of conducting polymer PANI/α-Fe_2O_3 composite gas sensor, it's still a huge task to dramatically improve their sensing performances (sensitivity, selectivity, response/recovery speeds, etc.) by carefully tuning the nanostructure and morphology of the composites [20,21].

In this work, by controlling the morphology and designing heterojunction [2,3,22], we developed a facile two-step solution route to prepare PANI/α-Fe_2O_3 nanocomposites. Firstly, ultra-uniform α-Fe_2O_3 nanotubes were synthesized by an anion-assisted hydrothermal route, which were then packaged by PANI through in-situ chemical oxidative polymerization method to form composites. Afterwards, the products were characterized by XRD, FESEM, TEM and HRTEM, TGA and FT-IR. The sensing properties of the composites to several typical gases at lower temperature were studied, and their sensing mechanism was also discussed.

2. Experimental section

2.1. Hydrothermal synthesis of hematite nanotubes

All chemicals were analytical-grade reagents and purchased from Sigma-Aldrich (Milwaukee, Wisconsin), and used as received without further purification. Deionized water was used throughout the experiments.

The hydrothermal synthesis of hematite nanotubes was described elsewhere but with some modifications [23,24]. Typically, 0.370 *g* of $FeCl_3$•$6H_2O$, 0.011 *g* of NaH_2PO_4 •$2H_2O$, and 0.015 *g* of Na_2SO_4 were added into 80 mL of deionized water, and mixed together to form aqueous solution. After vigorous stirring for 10 min, the above solution was transferred into a 100 mL of Teflon-lined stainless steel autoclave for hydrothermal reaction at 180 °C for 36 h. After the autoclave was cooled to room temperature, the precipitate was separated by centrifugation, washed with distilled water and anhydrous ethanol for five times, and dried overnight at 120 °C to obtain hematite nanotubes.

2.2. In-situ preparation of PANI/α-Fe_2O_3 composites

The PANI/α-Fe_2O_3 composites were obtained by chemical polymerization route [2]. 0.050 g of above hematite was dispersed into the conical flask with 20 mL of chloroform under sonication, then 0.100 g of aniline monomer was dissolved to the flask and stirred for several minutes. Afterwards, 0.440 g of $FeCl_3$ (n_{FeCl3} /$n_{aniline}$ = 2.6:1) was added to the mixture as oxidant. The color of the mixture gradually changed from brown to deep black, which indicated the successful formation of polyaniline shell packaging outside hematite nanotubes. After stirring for 2 h, the dispersion was filtered, and washed with anhydrous ethanol and water for six times to remove the residual iron chloride or chloroform solvent, finally after vacuum drying at 40 °C for 12 h to get PANI/α-Fe_2O_3 composites.

2.3. Characterizations

The phase, morphology and composition of the products were characterized by means of powder XRD analysis (Rigaku Ultima IV, Cu Kα radiation, λ = 1.5418 Å), FESEM (Hitachi SU5000) with EDS (Quantax, Bruker), TEM and HRTEM (Tecnai G2 20, FEI), TGA (Setaram Labsys Evo, France) and FT-IR (Autosorb-iQ, in the range of 400–4000 cm^{-1}, Quantachrome, USA).

2.4. Fabricating sensor and gas sensing test

The detailed processes of fabricating sensor and sensing test, also the working principle have been described in our previous reports [25,26], and some pictures of actual setup can be seen in Fig. 1. Briefly, a proper amount of the hematite and composite samples were separately mixed with several drops of distilled water to form slurry, then coated onto the alumina tube (diameter of 1 mm and lengthof 4 mm with one Au electrode and two Pt wires on each end, and a Ni–Cr alloy filament put through it as a heater by tuning the heating voltage, V_h), as can be seen in Fig. 1a, which were fixed on a special pedestal with six probes (Fig. 1b) to get the sensor unit (Fig. 1c) and put on the circuit board (Fig. 1d). A load resistance (R_L) was connected in series to the sensor.

Gas sensing test was carried out on the HW-30 A Gas Sensing Measurement System (Weisheng Electronics Co., Ltd., Henan, China) with a relative humidity (RH) of ~ 40%. The ambient air was used as the diluting and reference gas, while the operating temperatures were from 140 to 240 °C. The sensor was aged in the gas chamber at 200 °C for 24 h before testing, and different from the flow valve unit, tested gases were statically introduced into the gas chamber by injecting a calculated volume of liquid with a microsyringe onto the heating board. The gas concentrations were calculated according to the total volumes (18 L) of gas chamber (Fig. 1e). The sensor signal voltage (V_{out}) was collected by a computer at a test circuit voltage of 5 V (V_c) (Fig. 1f). The sensor was exposed to air again by opening the chamber when the test was completed.

The sensitivity (also called response) for the reducing gas is defined as R_a/R_g, where R_a is the sensor resistance in air, and R_g is the sensor resistance in a target gas, respectively [25]. The response time of the sensor was measured as the time taken for the sensor output to reach 90% of its saturation after applying the gas in a step function. The whole preparation and gas sensing test processes were illustrated in Fig. 2.

3. Results and discussion

3.1. Characterization

The morphological change is accompanied by packaging PANI outside the pure hematite sample. Fig. 3 (a–d) present the FESEM images of as-prepared α-Fe_2O_3 nanotubes and PANI/α-Fe_2O_3 nanocomposites. Ultra-uniform and tube-like α-Fe_2O_3 nanomaterial with a diameter of ~150 nm, and thickness of only ~20 nm can be seen in Fig. 3a and b, and the smooth surfaces and hollow structures of the nanotubes can be observed from the magnified image in Fig. 3b. This indicates an effective route in producing non-aggregated nanotubes even in the absence of structure-aiding agent. Fig. 3c and d shows the nanospheres of PANI/α-Fe_2O_3 nanocomposites, where PANI is uniformly dispersed inside and outside the walls of α-Fe_2O_3 to form cocoon-like heterostructures. Especially in Fig. 3d, the surface of the nanocomposite appears to be rough due to the chemical polymerization of PANI on the surface of α-Fe_2O_3 support. Apparently, the PANI layers were very thin since there is no obvious change of the thickness of nanotubes or nanococoons.

Fig. 4 (a, b) shows the XRD patterns of α-Fe_2O_3, and PANI/α-Fe_2O_3 nanocomposite. Both the dominant diffraction peaks in Fig. 4a and b can be ascribed to typical hexagonal α-Fe_2O_3 (JCPDS 33-0664) [27]. Besides, in Fig. 4b, the diffraction peak of 2θ = 25.7° can be indexed as (1 1 0) plane of PANI [28], and the existence of α-Fe_2O_3 in such nanocomposite proves the existence of PANI/α-Fe_2O_3 heterojunction or the distribution of PANI along the α-Fe_2O_3 matrix. Furthermore, the line in Fig. 4b is rougher than in Fig. 4a, which indicates that PANI is mainly amorphous and successfully coated on the α-Fe_2O_3 nanotube.

In order to further confirm the structure of the nanocomposites, several other analytical techniques were employed. TEM and HRTEM analyses of the composites were conducted and presented in Fig. 5(a, b). The TEM image in Fig. 5a shows clearly the tube-like structures packaged with PANI, where the inner walls of the α-Fe_2O_3 tubes are still maintained well after a series of treatments, and the thickness of PANI layers are just ~5 nm. Besides, there are also some globular PANI aggregates separated from the PANI/α-Fe_2O_3 nanocomposites, since PANI is more easy to assemble its own phase. However, the following gas sensing test has proved that single PANI component exhibited