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Ethanol gas sensing properties of lead sulfide quantum dots-decorated zinc oxide nanorods prepared by hydrothermal process combining with successive ionic-layer adsorption and reaction method

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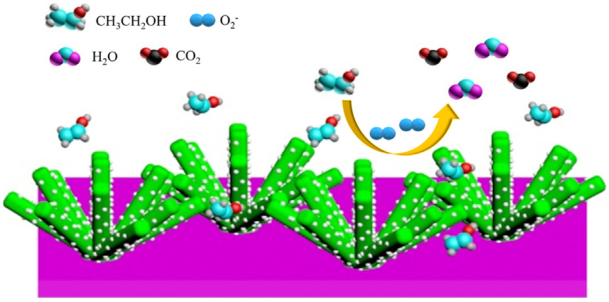
GRAPHICAL ABSTRACT



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ABSTRACT

An ethanol gas sensor based on lead sulfide (PbS) quantum dots (QDs)-decorated zinc oxide (ZnO) nanorods were demonstrated in this article. The PbS QDs/ZnO film was fabricated via tuning PbS QDs deposition onto the hydrothermally synthesized ZnO nanorods via successive ionic-layer adsorption and reaction (SILAR) method. The PbS QDs/ZnO nanorods nanocomposite was characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscope and transmission electron microscope. The ethanol gas sensing properties of the PbS QDs/ZnO nanorods-based sensor with different SILAR layers of PbS QDs was investigated at room temperature. The experimental results showed that high response, short response and recovery time, and good repeatability were yielded for the PbS QDs/ZnO nanorods-based sensor, and the optimal SILAR cycle of PbS QDs was discovered to achieve the best ethanol gas sensing performance. The possible sensing mechanism of the PbS QDs/ZnO nanorods-based sensor was attributed to the porous flower-like morphologies, heterojunction nanostructure and high ratio of accessible sites for gas diffusion.

1. Introduction

Ethanol gas sensors play a very important role in many fields, such as ethanol production, fuel processing, industrial monitoring, and drunk driving [1,2]. To this day, metal-oxide semiconductor (i.e., ZnO [3], Fe_2O_3 [4], SnO_2 [5]), conductive polymer [6] and carbon-based nanomaterials [7], have been used in seeking high-performance gas sensors with enhanced sensing properties [8]. As a n-type metal oxide semiconductor, ZnO has been investigated among these nanomaterials due to its unique chemical and stable physical properties [9,10]. Jia et al. synthesized ZnO dandelion-like spheres via solvothermal reaction method for acetone gas sensing [11]. Liu et al. used reduced graphene oxide-ZnO hybrids as sensing

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materials to detect NO_2 gas [12]. Zhang et al. fabricated an ethanol sensor based on ZnO nanorods/carbon nanotube film, and exhibited higher response at room temperature than that of ZnO [13]. Kim et al. found that Ni-doped ZnO nanorods exhibited better gas sensing properties than undoped ZnO nanorods [14]. Wongrat et al. introduced the gold nanoparticles into ZnO nanostructures (ZnO:AuNPs) by using a sputtering technique, and get wonderful ethanol gas sensing properties under UV illumination [15]. Wang et al. synthesized CdO-ZnO gas sensor for acetone gas sensing detection [16]. However, the pure ZnO gas sensors have some shortcomings, such as low long response and recovery times, low sensitivity, high operation temperature [17,18]. The modification of ZnO with other nanomaterials such as metal, metal oxide and carbon nanotube is an effective pathway to enhance its gas sensing properties.

Recently, quantum dots (QDs) have attracted much more attentions in many fields, including lighter emitters [19] solar cells [20,21] and light detectors [22]. The state of the art of the gas sensors indicated that quantum dots may be good alternative nanomaterials for high-performance gas sensing [23–25]. Liu et al. fabricated a flexible NO_2 gas sensor based on lead sulfide (PbS) colloidal quantum dots on a paper substrate, and highly sensitive, fully recoverable, and rapid-response was demonstrated at room temperature [24]. Liu et al. prepared NH_3 gas sensors based on PbS QDs/TiO_2 nanotubes arrays, indicating a good response, low detection limit and quite good selectivity towards NH_3 gas at room temperature [25]. The combination of PbS QDs and ZnO may yield tunable band gap at their interface, ultrafast electron transfer and quantum size effect, which may facilitate it to work at room temperature [24].

In this paper, an ethanol gas based on PbS QDs-decorated ZnO nanorods was reported. The PbS QDs/ZnO nanocomposite was prepared by hydrothermal process combining with successive ionic layer adsorption and reaction (SILAR) method. The PbS QDs/ZnO nanocomposite was characterized by means of XRD, XPS, SEM and TEM. The ethanol gas sensing properties of the PbS QDs/ZnO sensor was investigated at room temperature, and good response, selectivity, repeatability and short response/recovery times of the sensor were demonstrated. The sensing mechanism of the PbS QDs/ZnO sensor was discovered.

2. Experimental

2.1. Materials

The reagents of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, ≥99%), sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$, ≥96%), lead nitrate ($Pb(NO_3)_2$, ≥99%) and sodium hydroxide (NaOH, ≥98%) were offered by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All the received chemicals were used as received without any further purification.

2.2. Sensor fabrication

The fabrication of PbS QDs/ZnO nanorods-based sensor was illustrated in Fig. 1(a). The ZnO nanorods were fabricated by a cost-effective hydrothermal synthesis method. 2.08 g $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved into 140 mL deionized (DI) water (conductivity: 0.056 μS/cm) and stirred for 30 min. And then, 3.2 g NaOH was dissolved into the resulting solution, followed by stirring for 1 h and ultrasonication for 15 min. The obtained solution was transferred into a Teflon-lined autoclave and treated at 120 °C for 12 h. The final product of ZnO nanorods suspension was washed with DI water several times [26]. The related chemical reactions for the ZnO preparation are described as $Zn^{2+} + OH^- \rightarrow Zn(OH)_2$ and $Zn(OH)_2 \rightarrow ZnO + H_2O$. The ZnO nanorods were drop-casted on the printed circuit board (PCB) substrate with interdigitated electrodes (IDEs), which was microfabricated via photolithographic technology as reported in our previous work [27]. The device has an outline dimension of 8 × 8 mm, Cu/Ni electrode layer was deposited on the substrate, and the IDE width and gap both is 100 μm. PbS QDs were decorated on the ZnO nanorods through SILAR method [28]. 0.01 M $Pb(NO_3)_2$ and 0.01 M $Na_2S{\cdot}9H_2O$ were used as cationic and anionic precursor, respectively. The sensor was alternatively immersed into the $Pb(NO_3)_2$ solution and Na_2S solution for 1 min, respectively. After each step of immersing, the sensor was washed with DI water to remove the excess precursor solution. The above process was repeated with different cycles to yield ZnO/$(PbS\ QDs)_n$ nanocomposite, here n = 3, 5, 7, is the sensitized cycles of the sensor. Pure ZnO nanorods sensor without PbS QDs decoration was prepared by drop-casting method as reference for making comparison.

2.3. Instrument and experimental setup

The surface microscopes of ZnO, PbS QDs/ZnO nanocomposite were measured with field emission scanning electron microscopy (FESEM, Hitachi S-4800). The XRD spectrum for ZnO nanorods and PbS QDs/ZnO nanocomposite were characterized with an X-ray diffractometer (Rigaku D/Max 2500 PC, Japan) using Cu Kα (λ = 1.5418 Å) radiation. Transmission electron microscopy (TEM) measurement of as-prepared samples was performed on a FEI Tecnai G2 F20 electron microscopy with an accelerating voltage of 200 kV, and a carbon film copper net served as support for TEM studies. X-ray photoelectron spectroscopy (XPS) analysis on the samples was performed by a Thermo Scientific K-Alpha XPS spectrometer.

The ethanol-sensing experimental setup is shown in Fig. 1(b). The gas sensing measurement was performed by exposing the PbS QDs/ZnO-based sensors to an enclosed chamber, in which the ethanol gas concentration is varied from 5 ppm to 100 ppm by injecting with a syringe. The resistance response of the PbS QDs/ZnO-based sensors was measured by using a data logger coupled with a computer. The response of the sensor is defined as $S = R_a/R_g$, where R_a and R_g are the resistance of the sensor in the air and the ethanol gas, respectively.

3. Results and discussion

3.1. Characterization results

The SEM images for the samples are shown in Fig. 2. The morphology of ZnO nanorods with smooth surface is shown in Fig. 2 (a). The low-magnification and high-magnification SEM images of PbS QDs/ZnO nanorods are shown in Fig. 2(b) and (c), respectively. The PbS QDs are clearly observed on the ZnO nanorods surface. The PbS QDs-decorated ZnO nanorods form a porous flower-like nanostructure. Fig. 2(d) exhibits the XRD patterns of PbS QDs/ZnO nanorods with different SILAR layers of PbS QDs. The XRD pattern of ZnO nanorods shows major peaks at 31.97°, 34.58°, 36.47°, 47.72°, and 56.81°, which are attributed to the planes (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) of ZnO nanocrystals (JCPDS89-1397) [27]. In the XRD patterns of PbS QDs/ZnO nanorods with PbS QDs coated, four extra diffraction peaks at 26.03°, 30.26°, 43.31°, 53.66° corresponded to the (1 1 1), (2 0 0), (2 2 0) and (2 2 2) planes of PbS QDs (JCPDS5-592), respectively [25].

The TEM images of PbS QDs/ZnO nanorods are shown in Fig. 3. The nano-sized PbS QDs attached on the ZnO nanorods are obviously observed in Fig. 3(a) and (b). The high-resolution TEM images of PbS QDs/ZnO nanorods are shown in Fig. 3(c) and (d). The lattice