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Pt-decorated zinc oxide nanorod arrays with graphitic carbon nitride nanosheets for highly efficient dual-functional gas sensing

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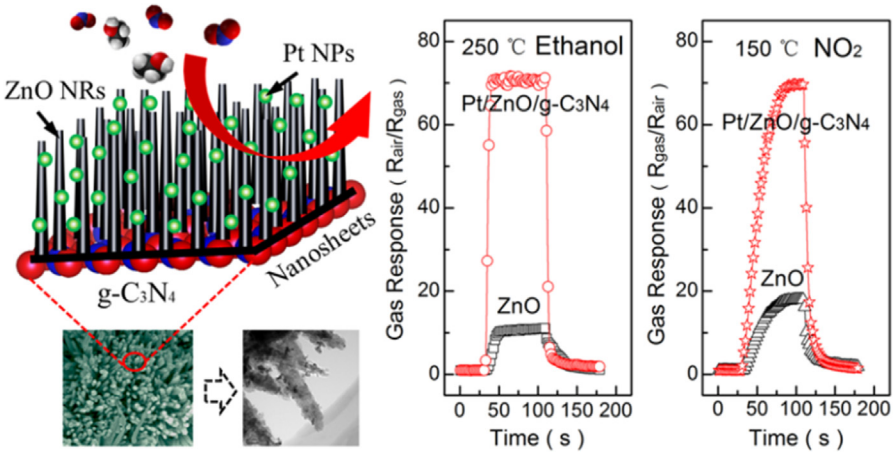
HIGHLIGHTS

- Pt/ZnO/g-C_3N_4 nanostructures were designed and prepared as a highly efficient gas sensing material.
- Pt/ZnO/g-C_3N_4 nanostructures could be applied to a dual-functional gas sensor for ethanol and NO_2.
- The gas sensing mechanism was demonstrated via the synergistic effect and the electronic structure of the materials.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, well-aligned ZnO nanorods were grown on the substrate of exfoliated g-C_3N_4 nanosheets via a microwave-assisted hydrothermal synthesis, and then Pt/ZnO/g-C_3N_4 nanostructures were obtained after the deposition of Pt nanoparticles. The growth of vertically ordered ZnO nanorods was occurred on g-C_3N_4 nanosheets through the bonding interaction between Zn and N atoms, which was confirmed by XPS, FT-IR data and molecular orbital theory. The Pt/ZnO/g-C_3N_4 nanostructures sensor exhibited the remarkable sensitivity, selectivity, and fast response/recovery time for air pollutants of ethanol and NO_2. The application of Pt/ZnO/g-C_3N_4 nanostructures could be used as a dual-functional gas sensor through the controlled working temperature. Besides, the Pt/ZnO/g-C_3N_4 nanostructures sensor could be applied to the repeating detection of ethanol and NO_2 in the natural environment. The synergistic effect and improved the separation of electron-hole pairs in Pt/ZnO/g-C_3N_4 nanostructures had been verified for the gas sensing mechanism. Additionally, Pt/ZnO/g-C_3N_4 nanostructures revealed the excellent charge carriers transport properties in electrochemical impedance spectroscopy (EIS), such as the longer electron lifetime (τ_n), higher electron diffusion coefficient (D_n) and bigger effective diffusion length (L_n), which also played an important role for Pt/ZnO/g-C_3N_4 nanostructures with striking gas sensing activities.

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1. Introduction

Semiconducting nanostructures, including nanoparticles, nanorods and nanosheets etc., have attracted tremendous attention due to their unique electrical, optical, magnetic and catalytic properties [1–5] and potential applications in the areas of energy storage, catalysts and sensors [6–8]. In particular, metal oxide gas sensors (MOGS), as fast, simple and portable applications, are widely used in air quality monitoring and detection of toxic, flammable, explosive gases [9]. However, the major challenge for MOGS is further the improvement of gas sensing properties. Nowadays, nano-materials are employed to improve their sensitivity, selectivity and stability by multitudinous synthetic strategies [10–14]. Although a great stride has been achieved in the preparation of nanostructures, constructed heterostructures with different materials are still quite attractive [15–17].

Two-dimensional (2D) nanosheets of graphitic carbon nitride (g-C_3N_4) have been fabricated via the exfoliation of bulk layered counterparts and exhibited remarkable electronic and optical properties in recent investigations [18–20]. The g-C_3N_4 nanosheets have already shown to be a promising metal-free catalyst for various other reactions [21–24], however, this 2D material for the detection or decomposition of hazardous gases is still in its infancy [25,26]. The g-C_3N_4 nanosheets not only can provide abundant grown sites for other semiconductors as a substrate, but also can increase transport of charges and reduce the recombination probability of charge carriers [27–29]. Thus, the g-C_3N_4 nanosheets should be a potential candidate for the gas sensing materials. Additionally, as a significant transition metal oxide, zinc oxide (ZnO) has attracted considerable attentions according to their abundant physical and chemical properties. It has been extensively applied in optoelectronic devices [30], solar cells [31] and gas sensors [32–34], which contribute to its advantages of high mobility of electrons, low cost and environmental friendliness. Meanwhile, ZnO not only can be easily synthesized at nanoscale, but also the morphology can be controlled [33]. It is believed that a highly oriented and ordered ZnO nanorods is beneficial for improving the gas sensing performance because of a high surface to volume ratio and average effect of assembled nanorods [35]. Noble metal such as Pt nanoparticles is effective in many catalyst systems [36–38], however, they tend to aggregation due to big surface energy and thus require a support to disperse and stabilize them. It is demonstrated that a binary or ternary heterostructure of metal nanoparticles and semiconductor with g-C_3N_4 has been successfully prepared for hydrogen production from water splitting and degradation of organic dyes under visible light irradiation [39–43]. Therefore, constructed Pt/ZnO/g-C_3N_4 nanostructures should be a feasible way to develop abilities of different materials. The synergistic effect of Pt/ZnO/g-C_3N_4 nanostructures can be effectively applied to gas sensing, and the stability of this material will be improved at the same time. Predictably, Pt/ZnO/g-C_3N_4 nanostructures should be a promising gas sensing material for the detection of harmful gases.

Herein, we designed and prepared Pt/ZnO/g-C_3N_4 nanostructures as a highly efficient gas sensing material. The well-aligned ZnO nanorods were grown on the substrate of exfoliated g-C_3N_4 nanosheets by a microwave-assisted hydrothermal synthesis in 140°C for 2 h. Subsequently, Pt nanoparticles were loaded on this material, and ultimately to obtain Pt/ZnO/g-C_3N_4 nanostructures. Compared with ZnO, the gas response of Pt/ZnO/g-C_3N_4 nanostructures for ethanol and NO_2 was increased above 7 and 4 times, respectively. The Pt/ZnO/g-C_3N_4 nanostructures sensor could be used as a dual-functional gas sensor through the adjustable working temperature. Constructed Pt/ZnO/g-C_3N_4 nanostructures had numerous merits for enhanced gas sensing properties, such as the synergistic effect, improved the separation of electron-hole pairs, and excellent charge carriers transport properties, which provided reliable evidences for studying the gas sensing mechanism.

2. Experimental

2.1. Preparation of exfoliated g-C_3N_4 nanosheets and Pt/ZnO/g-C_3N_4 nanostructures

The powder of bulk g-C_3N_4 was synthesized according to the previous work in our group [44]. Then, the exfoliated g-C_3N_4 nanosheets were prepared by using thermal exfoliation of bulk g-C_3N_4 in a vacuum tube furnace. In a typical synthesis, 10 g of the g-C_3N_4 powder was placed in an open alumina crucible and heated at 500 °C for 8 h with a ramp rate of 5 °C min^{-1} in the vacuum tube furnace, and an oxygen gas flow of 30 sccm was used to ensure the exfoliation atmosphere. Consequently, the light yellow and fluffy powder of g-C_3N_4 nanosheets could be obtained after cooling naturally to room temperature.

For synthesis of the aligned ZnO nanorods on the exfoliated g-C_3N_4 nanosheets, 50 mg of g-C_3N_4 nanosheets was dispersed in 30 mL deionized water to form a light yellow solution under ultrasonic bath and then 0.1 M zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and 1 M sodium hydroxide (NaOH) were added to the above solution. After stirring for 30 min at room temperature, the solution was transferred into a 100 mL Teflon-lined autoclave and maintained at 140°C for 2 h in the microwave workstation. (MDS-10, Sineo Microwave, Shanghai, China). The obtained precipitate was separated by centrifuging and washed with deionized water and ethanol several times and then dried at 70°C for 8 h in an oven. For comparison, ZnO nanorods were prepared through the same procedure without the addition of g-C_3N_4 nanosheets.

Subsequently, 0.1 g of ZnO/g-C_3N_4 was dispersed in 150 mL deionized water to form a homogeneous solution and 1.2 mL H_2PtCl_6 solution (8 mM) was added under magnetic stirring. 20 mL of sodium borohydride in methanol with 2.5 mg mL^{-1} was added dropwise in the above solution, the entire solution was stirred at 60°C for 2 h under oil bath. The black product of Pt/ZnO/g-C_3N_4 nanostructures was collected by centrifugation and washed with deionized water and ethanol several times and then dried at 70°C for 8 h in an oven. Also, Pt/ZnO was prepared through the same procedure as that for Pt/ZnO/g-C_3N_4 by using ZnO instead of ZnO/g-C_3N_4.

2.2. Characterization methods

Morphology and microstructure of samples were observed by using field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM; Tecnai F30G, FEI, Hillsboro, OR, USA). The crystal phase of the as-synthesized material was analyzed by using powder X-ray diffraction (XRD; X'pert PRO MPD, Philips, Eindhoven, The Netherlands) with Cu Kα radiation (λ = 1.5406 Å) in the range of 10−70°. Surface chemical element analysis of Pt/ZnO/g-C_3N_4 nanostructures was carried out by using X-ray photoelectron spectroscopy (XPS; VG ESCALA-B220i-XL, Thermo Scientific, Surrey, UK) with an Al Kα (hν = 1486.6 eV) source at a residual gas pressure below 10^{-8} Pa. Fourier transform infrared (FT-IR) spectra were recorded on a FTIR spectrometer (TENSOR27, Bruker, Billerica, MA, USA) with a resolution of 1 cm^{-1}. Ultraviolet-visble diffuse reflectance spectra (UV-vis DRS; Cary 5000, Agilent, Santa Clara, CA, USA) were obtained with the integrating sphere attachment. Nitrogen adsorption-desorption was performed on a nitrogen adsorption apparatus at 77 K (V-Sorb 2800P, Gold APP Corp., Beijing, China), the sample was degassed at 120°C for 2 h before measurement. Electrochemical impedance spectroscopy