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Ag nanoparticles modified TiO_2 spherical heterostructures with enhanced gas-sensing performance

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ABSTRACT

Monodispersed TiO_2 spherical colloids with diameters of about 250 nm were prepared by a sol–gel method. Heterostructural Ag–TiO_2 spheres were manipulated by surface engineering, in which the Ag nanoparticles with an average size of 10 nm were uniformly distributed on the surface of the TiO_2 nanospheres by in situ reduction and growth. The gas-sensing properties of the TiO_2 nanospheres and heterostructural Ag–TiO_2 nanospheres to ethanol and acetone were measured at 350 °C. The results indicated that Ag nanoparticles greatly enhanced the response, stability and response characteristic of TiO_2 nanospheres to the tested gases. Response times of Ag–TiO_2 sensor to 30 ppm acetone and 50 ppm ethanol were <5 s.

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1. Introduction

It is necessary to monitor colorless organic vapour concentrations in the environment for health and the workplace for safety due to their toxicity and explosive possibility [1]. Nanometer-scaled TiO_2, an important multifunctional n-type semiconductor, has stimulated considerable research efforts in seeking morphology-dependent physical properties and applications in gas sensors, solar cells, photocatalysis, *etc.* [2–6]. Especially, as an organic vapour sensing material, TiO_2 is nontoxic, highly chemically stable and low costing in comparison with other common metal oxides such as SnO_2 and ZnO. In fact, a variety of TiO_2 nanostructures with different sizes and morphologies, including nanoparticles, nanotubes, nanobelts, and nanowires, have been examined for ethanol and acetone sensing and exhibited good sensing characteristics [7–10]. However, several drawbacks, such as low response, poor selectivity and stability, and long response and recovery times, limited previously studied TiO_2 materials in the practical application. Recently, Hayakawa et al. [11] reported the Pt dispersed-TiO_2 nanoparticles with an improved selectivity to trimethylamine and NH_3. Hu et al. [12] reported that heterostructural Ag–TiO_2 nanobelts exhibited high sensitivity and rapid response for ethanol vapour detection. These two results remind us that the deposition of noble metal nanoparticles onto the surface of oxide nanostructures can improve the response and selectivity, and reduce response time [13–16]. For exploiting gas sensors, it is desirable to develop high performance, gas-sensing materials; for example, morphologically different, TiO_2 heterostructures modified by noble metal nanoparticles.

The nanometer-scaled TiO_2 spherical colloids have currently been one of the most active areas of material research due to their high refractive indices, excellent catalytic activities and chemical stabilities, along with potential applications widely spreading from photonic crystals to photocatalysis [17,18]. In particular, noble metal nanoparticles are easily deposited onto the surface of TiO_2 nanospheres through the strong synergistic interactions, which further enhance the catalytic activities and photoelectronic properties of TiO_2 nanospheres due to modulation of the energy band structures and surface-to-volume ratios by surface engineering [19–21]. Because of its unique physical and chemical characteristics, the Ag–TiO_2 spherical heterostructure is a remarkable candidate for organic vapour detection. However, the application of the Ag–TiO_2 spherical heterostructures in sensors remains unexplored. Here, we successfully prepared the monodispersed TiO_2 spherical colloids by a sol–gel method and Ag–TiO_2 spherical heterostructures by surface engineering of in situ reduction and growth. The gas-sensing properties of these two materials to vapour phase ethanol and acetone were measured. The results indicated that modified Ag nanoparticles could greatly enhance the response, stability and response characteristic of TiO_2 nanospheres to the tested gases.

2. Experimental

2.1. Synthesis of TiO_2 nanospheres

The TiO_2 nanospheres were synthesized following the reported procedure [17] with modifications. Tetraethyl titanate (3.5 mL) was

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added to ethylene glycol (50 mL) and magnetically stirred for 10 h at room temperature. Then, the mixture was poured into a solution containing 170 mL acetone and 2.7 mL water with vigorously stirring for 1 h. The white precipitate was harvested by centrifugation, followed by washing with distilled water and ethanol five times to remove free ethylene glycol from the surfaces of the glycolate particles. Finally, the precursor was dried at 60 °C for 2 h. The precursor was annealed at 500 °C for 1 h and ready for gas sensing applications.

2.2. *Preparation of Ag–TiO_2 spherical heterostructures*

TiO_2 precursor nanospheres (0.1 g) were suspended in 20 mL distilled water with stirring for 10 min. Then, 20 mL HCl solution with concentration of 0.02 mol/L containing 0.1 g $SnCl_2$ was added into the above solution while stirring and the mixture solution was observed to become yellow quickly. After 10 min, the precipitate was centrifuged and washed with distilled water five times. The obtained precipitate was immersed in 4 mL ethanol solution containing 5 mmol/L $AgNO_3$ while stirring, and then irradiated using UV light (340 nm, 30 mW cm^{-2}) for 5 h, yielding the pale-yellow precipitate. After centrifuged and washed with distilled water five times, the pale-yellow precipitate was dried at 60 °C for 12 h and then annealed at 500 °C for 1 h.

2.3. *Characterization*

Morphology and structure of the sample was examined with scanning electron microscopy (SEM) (FEI/Philips, XL-30). Phase and crystalline of the Ag–TiO_2 spherical powder annealed at 500 °C for 1 h were determined with X-ray diffractometer (XRD) (Rigaku, D/MAX-3B) with Cu Kα radiation (λ = 0.15405 nm). The sample was also analyzed by X-ray photoelectron spectroscope (XPS) (VG Scientific, ESCALAB 250) with Al Kα radiation ($h\nu$ = 1486.6 eV) within ±0.2 eV deviation in the binding energy position.

2.4. *Sensor fabrication and measurement*

Commercial Taguchi Gas Sensor (TGS), fabricated onto a cylindrical Al_2O_3 tube of a 4 mm length with two permanent gold coatings spaced 1 mm, was coated by three-layer paste, and then sintered at 350 °C for 3 h in air to form a thick sensing film. The detailed sensor fabrication procedure was reported previously [22]. The electrical resistance of the sensor in various gas concentrations was measured with a digital gas-sensitive electrometer (Qingdao, RQ-2, China) at various temperatures. Ethanol and acetone with different concentrations were injected into a 1 L vacuum container by a microsyringe and vapourous with heating. After resistance of the sensor reached a steady state in air, the sensor was immediately placed into the container with the desired concentration of the test gas. The response is defined as: Ra/Rg, where Ra and Rg are the sensor resistances measured in air and in tested gas, respectively. The time required for a sensor to reach 90% of the total resistance change was defined as the response time in case of adsorption, or the recovery time in case of desorption.

3. Results and discussion

3.1. *Structure and morphology*

The as-prepared precursor before calcinations is in an amorphous phase. The XRD pattern of the Ag–TiO_2 powders annealed at 500 °C for 1 h is shown in Fig. 1. The *d*-values calculated are in agreement with those given in the standard data (JCPDS, 21-1272), suggesting that the as-prepared precursor has crystallized in a pure anatase phase. No obvious peaks for metallic silver nanoparticles can be observed because the low diffraction intensity of ounce silver is immersed in that of TiO_2. Furthermore, a detail component analysis of the Ag–TiO_2 heterostructures was carried out with XPS measurements. Fig. 2a shows the Ti 2p spectra of the heterostructural Ag–TiO_2 nanospheres. The shape, binding energy and spin–orbit splitting of the Ti 2p photoemission envelope are characteristics of TiO_2 [22]. Fig. 2b exhibits the Ag 3d spectra of heterostructural Ag–TiO_2 nanospheres. The characteristic Ag 3d$_{5/2}$

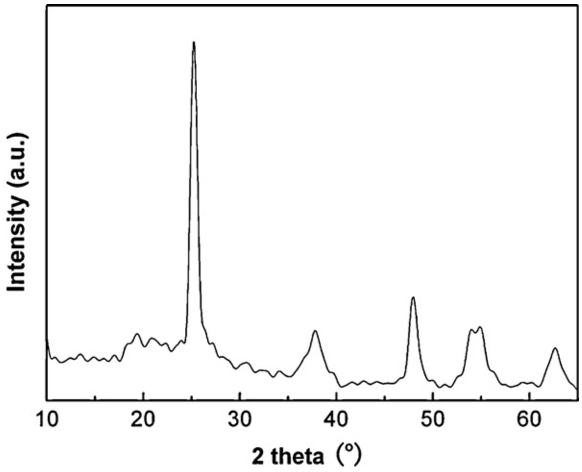

Fig. 1. XRD patterns of the Ag–TiO_2 powders annealed at 500 °C for 1 h.

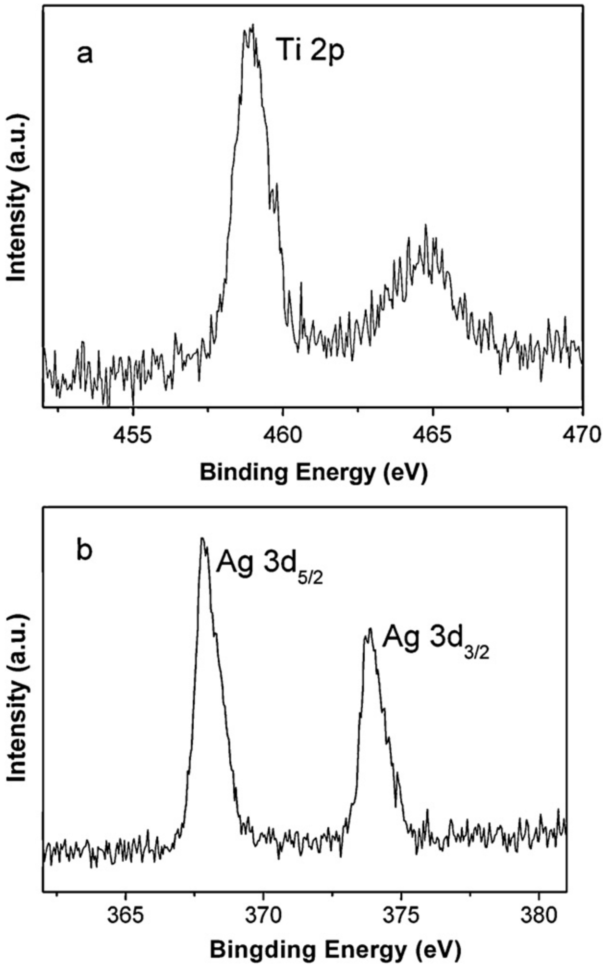

Fig. 2. XPS Ti 2p (a) and Ag 3d (b) spectra of the Ag–TiO_2 powder.

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