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Multi-applicative tetragonal TiO_2/SnO_2 nanocomposites for photocatalysis and gas sensing

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ABSTRACT

TiO_2-based mixed metal oxide heteronanostructures have multiple applications in photocatalysis and gas sensing because of their charge transport properties. In this study, we prepared tetragonal TiO_2/SnO_2 nanocomposites (NCs) with different weight percentages using a simple wet impregnation method. The physicochemical properties of the NCs were investigated using X-ray diffraction, Fourier transform-infrared spectroscopy, ultraviolet–visible spectroscopy, field-emission scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, and Brunauer–Emmett–Teller surface area analysis. The results showed that the surface area of the NCs increased significantly and the anatase TiO_2 was sensitized after the addition of a small amount of cassiterite SnO_2 NPs. We systematically studied the as-prepared NCs during the photocatalytic degradation of Congo Red dye under visible light irradiation ($\lambda > 420$ nm) and NH_3 gas sensing, which demonstrated the efficient photocatalytic performance and the superior sensing response of the catalyst with a weight composition of 25% SnO_2 in TiO_2 (4:1) compared with the other NCs or the bare individual nanoparticles. The improved photocatalytic and gas sensing performance of the TiO_2/SnO_2 (4:1) NCs may be attributed to the increased active surface area, the increased adsorption of the dye and target gas molecules, as well as efficient electron–hole charge separation and transfer.

1. Introduction

The development of single materials with multiple applications is an attractive area of research at present. Many studies have employed TiO_2 nanoparticles (NPs) as key materials, such as in solar energy harvesting, waste water management, gas sensing, and organic transformation, because of their openness and attractive physicochemical properties [1–4]. However, the bare TiO_2 is not very efficient because of the rapid recombination rate of photogenerated electron–hole pairs on its surface or interior region [5–7]. The optical band gap of bare TiO_2 is also very high ($E_g \sim 3.2$ eV), which hinders its use as a photocatalyst under visible light irradiation [8–10]. Many studies have employed various physical and chemical methods to tune the properties of metal oxides with various materials such as metals, non-metals, chalcogenides, and metal oxides, which can act as sinks for the photogenerated electrons and holes to improve the visible light activity [11–15]. TiO_2 is also among the best materials for sensing organic vapors, oxidizing as well as reducing gases. However, the main problem with TiO_2 in sensing applications is its cross-sensitivity and high resistivity (106 Ω cm). It also requires very high operating temperatures (300–500 °C) for sensing [16]. The effective resolution of these problems involves preparing nanosize TiO_2 and coupling it with another nanosize metal oxide semiconductor in order to enhance its selectivity and to increase the surface area by avoiding grain growth [17]. TiO_2 is usually coupled with M_xS_y or M_xO_y type semiconducting materials in various systems such as TiO_2/CdS [18], TiO_2/ZnO [19], TiO_2/CeO_2 [20], TiO_2/Fe_xO_y [21], TiO_2/WO_3 [22,23]etc.

The activity of doped or coupled TiO_2 may be enhanced by increasing its active surface area or due to the intermixing of electronic density states, which trap photoinduced electrons and holes to facilitate reduction–oxidation based catalytic effects [24,25]. In particular, SnO_2 has a comparable band gap ($E_g = 3.4$–3.8 eV) and it is a suitable material for

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coupling with TiO_2 because of its useful physical properties, and thus it is employed in a variety of commercial devices [26]. Furthermore, the similarities in the structure of TiO_2 and SnO_2 as well as the ionic radii of the cations ($Ti^{4+} = 0.605$ Å and $Sn^{4+} = 0.69$ Å) allow them to form a heterojunction hybrid between the two oxides [27]. This may result in the formation of intermixed electronic density states and reduce the grain size to allow appropriate separation of the photogenerated electrons and holes, which facilitates the degradation of organic pollutants [28,29] as well as providing the capacity to sense various gases [30]. The SnO_2/TiO_2 heterostructures exhibit enhanced photocatalytic efficiencies in the degradation of rhodamine B compared with the bare TiO_2 NPs, although this is only possible under ultraviolet (UV) light irradiation [31]. Rajkumar et al. [32] used an SnO_2/TiO_2 nanotube composite for the degradation of textile effluent under visible light, but a tedious experimental setup was required to obtain nanotubes with the appropriate morphology. Chung et al. [33] added 3–5 mol% TiO_2 to an SnO_2 matrix for gas sensing applications and reported a substantial improvement in the hydrocarbon sensing performance of SnO_2 thick films. MoO_3/TiO_2 and Bi_2MoO_6 materials have also been used for selective ammonia gas sensing [34], where the metal oxides were dispersed on the surface of anatase TiO_2 to catalyze the oxidative decomposition of hydrocarbons and ammonia. Hybrid structures comprising SnO_2 NPs incorporated into TiO_2 nanobelts exhibited enhanced gas sensing capacities, where they could sense many organic vapors and gases with rapid response/recovery speeds [35,36]. The recent uses of TiO_2-based nanocomposites (NCs) in photocatalytic and gas sensing applications have suggested that these materials can be improved to compete with conventional NCs.

In this study, we prepared inexpensive, simple, and non-toxic TiO_2/SnO_2 NCs under ambient experimental conditions. The materials obtained may be efficient for use in multiple applications, where they exhibited good photocatalytic activity under visible light irradiation. Congo Red (CR) is the most important secondary diazo dye used in the textile and paper industry, where it has good solubility and photostability in water as well as in ethanol. However, toxicity is the main issue that limits the widespread use of CR [37]. Thus, we employed this pollutant dye to investigate the photocatalytic properties of the materials obtained in the present study. Furthermore, these materials were tested in ammonia gas sensing applications. Ammonia gas sensors are important in various industries as well as in households, food processing, medical diagnosis, and pollution control [38,39]. The TiO_2/SnO_2 NCs exhibited a high sensing response with a good recovery time when sensing ammonia gas. The physicochemical properties of the prepared NCs were studied using various sophisticated instrumental techniques.

2. Materials and methods

2.1. Chemicals and reagents

Titanium (IV) isopropoxide (TTIP), acetyl acetone (AcAc), isopropyl alcohol, stannous chloride dihydrate, ammonia solution, and CR were purchased from Sigma Aldrich. All of the chemicals and reagents were analytical reagent (AR) grade. Deionized water (18 mΩ cm^{-1}) was used in all the experiments.

2.2. Preparation of anatase TiO_2 NPs

A facile sol–gel method where AcAc acted as the complexing and polymerizing agent was employed to prepare anatase TiO_2 NPs. TTIP (5 mL), AcAc (3 mL), and isopropyl alcohol (5 mL) were placed into a round-bottomed flask. The solution was then stirred at 40 °C for 1 h. The initial pH of the orange colored sol was 6. The solution was then refluxed in an oil bath at 120 °C for 3 h. After cooling, a deep orange-red colored gel was obtained, which was dried at 150 °C. The resulting powder was washed with deionized water and calcined at 450 °C for 3 h to obtain white colored TiO_2 NPs.

2.3. Preparation of cassiterite SnO_2 NPs

Stannous chloride dihydrate (2.5 g) was dissolved in AcAc (5 mL) with constant stirring at 60 °C for 2 h and 15 mL deionized water was then added with constant stirring for 1 h. Next, 10 mL of ammonia solution (0.5 M) was added in a dropwise manner with constant stirring at 40 °C for 2 h. A yellow colored gel was obtained, which was dried at 150 °C, washed with deionized water several times, and calcined at 450 °C for 3 h to obtain white colored SnO_2 NPs.

2.4. Preparation of anatase TiO_2/Cassiterite SnO_2 NCs

Typical syntheses of TiO_2/SnO_2 NCs with different weight percentages were performed using the wet impregnation method. During the synthesis of SnO_2 NPs, the appropriate amount of TiO_2 NPs was added relative to the desired stoichiometric ratio and the resulting mixture was stirred vigorously at 60 °C for 3 h. Finally, all of the samples were calcined at 450 °C for 3 h to obtain white colored NCs.

The NCs obtained with different weight percentages of SnO_2 NPs comprising 0.0%, 25.0%, 50.0%, and 100.0% in the TiO_2 host lattice were designated as bare TiO_2, TS (4:1), TS (2:1), and bare SnO_2, respectively.

2.5. Characterization

The structural properties of the prepared materials were analyzed by X-ray diffraction (XRD) using Ni-filtered Cu $K\alpha$ radiation at 1.54056 Å (X'pert PRO, Philips, Eindhoven). Fourier transform infrared (FTIR) spectra were obtained for the samples using an FTIR spectrophotometer (Perkin Elmer-Spectrum 100). Field-emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDAX) analysis was performed (FE-SEM, JEOL, JSM-7500F). The high resolution transmission electron microscopy (HRTEM) with selected area electron diffraction (SAED) was performed to obtain images (JEOL-3010 and Tecnai G2 F20). UV–visible (UV–Vis) diffuse reflectance spectra (DRS) were obtained for the samples and the time-dependent degradation spectra were recorded for CR dye using a LabIndia 3092 UV–visible spectrophotometer. The N_2 adsorption and desorption isotherms were measured using a Quantachrome Nova Win instrument. The gas sensing responses of the samples in the form of resistance were measured using a Keithley 6514 electrometer.

2.6. Photodegradation

In a typical procedure, 50 mg of photocatalyst was dispersed in 70 mL of aqueous CR solution (10 ppm). This solution was then stirred for 60 min in the dark to achieve an adsorption-desorption equilibrium between the dye molecules and the catalyst surface. A multi-lamp photoreactor (Model: MLR-16) was used with mercury vapor lamps at a wavelength of 520 ± 40 nm with 8 W power to illuminate the dye solution. Aliquots were withdrawn from the reactor every 15 min to monitor the progress of the degradation process. The aliquots were centrifuged and their corresponding UV–Vis spectra were obtained using an UV–Vis spectrophotometer (maximum absorption wavelength for CR = 498 nm).

2.7. Gas sensing

The gas sensing performance of the as-prepared tetragonal TiO_2/SnO_2 NCs was tested after deposition onto glass substrates. In a typical procedure, 0.5 g of the material was mixed with ethanol to make a paste. Gas sensor films were obtained using a simple doctor blade technique where the paste was coated onto the glass substrate. The sensing performance was evaluated with homemade computer-controlled static gas sensing equipment, which comprised a stainless steel container with a gas inlet-outlet and a gas volume capacity of 250 cm^3. The thin film of the material (10 mm $\times$ 10 mm) on the glass substrate was kept on a heating flat plate