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Synthesis and characterization of Ag–TiO_2–CNT nanoparticle composites with high photocatalytic activity under artificial light

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ABSTRACT

Carbon nanotube (CNT)-modified silver titania (Ag–TiO_2) nanoparticle composites were synthesized by photochemical reduction. Characterization of the composites was performed using field emission-scanning electron microscopy (FE-SEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (DRS), and Raman spectroscopy. It was found that TiO_2 particles were uniformly distributed on CNTs, and the silver particles were decorated on the surface of the TiO_2. The photocatalytic activity of Ag–TiO_2–CNT nanoparticle composites synthesized with various concentrations of CNTs was investigated using methylene blue (MB) dye solution. Adsorption and recovery of MB showed that Ag–TiO_2–CNT nanoparticle composites have a higher absorption efficiency than unadorned CNTs. The higher absorption demonstrates a synergistic effect between the CNTs and silver titania. Overall, novel photocatalytic nanoparticle composites that adsorb organic molecules, absorb light energy, and separate long-lived electron–hole pairs through spatial separation were developed. Minimization of electron–hole recombination allows efficient transfer of photochemical energy which affects the redox chemistry across the interfaces in the composites. The new composites were designed for environmental cleanup of organic pollutants.

1. Introduction

Major global environment issues imposed upon the 21st century include climate change, environmental pollution, and sustainable water management [1,2]. Photocatalysts are emerging as a key technology to meet these demands as they can be utilized to clean water, produce energy, and remediate polluted areas in a carbon neutral manner utilizing solar energy. In particular, titanium dioxide (TiO_2) is a semiconductor material that has received much attention because of its high photocatalytic activity, photosensitivity, nontoxicity, long-term stability, low cost, and antimicrobial properties [3–6]. Photocatalysis utilizing bulk TiO_2 is initiated through the generation of electron (e^-) and hole (h^+) pairs upon illumination with ultraviolet (UV) radiation at $\lambda < 380$ nm spanning the band gap, $E \geqslant 3.2$ eV. These electron–hole pairs can participate in redox reactions with adsorbed molecules on the surface. This redox chemistry is in competition with electron–hole recombination. We are developing a TiO_2-based nanoparticle composite to enhance photocatalytic activity under visible as well as UV sunlight to enable more environmentally-friendly applications as well as increasing the charge carriers available for desired redox chemistries.

Carbon nanotubes (CNTs) have attracted significant attention in a variety of scientific fields because of their unique structural, chemical, thermal, and electrical properties [7] and are utilized in our nanoparticle system design. CNTs have been reported to synergistically enhance the photocatalytic activity of TiO_2 based on the CNTs' ability to (1) inhibit recombination by acting as sinks for photogenerated electrons in TiO_2 [8–10] and (2) photosensitize the titania particle based on electron–hole pair generation in the CNT [8,11–13] due to the favorable energetics of their electronic-band structures[14]. As beneficial as the properties of TiO_2–CNTs composites may be, synthetic methods can be complicated and utilize non-environmentally friendly reagents such as strong acids and organic solvents. We introduce a simple and efficient photochemical reduction method to fabricate these nanocomposites.

Many other nanocomposite systems with high photoactivity have been studied such as silver modified TiO_2 (Ag–TiO_2). Both Ag–TiO_2 and CNT–TiO_2 materials have been applied to the degradation of dyes [10,15–18]. Zhang and coworkers [19] have utilized all three components and applied Ag–CNT/TiO_2 composite electrodes for methylene blue (MB) degradation.

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The present paper reports photochemical reduction synthesis and artificial light-induced catalytic activity of nanosized silver (Ag) doped titania (TiO_2) with carbon nanotubes (CNTs). Synthesis of the composite was achieved by a simple photochemical reduction process in slightly basic water under ultraviolet (UV) irradiation at room temperature. Field emission-scanning electron microscopy (FE-SEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (DRS), and Raman spectroscopy were used to characterize the resulting materials. The photocatalytic activity of Ag–TiO_2–CNT nanoparticle composites was investigated by measuring the degradation under artificial light of MB dye solution as an indicator of its photo-oxidation capabilities in regards to the removal of organic pollutants.

2. Experimental

2.1. Materials

Nanosized bicrystalline TiO_2 (P25, 50 m^2/g, 80% anatase and 20% rutile) was supplied by Degussa. ACS reagent grade silver nitrate ($AgNO_3$), ammonium hydroxide (NH_4OH, 30% v/v aqueous solution), ethanol (CH_3CH_2OH, 99.5%) and carbon nanotubes (CNTs multiwalled, >95%) were used as-received from Sigma Aldrich without any further purification. Solutions were prepared with high purity water produced by a Millipore Milli-Q system at 25 °C.

2.2. Photochemical reduction process

Ag–TiO_2 composite nanoparticles were synthesized as a comparison material by a method we have previously reported [15]. Ag–TiO_2–CNT nanoparticle composites were synthesized by the photochemical reduction process. The CNTs were multi-wall carbon nanotube (MWCNT) powders of 95% purity with outer diameter 6–9 nm and length of 5 μm. The CNTs were dispersed in 50 mL of ethanol and sonicated for 20 min after which 0.3 g of TiO_2 (P25) was added. CNT:TiO_2 mixtures of various weight ratios (0.5:100, 1:100, 5:100, 10:100) were then mixed with 50 mL of 15 mM $AgNO_3$ aqueous solution. The pH of the solution was adjusted to 8.5 by addition of NH_4OH. The solution was thoroughly mixed by stirring for 10 min and then irradiated under UV lamp (Ecolux, 40 W) with stirring at room temperature for 3 h. Synthesized Ag–TiO_2–CNT nanoparticle composites were collected by centrifugation (3000 rpm, 4 min) and rinsed with distilled water repeatedly followed by drying at 80 °C under vacuum overnight. Dark brown Ag–TiO_2–CNT composite nanoparticles were obtained.

2.3. Property and morphology characterization

The surface morphology and size of Ag–TiO_2–CNT nanoparticle composites were studied FE-SEM (Hitachi 8000), operating at 5 kV and by STEM at 30 kV. Samples were gold-covered for FE-SEM measurements. EDX data were obtained with a Bruker AXS (XFlash detector 5030) attachment on the FE-SEM. Three typical regions were analyzed and the average wt.% of Ag–TiO_2–CNT nanoparticle composites was determined. The crystallographic structures of the composite photocatalysts were observed by using XRD (AXS-Bruker D8 Discover Diffractometer) at room temperature with Cu Kα radiation source ($\lambda = 0.15418$ nm). UV–Vis diffuse reflectance spectra were measured on a UV–Vis spectrophotometer (UV-2550, Shimadzu, Japan) attached with an integrating sphere. The Raman scattering experiments were performed using a LabRAM ARAMIS (HORIBA Scientific) with excitation laser beam wavelength of 633 nm.

2.4. Photocatalytic MB degradation

The degradation of MB under artificial light irradiation was used to evaluate the photocatalytic activity of Ag–TiO_2–CNT nanoparticle composites and compare them to Ag–TiO_2 nanoparticle catalyst. About 20 mg of photocatalyst was mixed with 50 mL of 5 mg/L concentration MB aqueous solution. The solution was stirred with a magnetic bar throughout the experiment. The dark adsorption/desorption time was 60 min and the reactions were carried out at room temperature (25 ± 1 °C) for 180 min. A 32 W Ecolux lamp was used as light source. In order to simulate sunlight, the incident light was impinged directly on the MB suspension without using a filter with the distance from the lamp maintained at about 15 cm. The MB concentration was followed by measuring the absorbance of aliquots with a UV–Vis spectrophotometer (SEC2000, ALS-Japan) at a wavelength of 655 nm.

2.5. MB adsorption and recovery

For degradation/adsorption effect studies, adsorption/recovery capacity experiments utilizing only CNTs and the nanoparticle photocatalysts of Ag-TiO_2 or Ag–TiO_2–CNT were performed. In the case of CNTs, different amounts of CNTs (0.5, 1, 2, 3, 4, 5 mg) were added into 50 mL of aqueous solution. The mixtures were stirred in darkness for 1 h and adsorption/recovery experiments were performed for one hour. For nanoparticle photocatalyst, we added 20 mg of Ag–TiO_2 or Ag–TiO_2–CNT particles to this aqueous solution and adsorption rate was measurement at hourly intervals. The whole experiments were carried out at room temperature (25 ± 1 °C) for 4 h, including adsorption/desorption for first 60 min in darkness and then degradation for next 180 min under artificial light. The solids were separated by centrifugation and the concentration of MB in the supernatant was measured. The nanoparticle composites were washed with distilled water repeatedly to remove non-adsorbed MB. The adsorbed MB on the nanoparticle composites were removed by addition of 50 mL ethanol of pH 3 adjusted by 0.1 M HCl solution with agitation. After the solids were removed by centrifugation, the supernatant solutions were analyzed by UV–Vis spectrometer.

3. Results and discussion

The microsurface structures of the Ag–TiO_2–CNT nanoparticle composites were characterized by FE-SEM and STEM. Unadorned CNTs are shown in Fig. 1(a). As shown in Fig. 1(b and c), Ag–TiO_2 particles are attached well on the surface of the CNTs and uniformly distributed. The dispersion of small particles is optimal for surface catalysis as this can provide more reactive sites for the reactants than aggregated particles [11]. STEM was used to further examine the surface structure of Ag–TiO_2–CNT nanoparticle composites. In Fig. 1(d–f), images of unadorned CNTs and Ag–TiO_2–CNT nanoparticle composites are shown at different magnifications. The images confirm that the surface of the CNTs have been uniformly decorated with AgTiO_2 particles of size ~20–30 nm. Also, Ag–TiO_2–CNT nanoparticle composites were found to be covered with “aciniform” structures of Ag–TiO_2, as shown in Fig. 1(c and e).

The EDX spectra of the various Ag–TiO_2–CNT nanoparticle composites presented in Fig. 2 are consistent with the proposed composition of Ag, Ti, O, and C. The results of EDX elemental microanalysis of the nanoparticle composites are listed in Table 1 with prepared Ag–TiO_2 nanoparticles. The greater the CNT:TiO_2 the synthesized weight (%) increased, and the contents of Ag, Ti, and O component tended to decrease compared to C composition as expected.