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Synthesis of multiwall carbon nanotubes/TiO_2 nanotube composites with enhanced photocatalytic decomposition efficiency

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ABSTRACT

Multiwall carbon nanotubes (MWCNT)-loaded TiO_2 nanotube (TNT) composites were synthesized by hydrothermal method. Scanning electron microscopy and transmission electron microscopy revealed the tubular morphology of the prepared TNT and MWCNT/TNT composites, which was further confirmed by the increase in their surface area. The MWCNT/TNT photocatalysts show high photocatalytic decomposition efficiency (PDE) for the degradation of rhodamine 6G (RhB-6G) dye, with excellent stability and reusability. Among the MWCNT/TNT composites, 10% loading of MWCNT results in a significantly higher PDE (89%) as compared with that of bare TNT (78%), Degussa P-25 TiO_2 (P25, 60%), and TiO_2 nanoparticles (56%). The enhanced PDE of MWCNT/TNT composites is due to the ability of the MWCNTs to promote the electron transfer process and reduce the electron-hole pair recombination rate, as also confirmed by photoluminescence measurements. Moreover, chemical oxygen demand (COD) and total organic carbon (TOC) analyses were performed to verify the RhB-6G dye degradation. Tubular morphology, enriched adsorption, synergic effect, and efficient separation of photogenerated electron-hole pairs account for the enhanced PDE of MWCNT/TNT composites in the decomposition of RhB-6G dye under the current experimental conditions.

1. Introduction

Titanium dioxide (TiO_2) is an eco-friendly photocatalyst, which has been broadly exploited for environmental remediation and energy application under UV and solar light irradiation, because of its unique advantages [1–6]. However, the major drawbacks associated with TiO_2-based systems, i.e., low adsorption capacity, low photon utilization efficiency, high rate of electron-hole pair recombination, and poor performance in visible light irradiated photoreactions, limit their practical application. In order to overcome these issues and enhance the photocatalytic efficiency, much effort has been directed toward the development of composite catalysts with TiO_2 supported on various high surface area solids, such as silica, zeolite, carbon (carbon nanotubes, graphene, and activated carbon), metal oxides, and metal organic frameworks (MOFs) [7–12]. Composite materials have unique adsorption and condensation properties, which facilitate the degradation of organic contaminants. Among these, carbon-containing composites, especially carbon nanotubes (CNTs), have attracted considerable interest owing to their distinctive tubular structure, electrical properties, high mechanical strength, and large specific surface area, which are important features for superior catalyst support materials. Moreover, CNTs play an important role in the inhibition of the recombination process by harvesting the electrons from TiO_2 and enhance the photocatalytic decomposition efficiency (PDE) [13,14]. Remarkable efforts have been then devoted to the synthesis of single-walled CNT (SWCNT), multi-walled CNT (MWCNT)/TiO_2(TNP) composites, used for the treatment of wastewater containing pollutants, for sensors, for dye-sensitized solar cells, etc [15–20]. However, the photocatalytic decomposition efficiency was still insufficient for commercial applications, due to the low surface area of TiO_2 and thus low adsorption capacity.

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One-dimensional TiO_2 nanotubes (TNTs) have received major attention for their distinctive characteristics including high specific surface area, high adsorption capacity, good ion-exchange property,and low recombination rate by long electron transport distance along the tubular structure [21–26]. Subsequently, the synthesis of CNT/TNT composites has attracted research interest because two nanotubular structures can efficiently increase the lifetime of photogenerated charge carriers and enhance the decomposition efficiency. Ping et al. [27]. reported the first MWCNT/TNT composite synthesized by a combination of sol-gel and hydrothermal methods and used for the degradation of humic acid under UV irradiation. Tang et al. [28] studied the gas-phase degradation of benzene using hydrothermally synthesized one-dimensional CNT/TNT composites. Vijayan et al. [29] reported acetaldehyde degradation by a SWCNT/TNT composite synthesized by hydrothermal and evaporation methods. The electrons are effectively transferred from TNT to SWCNT suppressing the recombination rate. Subsequently, Jiang et al. [30] described a CNT/TNT composite for the decomposition of methyl orange (MO) dye. However, a detailed study of the synthesis of MWCNT/TNT composites, the nature of electron-hole recombination, and their applications has not yet been fully performed.

Herein we report MWCNT/TNT composites with different weight percentages of MWCNT, synthesized by simple hydrothermal method by *in-situ* addition of MWCNT. The composites are thoroughly characterized using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) surface area, UV–vis diffuse reflectance spectroscopy (UV-vis-DRS), and Fourier transform infrared (FT-IR) analysis. The PDE of MWCNT/TNT composite materials was evaluated by the decomposition of rhodamine 6G (RhB-6G) dye under UV irradiation. The MWCNT/TNT composites exhibited remarkably enhanced photocatalytic decomposition efficiency and a plausible degradation mechanism was proposed. In order to highlight the efficiency of our system, the PDE was compared with literature reports.

2. Experimental section

2.1. Materials and methods

Multiwall carbon nanotubes (MWCNT, >95%, OD = 60–100 nm, ID = 5–10 nm and length = 0.5–500 μm), anatase TiO_2 (AT, >99%) and rhodamine 6G (RhB-6G) dye were purchased from Sigma Aldrich. Sodium hydroxide (NaOH), nitric acid (HNO_3), and hydrochloric acid (HCl) were purchased from S.D. Fine Chemicals Ltd, Mumbai, India. Double distilled water was used to prepare the experimental solution.

2.2. Functionalization of MWCNT

Prior to MWCNT/TNT composite synthesis, the MWCNT was functionalized by acid treatment. Typically, MWCNT was suspended in concentrated HNO_3 (25 mL), sonicated, and refluxed for 20 h at 80 °C. After 20 h, the reaction mixture was centrifuged, continuously washed with distilled water until neutrality, and oven-dried at 110 °C for 12 h. The powdered MWCNT was then treated with 50% HNO_3 and refluxed at 130 °C for 24 h. MWCNT was centrifuged, repeatedly washed with distilled water until neutrality, and heated at 70 °C for 12 h for complete drying. The modified MWCNT was labeled as MWCNT-A.

2.3. Synthesis of MWCNT/TiO_2 nanotube composites

MWCNT/TiO_2 nanotube composites were prepared by hydrothermal method, as schematically represented in Fig. 1. A solution containing 10 N NaOH (50 mL) and 1.2 g of anatase

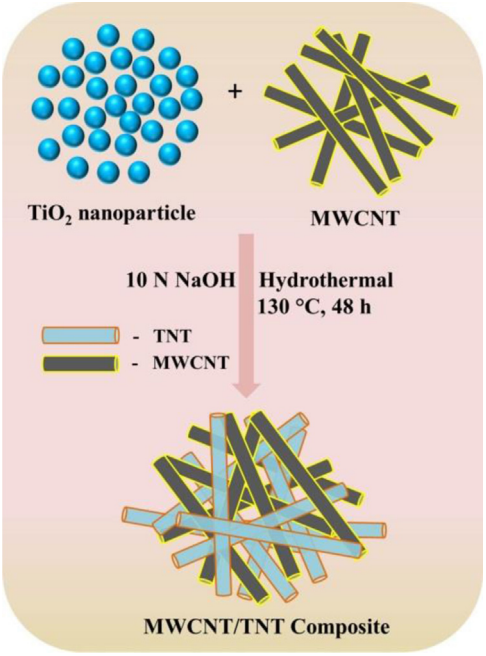

Fig. 1. Schematic representation of MWCNT/TiO_2 nanotube composite synthesis.

TiO_2 powder (AT) was sonicated (5 min) and transferred to a 75 mL Teflon-lined stainless steel autoclave. Calculated amounts of MWCNT-A were then added and the autoclave was heated at 130 °C for 48 h with stirring (250 rpm). The autoclave was cooled and the formed MWCNT/TNT composite was washed with distilled water until the pH of the supernatant was lower than 7. Next, the synthesized MWCNT/TNT composites were treated with HCl solution (0.1 M) under stirring at room temperature for 12 h, washed with water until the supernatant was free of chloride ions (silver nitrate test), dried at 70 °C for 12 h, and then calcined at 250 °C for 2 h under N_2 with a ramp rate of 2 °C/min. The synthesized MWCNT/TNT composites were designated as x%MWCNT/TNT (x = 1, 3, 5, 7, and 10). Similarly, pristine TNT was synthesized without addition of MWCNT.

2.4. Characterization

The crystal configuration of composites was analyzed by PXRD analysis using Rigaku MiniFlex X-ray diffractometer with Cu Kα1 radiation (λ = 0.15406 nm). The surface area was measured by nitrogen adsorption analysis at 77 K using an ASAP 2010, Micromeritics, USA surface area analyzer. FT-IR spectroscopic analysis of the composites was performed on a Perkin Elmer FT 1730 spectrophotometer. UV–vis-DRS were recorded over the wavelength range of 200–800 nm using a Shimadzu UV-3101 PC UV–vis spectrophotometer. The UV–vis-DRS were utilized for estimating the band-gap values of synthesized MWCNT/TNT composite samples using mathematical methods from Kubelka-Munk model as reported elsewhere [31] and the values were tabulated in Table 2. XPS analysis of the composite samples was carried out using a ULVAC-PHI Quantera SXM™ scanning XPS microscope with Al-Kα as an X-ray source. The tubular morphology of MWCNT, TNT, and MWCNT/TNT composites was observed by SEM (Leo Series VP1430) and TEM (JEOL JEM-2010 electron microscope).The percentage loading of MWCNT was analyzed by CHNS analysis.The photoluminescence spectra of the photocatalysts were recorded on an Action research (Spectra Pro 215i) photoluminescence spectrophotometer at an excitation wavelength of 320 nm.

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