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Original Research Paper

Visible light photocatalytic activities of carbon nanotube/titanic acid nanotubes derived-TiO_2 composites for the degradation of methylene blue

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ABSTRACT

Carbon nanotube/TiO_2 composites were synthesized by hydrothermal method using titanic acid nanotubes as the TiO_2 precursor. The crystalline structures, morphologies, light absorption properties, specific surface areas of the prepared powders were investigated with XRD, TEM, UV–Vis absorption spectra and N_2 adsorption–desorption. The photocatalytic activities of the composites were evaluated by monitoring the degradation rate of methylene blue (MB) under the visible light irradiation. The mechanism of the improved photocatalytic activity of the photocatalyst was discussed. It was found that all of the composites upon 24 h of hydrothermal reaction show the diffraction peaks indexed to anatase TiO_2 and the critical reaction time for anatase TiO_2 nanoparticles to form is 3 h. The visible light photocatalytic activities of the catalysts in this experiment were affected by a combination of BET specific surface area, MWCNT content and hydrothermal reaction time.

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1. Introduction

Semiconductor photocatalysts have been an attractive research field because of their applications in environmental pollution mediation and solar energy conversion [1–5]. Of the well-known photocatalysts, titanium dioxide (TiO_2) has received extensive attention due to its efficient photocatalytic activity, high stability, low cost, and innocuousness [6–9]. However, TiO_2 is a wide band gap energy semiconductor, active only under the UV light irradiation, which is only a small fraction (ca. 4%) [10] of solar radiation. Therefore, it is one of the key objectives in the field of material science research to develop visible light active photocatalysts.

The solutions include combining narrow-band semiconductor [11,12], doping metal or metal ion [13,14], and non-meta [3,15,16]. Of those attempts, combining TiO_2 with carbonaceous materials is being increasingly investigated as a means to increase photocatalytic activity, and demonstrations of enhancement are plentiful [17]. Since the landmark paper by Iijima [18], carbon nanotubes (CNTs) have attracted significant attention in a variety of scientific fields because of their unique properties: structural, chemical, thermal, electrical and more [19]. Recently, CNTs have been developed and are considered one of the special carbon nanomaterials for the enhancement of TiO_2 photocatalysis. Leary and Westwood [17] have summarized a variety of different structural forms of CNT–TiO_2 photocatalysts. The synthesis routes include simple mixing, sol–gel, hydrothermal, solvothermal, electrophoretic deposition (EPD), electrospinning, electroplating, chemical vapour deposition (CVD), metal–organic chemical vapour deposition (MOCVD) and sputtering deposition. The TiO_2 precursors include P25 TiO_2, titanium sulphate, titanium-n-butyloxide, titanium tetraisopropoxide, titanium tetrachloride, sol–gel derived TiO_2 and commercial purity Ti.

In 2004, Bonnamy' group [20] has synthesized TiO_2 coated carbon multiwall nanotubes by a sol–gel method using classical alkoxides as $Ti(OEt)_4$ (tetrabutyl titanate) and $Ti(OPr^i)_4$ (tetraisopropyl titanate) and by hydrothermal hydrolysis of $TiOSO_4$. Fu' group [21] has synthesized the bonding TiO_2/single-walled carbon nanotube composites through a sol-solvothermal technique in 2010. Besides, in recent years, a number of groups have reported the synthesis and photocatalytic activities of TiO_2/carbon nanotubes nanocomposite [22–24]. However, up to date, few reports are currently available about the preparation and photocatalysis of CNT–TiO_2 nanocomposites by using titanic acid nanotubes (TANs) as the TiO_2 precursor. There are three advantages of combining TANs derived TiO_2 with CNTs: (i) Combined CNTs can transfer electrons to TiO_2 by acting as a photosensitizer or inhibit the recombination of electron–hole pairs by acting as sinks for photogenerated

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electrons in TiO_2. (ii) Not only CNTs but also TANs have high BET specific surface areas, which facilitate the adsorption of contaminations on the catalysts. (iii) The TANs derived TiO_2 have shown capabilities of improving visible light photocatalytic properties [25].

In this paper, we report on a facile process to prepare a CNT/TiO_2 (CNT/T) nanocomposite by hydrothermal method with TANs as TiO_2 precursors. The novel composite has shown higher visible light photocatalytic activities for the degradation of methylene blue (MB). Moreover, the CNT weight percentage of the most active photocatalyst is only 1%, indicating a potential practical application value.

2. Experimental section

2.1. Synthesis of TANs

The preparation of TANs was reported elsewhere [26]. Briefly, a proper amount (3 g) of TiO_2 was immersed in 10 mol L^{-1} NaOH solution at 120 °C and allowed to react for 24 h under magnetic stirring. At the end of reaction, the precipitate was cooled to room temperature and diluted with distilled water to a pH value of about 7.0; then it was immersed in a HCl solution (pH 1.0) for 24 h and washed again with distilled water to remove Cl^- before being dried at 60 °C overnight.

2.2. Synthesis of CNT/T composites

CNT/T composites with different compositions were prepared by a hydrothermal method. Briefly, TAN and multiwalled carbon nanotube (MWCNT, purchased from Shenzhen Nanotech Port Co., Ltd., China) with calculated amount (referring to MWCNT mass ratio of 0.2, 1, 10, and 20 wt% in CNT/T composites) was added in a mixed solvent consisting of 30 mL of deionized water and 15 mL of anhydrous ethanol under vigorous stirring for 2 h to allow good dispersion. Resultant suspension was transferred to a 200 mL Teflon-sealed autoclave and maintained at 120 °C for 24 h to allow the conjunction of TAN and the CNT. Upon completion of the reaction, the products were collected by filtration, washed by water, and fully dried at 80 °C in an oven for 2 days to provide final CNT/T composites with different CNT mass ratio. The CNT/T composites were denoted as *x*-CNT/T-24 h (*x* is the MWCNT mass percent and 24 h is the hydrothermal reaction time). To investigate the effect of hydrothermal reaction time on the structure, morphology and property of the CNT/T composites, 1-CNT/T-3 h, 1-CNT/T-6 h and 1-CNT/T-12 h were also prepared by the same process. For a comparison, 1-CNT/P25-24 h was also prepared by the same process.

2.3. Characterization of CNT/T

The microstructures of composites were analyzed using a JEM-2010 transmission electron microscope (TEM) (JEOL Ltd., Japan). X-ray diffraction (XRD) patterns of composites were measured using a Philips X'Pert Pro X-ray diffractometer (Philips, Netherland). Ultraviolet–visible light (UV–Vis) absorption spectra were obtained with an UV–Vis–NIR U-4100 spectrophotometer (spectral range: 200–800 nm) (Hitachi Ltd., Japan). N_2 adsorption and desorption isotherms of the samples were obtained at 77 K with an automated surface area and pore size analyzer (Quadrasorb *SI*, Quantachrome Instrument, USA) equipped with a turbo molecular pump (MVP 040-2, Pfeiffer Vacuum, Germany). Prior to the adsorption experiments all samples were degassed for at least 24 h at 373 K under vacuum. The BET surface area (S_{BET}) were calculated by using the multi-point BET method. The corresponding pore size distribution (PSD) were calculated with the desorption data based on the BJH method.

2.4. Evaluation of photocatalytic performance

The photocatalytic activity of the composites was evaluated by monitoring the degradation rate of methylene blue (MB). Briefly, 100 mL aqueous solution of the MB (10 mg L^{-1}) containing 0.1 g of photocatalyst powder was mixed in a 100 mL cylindrical quartz vessel. Resultant mixed solution in the reaction vessel was irradiated with a 150 W xenon arc lamp installed in a light-condensing lamp housing while a 420 nm cutoff filter ($\lambda > 420$ nm; Schott glass, Germany) was installed in front of the reaction vessel. The distance between the lamp and the liquid surface is 5 cm. The suspension was kept in dark under stirring for 120 min prior to irradiation to ensure the establishing of an adsorption/desorption equilibrium. At given time intervals, 5 mL aliquots were collected from the suspension and immediately filtrated and analyzed by recording variations of the absorption band maximum (664 nm) of MB using a UV–visible spectrophotometer (UV 2550, Shimadzu). For a comparison, the degradation tests of MB were also conducted under the same conditions while commercial P25 TiO_2 powder was adopted as the catalyst. An experiment in the absence of catalyst was also performed as blank in order to calculate the contribution from direct photolysis.

3. Results and discussion

3.1. Photocatalyst characterizations with XRD and TEM

Fig. 1 shows X-ray diffraction patterns of P25 TiO_2, MWCNT and as-prepared CNT/T composites. From Fig. 1a, in the top pattern, two diffraction peaks at 2θ of 26° and 43° are indexed to the (002) and (101) reflections of MWCNT, respectively. Although containing different MWCNT mass ratio (0.2%, 1%, 10% and 20%,

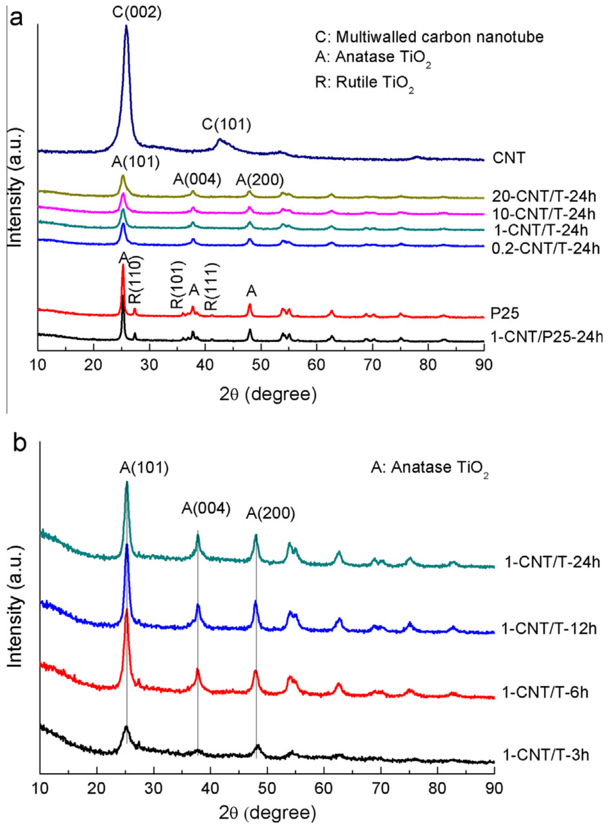

Fig. 1. XRD patterns of P25, MWCNT, 1-CNT/P25-24 h and CNT/T composites consuming 24 h of hydrothermal reaction time (a) and 1-CNT/T composites consuming different hydrothermal reaction times (3 h, 6 h, 12 h and 24 h) (b).

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