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Research Article

Modified Sol-Gel Synthesis of Carbon Nanotubes Supported Titania Composites with Enhanced Visible Light Induced Photocatalytic Activity

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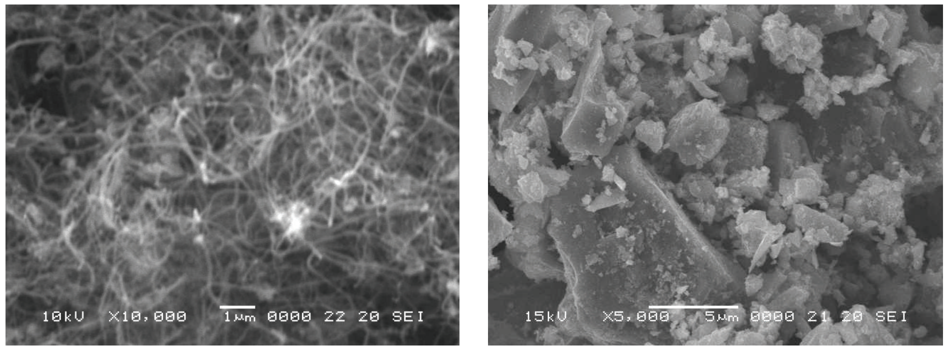
Multiwalled carbon nanotube (MWCNT) enhanced MWCNT/TiO_2 nanocomposites were synthesized by surface coating of carbon nanotube with mixed phase of anatase and rutile TiO_2 through a modified sol-gel approach using tetrabutyl titanate as raw material. The morphological structures and physicochemical properties of the nanocomposites were characterized by FT-IR, XRD, DTA-TG, TEM, and UV-Vis spectra. The results show that TiO_2 nanoparticles with size of around 15 nm are closely attached on the sidewall of MWCNT. The nanocomposites possess good absorption properties not only in the ultraviolet but also in the visible light region. Under irradiation of ultraviolet lamp, the prepared composites have the highest photodegradation efficiency of 83% within 4 hours towards the degradation of Methyl Orange (MO) aqueous solution. The results indicate that the carbon nanotubes supported TiO_2 nanocomposites exhibit high photocatalytic activity and stability, showing great potentials in the treatment of wastewater.

1. Introduction

Treatment of the industrial wastewater, especially the organic pollutants which are difficult to be biochemically degraded, is currently viewed as an active research area [1, 2]. Titanium dioxide (TiO_2) is an environmental-friendly photocatalyst material due to its high catalytic activity, thermal stability, strong oxidizing power, and nontoxic, low cost, and other unique advantages [3–5]. However, its photoefficiency is not high enough and the speed of ultraviolet photoresponse is not satisfactory [6, 7]. On the other hand, there is a measurable reduction in the photocatalytic activity for the recycled use of the photocatalysts. The disadvantage of TiO_2 semiconductor is that it only absorbs a small portion of solar spectrum in the ultraviolet region, which limits its applications. Therefore, the development of modified TiO_2 with enhanced visible light induced properties is needed to increase the photocatalytic activity for the organic pollutants [8–10].

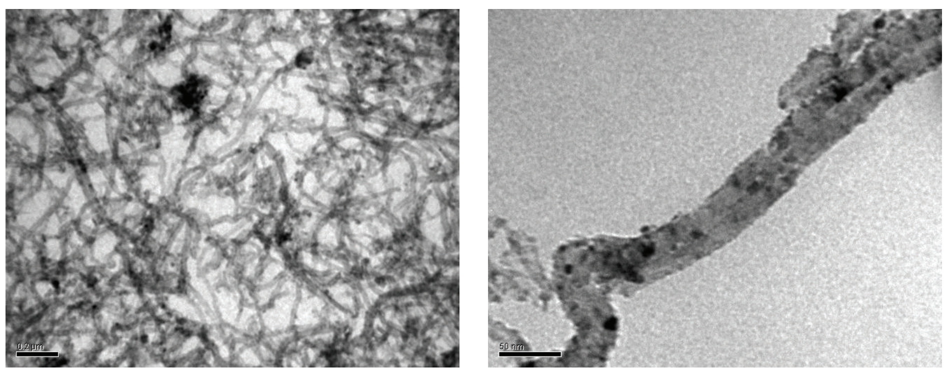
Carbon nanotube (CNT) is a new category of carbon structure, which was founded in 1991 by Iijima [11]. The ideal carbon nanotubes own seamless, hollow tube structure rolled by graphite surfaces slice layer composed of hexagon carbon atom. According to the number of graphite surface layers, they can be divided into single walled carbon nanotube (SWCNT) and multiwalled carbon nanotube (MWCNT). CNTs are considered to be ideal catalyst carriers due to their huge specific surface area, remarkable chemical stability, unique electronic structure, nanoscale hollow tube property, and good absorbability [12–15].

It was demonstrated in the paper that CNTs are regarded as the carrier of TiO_2 nanoparticle with the aim of improving the photocatalytic activity effectively and make TiO_2 easy to recycle. Herein, MWCNT/TiO_2 nanocomposites were synthesized by surface coating of carbon nanotubes with anatase and rutile types TiO_2 through a modified sol-gel approach using tetrabutyl titanate as the raw material. The obtained



(a) (b)

Figure 1: Typical SEM morphology of (a) modified MWCNT and (b) MWCNT/TiO_2 nanocomposites.



(a) (b)

Figure 2: Typical TEM images of acid modified MWCNT coated with nanosized TiO_2 materials in low magnification (a) and high magnification (b).

photocatalysts exhibit higher performance for Methyl Orange (MO) than pure TiO_2.

2. Results and Discussion

The morphology and microstructure of the acid modified MWCNT and MWCNT/TiO_2 nanocomposites were observed by Scanning Electron Microscope (SEM) and transmission electron microscope (TEM) investigations, respectively. As shown in Figure 1(a), the acid modified MWCNTs were dispersed uniformly with no or less aggregation. The weaved interconnected networks of carbon nanotubes contribute largely to the homogenous supporting of photocatalyst nanoparticles. After being supported by TiO_2 photocatalysts, as shown in Figure 1(b), the interval space of these weaved MWCNT networks was filled with nanosized TiO_2.

In the TEM image with low magnification (Figure 2(a)), MWCNTs coated with TiO_2 nanoparticles are identified with minor agglomeration of MWCNT. From the TEM image with higher magnification (Figure 2(b)), it can be seen that the TiO_2 nanoparticles with an average size of 15 nm are closely attached on the walls of MWCNT, which agrees with the XRD results below. Furthermore, the long and tube-like aperture structure of carbon nanotubes with large surface area contributes to the adsorption of the organic molecules. On the other hand, it is observed that the surfaces of MWCNT were not fully covered by TiO_2 nanoparticles, since the number of active sites on MWCNT generated by the acid treatment is not sufficient for the full covering [16].

Figure 3 presents the Fourier transform infrared (FT-IR) spectroscopy spectrum of MWCNT/TiO_2 nanocomposites. The appearance of two strong absorption peaks at 2920 cm^{-1} and 2850 cm^{-1} is attributed to symmetrical and asymmetric telescopic vibration of methylene group (-CH_2-) of carbon nanotubes, which indicates that the methylene structure of carbon nanotubes is not destroyed. Two absorption peaks at 1728 cm^{-1} and 1160 cm^{-1} demonstrate the formation of carboxyl groups and carbonyl groups in the modification stage [17]. Additionally, the band in the low wavenumber around 670 cm^{-1} in the spectrum corresponds to the characteristic absorption peak of TiO_2 [18].

In order to describe the crystalline structure of the obtained nanocomposites, X-ray diffraction (XRD) spectra were involved in the characterization. As shown in Figure 4, a characteristic diffraction peak at $2\theta = 26.23^\circ$ is the typical feature of carbon nanotubes. In curve (b), the peaks at $2\theta = 25.33^\circ$ and 27.48° are attributed to anatase and rutile structure

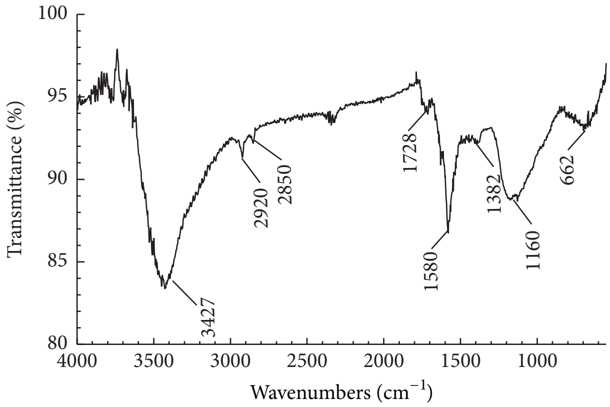
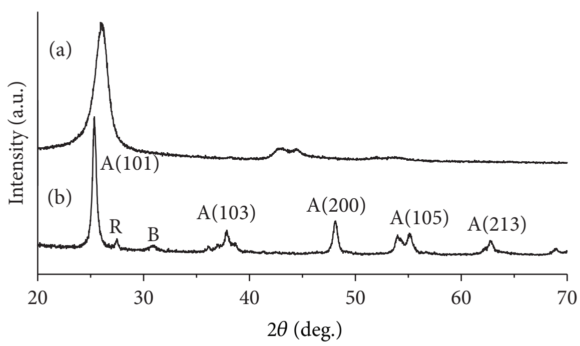


Figure 3: FT-IR spectrum of MWCNT/TiO_2 nanocomposites.



A: anatase
R: rutile
B: brookite

Figure 4: XRD patterns of MWCNT (a) and MWCNT/TiO_2 (b) nanocomposites.

of TiO_2, respectively [19]. The main characteristic diffraction peak of carbon nanotubes at 25.33° is overlapped with characteristic feature of TiO_2. Furthermore, the obtained TiO_2 particles with around 15 nm were calculated by Scherrer equation using the peak of $2\theta = 25.33°$ [20], which is consistent with TEM images.

In order to evaluate and confirm the chemical compositions of the prepared samples, differential thermal analysis and thermogravimetric (DTA-TG) analysis of carbon nanotubes and MWCNT/TiO_2 nanocomposites is shown in Figure 5. There is an obviously exothermic peak at 650°C, which is attributed to the peak of carbon nanotube. TG curve shows that a weight loss happens at 600°C and it can be supposed that the framework of carbon nanotubes was destroyed and then volatilized. The loading amount of MWCNT in the MWCNT/TiO_2 nanocomposites is about 12 wt.%, which is in agreement with the results of previous reports that the low ratio of carbon-based supporter contributes to the dispersion of catalysts on the supporters [21].

Figure 6 shows the UV-Vis spectra of the pure TiO_2, MWCNT, and MWCNT/TiO_2 nanocomposites. The absorption spectrum for the composites in 400 nm is much higher than that of pure TiO_2. The composites also have stable absorption in the region of visible light from 400 to 800 nm with slight increase of absorption intensity between 700 and 800 nm in the wavelength. The composites have good absorption properties not only in the ultraviolet area but also in the visible light region, which is of significance for us to exploit and utilize solar energy resources in the application of environmental remediation [22].

To explore the photocatalytic activity of MWCNT/TiO_2 nanocomposites, photocatalytic experiments are performed using MO as the model pollutant under irradiation of ultraviolet lamp. Figure 7 shows the relation of the irradiation time and the degradation of MO by MWCNT/TiO_2, pure TiO_2, and MWCNT. The prepared composites have higher degradation efficiency than pure TiO_2, which is comparable with the previous result that metal-doped TiO_2 (P25) has a much higher photocatalytic activity than pure TiO_2 with a degradation ratio of less than 10% under visible light and around 30% even under a 500 W high-pressure Hg lamp [23]. Within 4 h, the highest photodegradation efficiency can reach 83%. However, only about 53% and 34% of MO were degraded by using pure TiO_2 and MWCNT, respectively. The photocatalytic activities of TiO_2 were largely improved through the addition of MWCNT. The reason can be concluded as follows: firstly, MWCNT can absorb dissolved oxygen and organic matter on the outside of its surface due to the large surface area and special aperture structure; secondly, MWCNTs are eminent electronic conductors that can orderly export electrons from the surface of TiO_2 and quickly reduce electronic accumulation on TiO_2 [24, 25].

3. Experimental Section

3.1. Materials. MWCNT (diameter 10–20 nm, length 1-2 μm, purity: 98%, and ashes 0.2 wt.%) was purchased from Nano Port of Shenzhen Inc.; tetrabutyl titanate (CP) and other chemicals were purchased from Sinopharm Chemical Reagent Limited Corporation.

3.2. Purification of MWCNT. 1.0 g MWCNT were acidified in a mixed solution of concentrated sulfuric (98%) and nitric acids (65%–68%) with a volume ratio of 3 : 1 under ultrasonication at 70°C for 3 h. Then, the MWCNTs were separated by filtration, followed by the washing with distilled water until pH = 7. The purified MWCNTs were dried at 100°C and ground for the further using.

3.3. Preparation of MWCNT/TiO_2 Composites. In a typical experiment for the preparation of composites, titanium dioxide coated MWCNT was prepared by the following procedure. A precursor solution was prepared by the mixing of 5 mL of ethanol and 1.5 mL of glacial acetic acid as inhibitors. 20 mL of tetrabutyl titanate as a TiO_2 precursor was added dropwise to the solution under stirring. The resulting solution was designated as A. 20 mg of surface modified carbon nanotubes was dispersed in a mixture solution of nitric acid, deionized water, and ethanol. After ultrasonic vibration for 20 min, the obtained suspension was mixed with solution A under constant stirring until the gel formation. The gel was

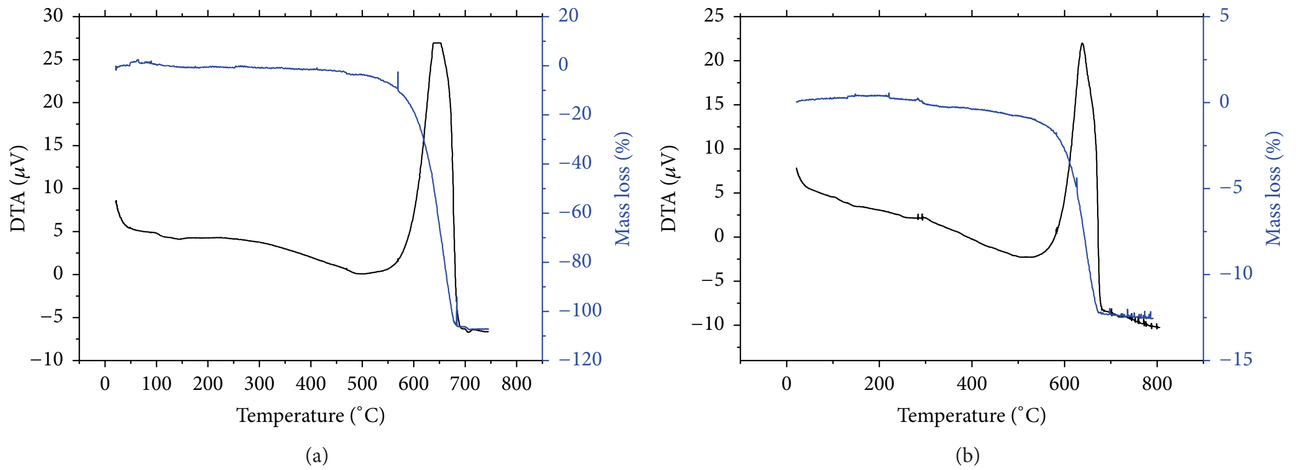


Figure 5: DTA-TG curves of MWCNT (a) and MWCNT/TiO_2 (b) nanocomposites.

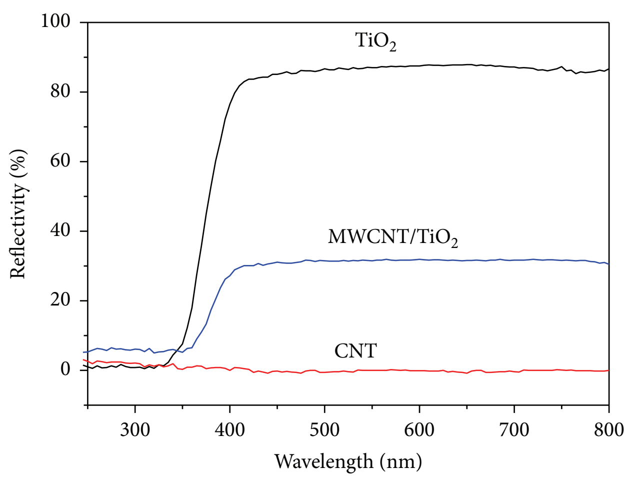


Figure 6: UV-Vis absorption spectra of pure TiO_2, MWCNT, and MWCNT/TiO_2 nanocomposites.

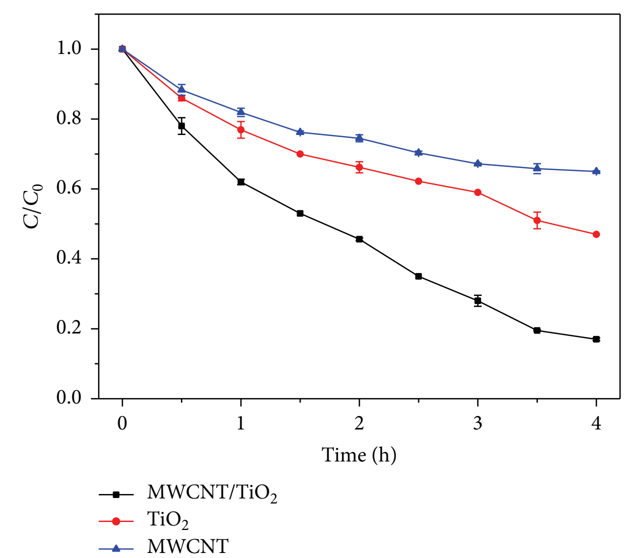


Figure 7: Effect of photocatalytic decomposition of Methyl Orange with irradiation time.

aged for 48 h at room temperature, followed by the drying in air at 105°C for about 8 h and the further grinding to a powder. The powder was then calcined at 450°C in air for 2 h to produce MWCNT/TiO_2 nanocomposites.

3.4. Photocatalytic Degradation Experiment. 200 mg nanocomposites were added into 250 mL Methyl Orange (MO) solution with concentration of 20 mg/L. After the pH value of degradation solution was adjusted to about 3, the solution under vigorous stirring was irradiated by 200 W medium mercury lamp with a main wavelength of 365 nm (Beijing Institute of Light Sources). The dispersion was kept in the dark for 60 min for dark adsorption experiments, after which photodegradation was carried out. The dark adsorption was designed to be 60 min because the adsorption results indicate that MO molecules were absorbed to saturation on the surface of catalysts (data not shown). A certain amount of aliquots (3 mL) was taken from solutions every 30 min to determine the concentration of the sample. The concentration of the MO dye was monitored by UV-Vis spectroscopy by recording the absorbance of the characteristic peak of MO at 465 nm. The change of MO concentration was regarded as the evaluation of photocatalytic activity of the composites.

3.5. Characterization and Testing. The FT-IR spectra were recorded on a Shimadzu IR-440 infrared spectrometer. The morphology of the particles was observed by JEM-1230 transmission electron microscope and JSM-5610LV scanning electron microscope. DTA-TG measurement was carried out in static air condition at room temperature. The X-ray diffraction (XRD) patterns were recorded by a PANalytical X'Pert PRO diffractometer operating at 50 kV with Cu kα radiation. The XRD intensity was measured by step scanning in the 2θ range 10°–70° with a step of 0.0167°. The UV-Vis spectra of the powder solids were measured on TU-1901 UV-Vis spectrophotometry.

4. Conclusions

In conclusion, MWCNT-based MWCNT/TiO_2 nanocomposites have higher photocatalytic activity than single TiO_2 photocatalyst for the degradation of MO aqueous solution under ultraviolet light irradiation, which is attributable to the uniform coating of TiO_2 nanoparticles and widening of absorption wavelength. This study provides an avenue for the preparation of carbon nanotube-based photocatalysts that utilize ultraviolet as an energy source in the application of environmental remediation. Researches on the composites of including both highly dispersed TiO_2 nanoparticles and highly dispersed carbon nanotubes are anticipated.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors' Contribution

The paper was written by contributions of all authors. Yanqing Wang designed the project, conducted the preparation of photocatalysts, the characterization, and its application test, analyzed the results, and was responsible for paper writing. Quanjie Wang analyzed the results and contributed importantly to the paper writing. Baorong Duan and Mengmeng Zhang analyzed the results and gave suggestions. All authors have given approval to the final version of the paper.

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