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

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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].

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 photosresponse 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].
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 $27.48^\circ$ are attributed to anatase and rutile structure.
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/TiO₂ 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 TiO₂ 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
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 nano-composites 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 k$\alpha$ radiation. The XRD intensity was measured by step scanning.
in the $\theta$ range $10^\circ$–$70^\circ$ with a step of $0.0167^\circ$. 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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