

Research Article

The Improved Photocatalytic Properties of Methylene Blue for $V_2O_3/CNT/TiO_2$ Composite under Visible Light

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Multiwall carbon nanotube (MWCNT), vanadyl acetylacetonate ($V(acac)_3$), and titanium *n*-butoxide (TNB) were used as carbon, vanadium oxide, and titanium oxide precursor to prepare $V_2O_3/CNT/TiO_2$ composite. The obtained composite was characterized by BET surface area measurement, X-ray diffraction, transmission electron microscopy, and energy dispersive X-ray analysis. In addition, we used methylene blue (MB) solution under condition of visible light irradiation to determine their photocatalytic degradation efficiency. In conclusion, the $V_2O_3/CNT/TiO_2$ composite had excellent photocatalytic degradation for MB solution under visible light.

1. Introduction

In recent years, a great deal of interest has been devoted to the photocatalytic degradation of organic water pollutants on semiconductor particles. Anatase TiO_2 has been widely employed in these studies, mainly due to its outstanding photocatalytic activity and stability. The current bottleneck with TiO_2 photocatalysis lies in its low quantum yield, which depends on the ratio of the surface charge carrier transfer rate to the electron-hole recombination [1]. The influence of various transition metal ions on the photoactivity of TiO_2 for many reactions has been studied with the aim of improving the efficiency of the photocatalytic process. Different doping effects have been reported in the literature, perhaps due to the widely varying experimental conditions for sample preparation and for the determination of photoactivity employed by different researchers [1–8]. Among the transition metal ions, vanadium ion is attractive because vanadium doping can increase carrier lifetime [2] and apparently also extend the absorption range of TiO_2 [2, 3, 8]. Vanadium-doped TiO_2 samples have been the object of many papers, including preparation and characterization, spectroscopic features, dynamics of charge-transfer trapping, and photocatalytic behavior [2–15]. Under visible light

irradiation, doping of vanadium in TiO_2 increased its photocatalytic activity [10–15].

Carbon materials can be used as support materials, due to their flexibility as support in tailoring the catalyst properties to specific needs [16]. Activated carbon has many advantages if utilized as catalyst support: resistant to acidic or basic media, stable at high temperatures in an inert atmosphere, possible to tailor its pore structure and chemical nature of the surface, and so forth [17]. However, activated carbon support also suffers several drawbacks: low mechanical stability which induces the formation of fines during operation and high tortuosity, with the presence of a large amount of micropores which could hinder the full accessibility of the reactants to the active sites. Carbon-based materials also severely suffer from their low oxidation resistance which does not allow their use at high temperature under an oxidative atmosphere [18].

Carbon nanotubes outperform activated carbon due to their exceptionally high mechanical strength, high thermal conductivity, medium to high specific surface areas, and high external surface area, which render them interesting candidates for use as catalyst supports for preparing nanosized metal and metal oxide particle catalysts [17, 19–23].

In this study, we prepared the $V_2O_3/CNT/TiO_2$ composite using multiwall carbon nanotube (MWCNT), organometallic compounds vanadyl acetylacetonate $\{V(acac)_3, VO(C_5H_7O_2)_2\}$ and titanium *n*-butoxide (TNB, $Ti\{OC(CH_3)_3\}_4$) as carbon, vanadium oxide, and titanium oxide precursors, respectively. The prepared composites were analyzed by BET surface area measurement, X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray (EDX) analysis. For determining their photocatalytic activity, the methylene blue (MB, $C_{16}H_{18}N_3S \cdot Cl \cdot 3H_2O$) solution and visible light were used as fictitious organic dye and light source.

2. Experimental

2.1. Materials. Crystalline MWCNT (95.9%) powder with diameter of 20 nm and length of 5 μm was purchased from Carbon Nano-material Technology Co., Ltd, Korea. For the oxidization the surface of MWCNT, *m*-chloroperbenzoic acid (MCPBA), used as an oxidized reagent, was also purchased from Acros Organics, New Jersey, USA. Benzene (99.5%), used as solvents, was purchased from Samchun Pure Chemical Co., Ltd (Korea). Vanadyl acetylacetonate, titanium *n*-butoxide and methylene blue were purchased from Sigma-Aldrich Chemistry (USA), Acros Organics (New Jersey, USA) and Duksan Pure Chemical Co., Ltd (Korea). The pure TiO_2 and CNT/TiO_2 photocatalysts were used as compare materials for comparison of photodegradation effect of MB solution. The pure TiO_2 , with anatase structure, is obtained from Duksan Pure Chemical Co., Ltd (Korea). The CNT/TiO_2 photocatalyst was prepared from MWCNT, and TNB and its properties and photocatalytic activity had been studied in our previous work [24].

2.2. Synthesis of $V_2O_3/CNT/TiO_2$ Composites. Firstly, we used the MCPBA to oxidize the MWCNT. 1.0 g MCPBA was dissolved in 60 mL benzene to prepare oxidizing agent. Then 0.2 g MWCNT was put into the oxidizing agent. The mixture was stirred with a magnet for 6 hours at 343 K. Then the MWCNT was dried at 373 K.

$V(acac)_3$ was dissolved in benzene to prepare 0.01 M $V(acac)_3$ -benzene solution. A certain amount of MWCNT was put into a certain volume of $V(acac)_3$ -benzene solution. Then the solutions were homogenized at 343 K for 5 hours using a shaking water bath (Lab house, Korea) with a shaking rate of 120 rpm/min. After a 5-hour reaction, the solutions were transformed to the V_2O_3/CNT gels, and these gels were heat treated at 873 K for 1 hour with a heating rate of 279 K/min. Then V_2O_3/CNT composite was prepared. Meanwhile, 2 mL of TNB was dissolved in 50 mL of benzene to get the sol. The V_2O_3/CNT composite was put into the sol, after homogenized at 343 K for 5 hours using a shaking water bath (Lab house, Korea) with a shaking rate of 120 rpm/min, the $V_2O_3/CNT/TiO_2$ gels were obtained. These gels were heat treated at 873 K for 1 hour to form the $V_2O_3/CNT/TiO_2$ composite.

2.3. Characterization. Synthesized $V_2O_3/CNT/TiO_2$ composite was characterized by various techniques. BET surface area was measured using a Quantachrome surface area analyzer (Monosorb, USA). XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were obtained at room temperature by using an X-ray generator (Shimada XD-D1, Japan) using $CuK\alpha$ radiation. TEM used to observe the surface state and structure of $V_2O_3/CNT/TiO_2$ composite was carried out by a JSM-5200 JOEL electron microscope (Japan). EDX was used to measure the elemental analysis of $V_2O_3/CNT/TiO_2$ composite. The light absorption spectra of degraded MB solution were recorded with a UV-VIS spectrophotometer (Optizen POP, Mecasys Co., Ltd, Korea) in a range of 200–750 nm.

2.4. Photocatalytic Activity of $V_2O_3/CNT/TiO_2$ Composite. The photocatalytic activity of $V_2O_3/CNT/TiO_2$ composite was taken out by decomposition of MB solution under irradiation of visible light. In an ordinary photocatalytic test performed at 25°C, 0.05 g photocatalyst was added to 50 mL of 1.0×10^{-5} mol/L MB solution and maintained in suspension by magnetic stirring. After stirring continuously in the dark for 2 hours to ensure establishment of adsorption/desorption equilibrium of MB, the suspension was irradiated by visible light (8 W, $\lambda > 420$ nm, KLD-08L/P/N, Fawoo Technology), and it was treated as the starting point ($t = 0$) of the reaction, which designated as c_0 . At specific time (30 minutes, 60 minutes, 90 minutes, and 120 minutes) intervals, a certain volume of the sample was withdrawn and centrifuged to remove the catalyst before analysis. The concentration of MB (c) solution during the photocatalytic degradation reaction was monitored through measuring the absorbance of the solution samples with UV-VIS spectrophotometer at $\lambda_{max} = 660$ nm [25, 26].

3. Results and Discussion

3.1. Characterization. The BET surface area of pristine MWCNT is 299 m^2/g , and the prepared V_2O_3/CNT and $V_2O_3/CNT/TiO_2$ composites have a decreased BET surface area 130 m^2/g and 90 m^2/g , respectively. It can be considered that the vanadium oxide and titanium oxide particles dispersed on the surface of MWCNT, which can clog the pore of MWCNT, thus decreased the surface area.

The calcinations of V_2O_3/CNT and $V_2O_3/CNT/TiO_2$ composites were performed at 873 K to obtain black-colored materials. Figure 1 shows the XRD patterns of V_2O_3/CNT and $V_2O_3/CNT/TiO_2$ composites. Diffraction peaks corresponding to the graphite, rutile, anatase, and V_2O_3 have been marked with “C,” “R,” “A,” and “V,” respectively. Both of V_2O_3/CNT and $V_2O_3/CNT/TiO_2$ composites have broad peaks at $2\theta = 25.88^\circ$ due to graphite structure of MWCNT [27]. V_2O_3/CNT composite has peaks at $2\theta = 32.9^\circ, 36.2^\circ, 41.2^\circ, 49.8^\circ, 54^\circ,$ and 65.2° due to V_2O_3 [28]. $V_2O_3/CNT/TiO_2$ composite has not only peaks at $2\theta = 36.2^\circ, 41.2^\circ, 49.8^\circ,$ and 70.6° due to V_2O_3 [28], but also has peak at $2\theta = 27.4^\circ$ due to rutile structure of TiO_2 and peak

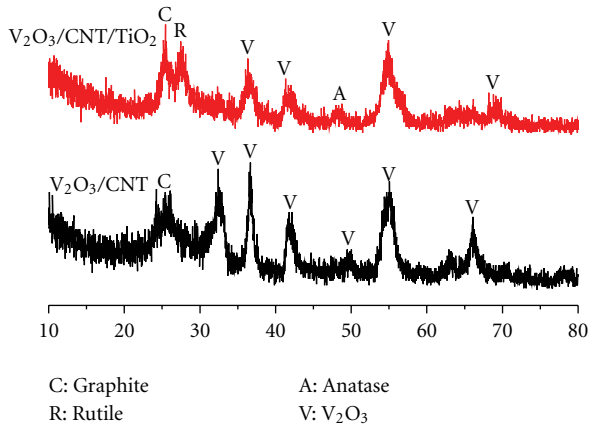


FIGURE 1: The XRD patterns of V₂O₃/CNT and V₂O₃/CNT/TiO₂ composites.

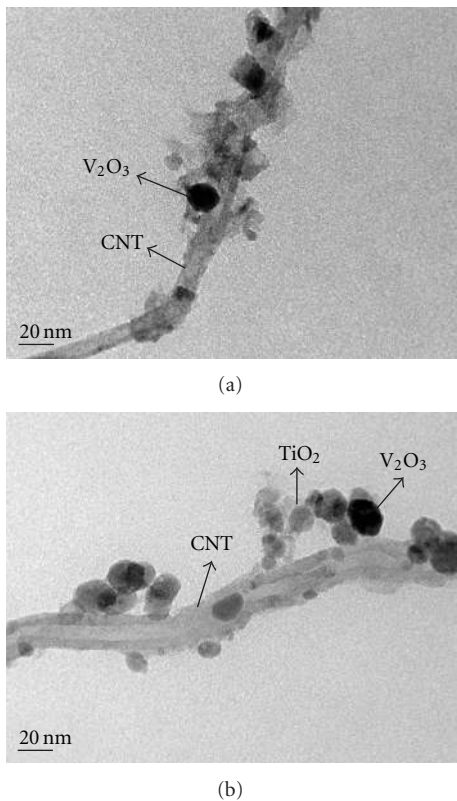


FIGURE 2: TEM images of V₂O₃/CNT (a) and V₂O₃/CNT/TiO₂ (b) composites.

at $2\theta = 48^\circ$ due to anatase structure of TiO₂ [29, 30]. It can be indicated that after heat treatment at 873 K for 1 hour, the organometallic compound precursors V(acac)₃ and TNB have been changed to V₂O₃ and TiO₂.

The TEM images in Figure 2 show the morphologies of V₂O₃/CNT and V₂O₃/CNT/TiO₂ composites. Figure 2(a) shows that, when MWCNT were reacted with V(acac)₃, the V₂O₃ particles deposited are spherical with the average diameters about 20 nm. Figure 2(b) shows the morphologies

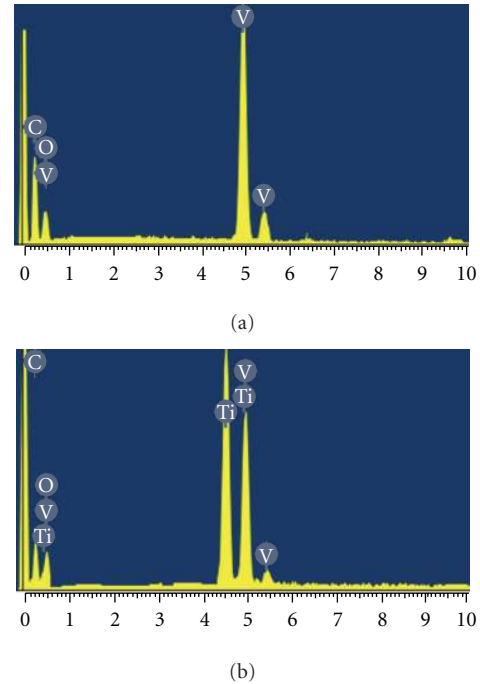


FIGURE 3: EDX elemental microanalysis of V₂O₃/CNT (a) and V₂O₃/CNT/TiO₂ (b).

of the V₂O₃/CNT/TiO₂ composite. TiO₂ particles with some agglomerates disperse on the surface of MWCNT together with V₂O₃ particles. Figure 3 shows the EDX microanalysis of V₂O₃/CNT and V₂O₃/CNT/TiO₂ composites. The elements C, V, and O can be found in V₂O₃/CNT composite, and the elements C, V, Ti, and O can be found in V₂O₃/CNT/TiO₂ composite. It can be indicated that the V₂O₃/CNT and V₂O₃/CNT/TiO₂ composites were successfully prepared in this study.

3.2. Degradation of MB Solution. As described above, the degradation process of MB solution could fall into two parts: adsorption in dark for 120 minutes and irradiation under visible light for 120 minutes. The percentage of MB solution degraded by adsorption effect after 120 minutes in dark is shown in Figure 4. The BET surface area is mainly influenced on adsorption effect. According to the results of BET surface area, the V₂O₃/CNT composite has larger surface area than the V₂O₃/CNT/TiO₂ composite has. So the adsorption capacity of V₂O₃/CNT composite is larger than that of V₂O₃/CNT/TiO₂ composite, as showed in Figure 4.

The photocatalytic degradation efficiency is calculated by comparing its concentration before and after irradiation under visible light by different time, using the formula

$$\frac{(c_0 - c)}{c} \times 100, \quad (1)$$

where c_0 and c are the initial and residual concentration of MB solution, respectively. The relative concentration of degraded MB solution by different samples after irradiation under visible light by different time is showed in Figure 5.

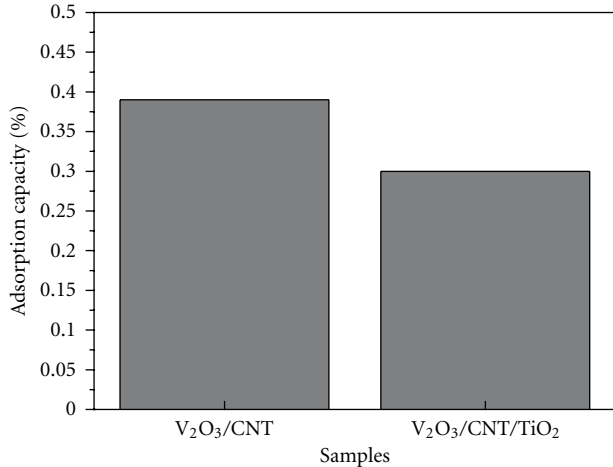
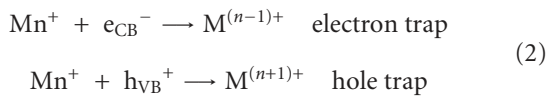


FIGURE 4: The adsorption capacity of V₂O₃/CNT and V₂O₃/CNT/TiO₂ for MB solution after 120 minutes in dark.

As shown in Figure 5, the pure TiO₂ has almost no photocatalytic degradation activity under irradiation of visible light. The V₂O₃/CNT and CNT/TiO₂ composites have almost same photocatalytic degradation activity, which can degrade 40% MB solution after irradiation of visible light for 120 minutes. In our previous works [24, 31, 32], it has been indicated that the MWCNT could act the photoabsorption character to absorbed photons from irradiation light. These photons can transfer to the conduction bands (CBs) of V₂O₃ and TiO₂, and increase the amount of photoelectron (e⁻) in the conduction bands (CBs) of V₂O₃ and TiO₂, thus increasing the photocatalytic activities of V₂O₃ and TiO₂ under irradiation of visible light. The V₂O₃/CNT/TiO₂ composite has more excellent photocatalytic degradation activity under irradiation of visible light than any other samples, which can degrade 70% MB solution after irradiation of visible light for 120 minutes. Apart from the factor of MWCNT, the enhanced photocatalytic degradation activity can be affect by the vanadium which can lead the absorption band of V₂O₃/CNT/TiO₂ composite shifted to the visible light region [2, 3] and their charge trapping effect [33]. The electron and hole traps are shown as follows:



The trapped electron may thus be readily transferred to oxygen molecule to form a superoxide radical anion (O₂^{·-}). In addition, the trapped hole can be easily transferred to hydroxyl anion adsorbed on the surface forming hydroxyl radical (OH[·]), or it can also be transferred to adsorbed dye molecule for form a dye radical.

4. Conclusions

We used MWCNT as basic material and then reacted with organometallic compounds V(acac)₃ and TNB to prepare V₂O₃/CNT/TiO₂ composite. In a comparison with BET

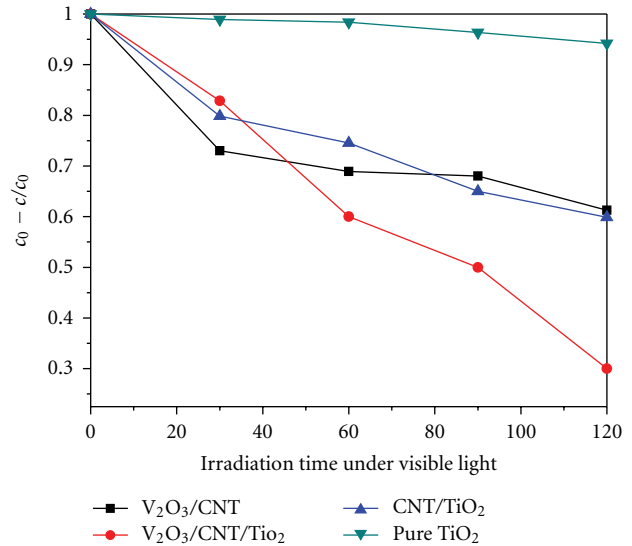


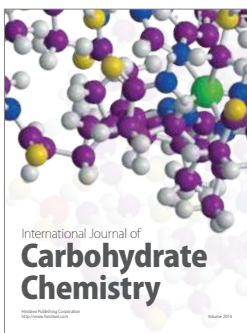
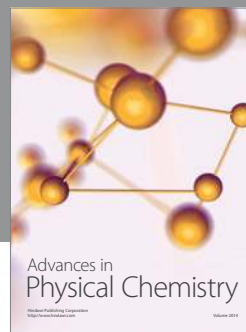
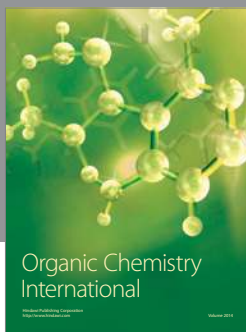
FIGURE 5: The relative concentration of MB solution degraded by different samples after irradiation under visible light.

surface area of pristine MWCNT, V₂O₃/CNT/TiO₂ composite has decreased surface area. From XRD patterns, the V₂O₃ structure and both of rutile and anatase structure of TiO₂ could be observed. TEM images showed that TiO₂ particles with some agglomerates disperse on the surface of MWCNT together with V₂O₃ particles. The elements C, V, Ti, and O could be found in V₂O₃/CNT/TiO₂ composite from EDX data. The V₂O₃/CNT/TiO₂ composite showed the most excellent photocatalytic degradation activity of MB solution under irradiation of visible light, since the MWCNT could act as the photoabsorption character to absorbed photons from irradiation light and the vanadium could lead the absorption band of V₂O₃/CNT/TiO₂ composite shifted to the visible light region and charge trapping effect of vanadium.

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