



Prevenient dye-degradation mechanisms using UV/TiO₂/carbon nanotubes process

Chao-Yin Kuo*

Department of Safety Health and Environmental Engineering, National Yunlin University of Science and Technology, 123, Section 3, University Road, Douliu, Yunlin, Taiwan

ARTICLE INFO

Article history:

Received 29 January 2008
Received in revised form 27 April 2008
Accepted 24 June 2008
Available online 1 July 2008

Keywords:

Carbon nanotubes
Titanium dioxide
Photocatalytic oxidation
Azo dye

ABSTRACT

Photocatalysis research heavily emphasizes increasing photo-efficiency. This study presents the application of carbon nanotubes (CNTs) to increase the photocatalytic activity of TiO₂. It elucidates the effect of CNTs dose on the decolorization efficiency of aqueous azo dye, C.I. Reactive Red 2 (RR2), determines the effects of SO₄²⁻ formation and removal of total organic carbon (TOC), and measures the effects of various ultraviolet wavelengths. Scanning electron microscopy was used to elucidate the mixing phenomenon and the size of TiO₂ and CNTs; X-ray diffraction was used to determine crystallinity; a BET meter was used to measure surface area and a spectrophotometry was used to determine the decolorization of RR2. Experimental results indicated significant effects of photodegradation on the combination of TiO₂ with CNTs and electron transfer is higher for 410 nm irradiation than for 365 nm, revealing that solar light can be used. The electron transfer in the TiO₂/CNTs composites reduced the electron/hole recombination and increased the photon efficiency and the prevenient dye-degradation mechanisms using UV/TiO₂/CNTs were established.

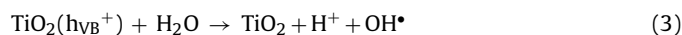
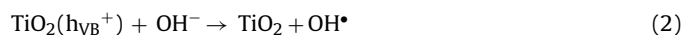
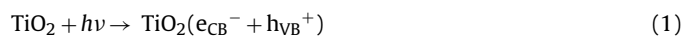
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Azo dyes, which contain at least one azo bond, are among the most widely used synthetic dyes and typically are major pollutants in dye wastewaters [1,2]. Owing to their toxicity and slow degradation, they are categorized as environmentally hazardous materials. Treatment costs are large for most textile factories, explaining the need to develop more efficient and economic methods, which consume less chemical and energy. Conventional treatments of dye effluents include biological oxidation and adsorption [1,2]. Although less costly than other procedures, biological treatment is not used in decolorization because the dyes are toxic. Adsorption onto activated carbon transfers most of the contaminant from the wastewater to the solid phase [1].

Photocatalytic oxidation is an alternative means of completely degrading azo dyes [1–4]. The following mechanism is widely accepted for the photodegradation of organic species by UV/TiO₂ [5]. Most advanced oxidation processes (AOPs) involve the generation of a very powerful and non-selective oxidizing agent, the hydroxyl radical (OH•), to destroy hazardous pollutants. Photogenerated holes are formed after TiO₂ particles when irradiated with

UV light (Eq. (1)). Hydroxyl radicals are generated mainly in the oxidation of OH⁻ or H₂O by these photogenerated holes (Eqs. (2) and (3)), and are principally responsible for the destruction of organic species. Oxygen is primarily used as an efficient electron trap (Eq. (4)), preventing the recombination of electrons and photogenerated holes.



However, the use of semiconductors as photocatalysts is limited mainly to the recombination of the generated photo-holes and photo-electrons. Photocatalysis involves the oxidation of a chemical by photo-holes from the semiconductor, so every recombination event involves the loss of holes that might otherwise have promoted degradation. Therefore, the vectorial transfer of photogenerated electrons and holes between the valence and conduction bands of semiconductors is important to photocatalysis. Hence, current photocatalysis research highly prioritizes improving the separation characteristics and photo-efficiency.

Various methods have been reported to increase photocatalytic efficiency [3,6–13]. These include increasing the surface area of

* Tel.: +886 5 534 5601x4423; fax: +886 5 531 2069.

E-mail addresses: kuocy@ms35.hinet.net, kuocy@yuntech.edu.tw.

TiO₂, the generation of defect structures to induce space-charge separation, and the modification of TiO₂ with metal(s) or other semiconductor(s) [3,6–9]. Another method that could increase the photocatalytic efficiency of TiO₂ is to add a co-sorbent such as silica, alumina, zeolites or clay, but observations do not support this suggestion [10–13]. Accordingly, the development of new materials for modifying TiO₂ is urgently required to increase the photocatalytic activity of TiO₂ for treating organic pollutants.

Carbon nanotubes (CNTs) have attracted considerable attention since their discovery [14] because they have a special structure, extraordinary mechanical and unique electronic properties and can be semiconducting [15]. Recently, researchers found that CNTs are efficient adsorbents of copper and dyes [16–18]. Furthermore, researchers have shown that CNTs increase the adsorption and photocatalytic activity of TiO₂ [19,20]. Accordingly, CNTs can be used as a promising material for environmental cleaning. The surface area of CNTs is much less than that of activated carbon. Therefore, adsorption is not the only factor for enhancing the photocatalytic activity of TiO₂ by CNTs. CNTs are 1D carbon-based ideal molecules with the nanocylinders, which can conduct electricity at room temperature with essentially no resistance. This phenomenon is known as ballistic transport [21,22], by which the electrons are considered to move freely through the structure, without any scattering from atoms or defects. While the electrons formed by the UV irradiation migrate to the surface of TiO₂, they are easily transported in CNTs which are bound with TiO₂. Hence, the high rate of electron/hole pair recombination, which reduces the quantum yield of the TiO₂ process, declines. Accordingly, the application of CNTs to establish the convenient dye-degradation mechanisms is proposed.

The aims of this study are as follows: (i) determine the decolorization efficiency of dye at various reaction times; (ii) elucidate the effect of CNTs dose on decolorization efficiency; (iii) determine the effects of SO₄²⁻ formation and degradation of total organic carbon (TOC); (iv) measure the effects of ultraviolet wavelength; and (v) establish the convenient dye-degradation mechanisms using UV/TiO₂/CNTs.

2. Materials and methods

2.1. Materials and analysis of TiO₂ and CNTs

TiO₂ mainly of the anatase type with a specific surface area of 2 m²/g, was obtained from the Merck Co. CNTs were formed by the pyrolysis of methane gas on particles of Ni by chemical vapor deposition (CVD) and the CNTs used herein were multi-walled carbon nanotubes (CBT, MWNTs-2040). The parent compound, C.I. Reactive Red 2 (RR2), was obtained from the Aldrich Chemical Company. The formula and molecular weight of RR2 are C₁₉H₁₀Cl₂N₆Na₂O₇S₂ and 615 g/mol, and its maximum light absorption wavelength (λ_{\max}) is 538 nm. The pH of the solution was controlled by adding HCl and NaOH using an automatic titrator. All solutions were prepared from deionized water (Milli-Q) and reagent-grade chemicals.

Scanning electron microscopy (SEM) (HITACHI S3000N) revealed the mixing phenomenon and the size of TiO₂ and CNTs. The crystallinity of the TiO₂ and CNTs was elucidated by X-ray diffraction (BRUKER AXS D8-Advanced). Table 1 presents the surface areas of CNTs, TiO₂, and the mixture of TiO₂ and CNTs with the weight ratio 10:1. BET surface areas (S_{BET}) and porous structure were determined using a Micromeritics ASAP 2010 nitrogen adsorption apparatus (Norcross, USA). Meanwhile, the obtained solid TiO₂ and mixed TiO₂ plus CNTs were detected using a BET adsorption apparatus to measure the surface property of the recovered photocatalysts after degradation.

Table 1
Surface area of the various catalysts

Catalysts	Material abbreviations	S_{BET} (m ² /g)
TiO ₂	T	2.18
CNT	C	106.90
TiO ₂ :CNT = 10:1 ^{a,c}	TC1	16.59
TiO ₂ :CNT = 10:1 ^b		15.67
TiO ₂ :CNT = 10:2 ^a	TC2	20.33
TiO ₂ :CNT = 10:2 ^b		18.98
TiO ₂ :CNT = 10:3 ^a	TC3	27.33
TiO ₂ :CNT = 10:3 ^b		25.51

^a Before photoreaction.

^b After photoreaction.

^c The weight ratio of TiO₂ and CNTs.

2.2. Photoreactor, procedures and analyses

Decolorization experiments were performed in a 3L hollow cylindrical glass reactor. The inner tube was made of quartz with an 8 W and 254, 365 and 410 nm UV lamp (Philips) inside it as the source of irradiation. All of the systems were controlled at pH 7, 25 °C, 7–9 mg/L dissolved oxygen and stirred continuously at 300 rpm. The RR2 and TiO₂ concentrations were 20 mg/L and 0.5 g/L in all experiments. The suspended solids in the UV/TiO₂/CNTs system were separated by centrifugation at 5000 rpm for 10 min, and then filtered through a 0.22 μm filter (Millipore). Vaporization, adsorption and direct photolysis were conducted to compare the decolorization efficiency of RR2 across all of these reactions.

The effect of CNTs on the photocatalytic activity of TiO₂ was studied by adding TiO₂ and CNTs in weight ratios of 10:1, 10:2 and 10:3 to solution, which contained 20 mg/L of RR2. Before the UV light lamp, with wavelengths of 254, 365 and 410 nm, at an intensity of 4 mW/cm² was turned on, the above aqueous dispersions were mixed in the dark for 60 min, as part of a hydration process. During the photocatalytic process, at given time intervals, 5 mL sample was collected and centrifuged to enable the colorimetric determination of dye concentration. Decolorization of RR2 was detected using a spectrophotometer (HACH DR/4000U) at 538 nm and the concentration was determined from the calibration curve using Beer–Lambert's law. The decolorization efficiency was calculated from the difference between the dye concentrations before and after the experiment. Ionic chromatography (Dionex DX-120) was adopted to determine concentrations of sulfate during decolorization.

The effects of CNTs on the TOC of the dye solution with TiO₂ and the mixture of TiO₂ and CNTs in a weight ratio of 10:1 as photocatalysts were determined under experimental conditions similar to those under which decolorization was determined. Following photocatalytic degradation, the suspensions were centrifuged and then filtered through a 0.22 μm filter (Millipore). The filtrates were used to detect TOC content using a Systematic-1010 TOC analyzer and the mineralization of RR2 was identified by the reduction in TOC.

3. Results and discussion

3.1. Characteristics of TiO₂ and CNTs

Before the effect of photodegradation was examined, background experiments, including adsorption and UV light direct degradation were conducted. The results indicated that the maximum adsorption effect of RR2 after 180 min was about 5% in the TC3 process. Furthermore, the results revealed no significant (less than 3%) direct degradation of RR2 after 180 min. The adsorption and direct photolysis of RR2 were tested at pH 7 and given that no signif-

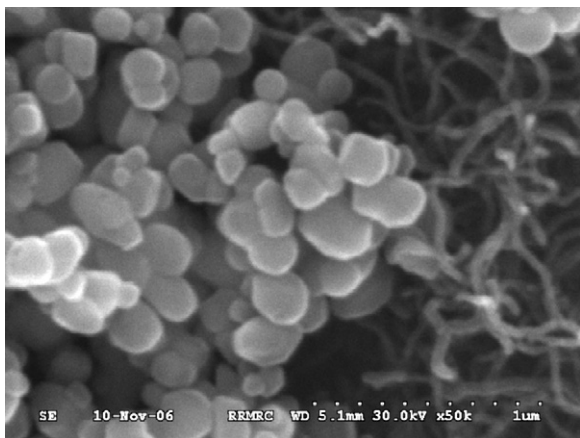


Fig. 1. SEM image of TiO_2 photocatalysts mixing CNTs (TC1, $\times 50,000$).

icant degradation occurred during adsorption or direct degradation by UV light, the disappearance of RR2 was caused by photocatalytic oxidation.

The specific surface areas of TiO_2 and TiO_2 mixed with CNTs as TC1, TC2 and TC3 were calculated to be 2.18–106.90 m^2/g using the BET method. Those of TiO_2 mixed with CNTs as TC1, TC2 and TC3 were calculated before and after photocatalytic oxidation, as presented in Table 1. The results indicated that the specific surface areas of TC1, TC2 and TC3 differed and were related to the weight ratios 10:1, 10:2 and 10:3, respectively. Moreover, before photocatalytic oxidation, the specific surface areas of TC1, TC2 and TC3 exceeded those after photocatalytic oxidation. The difference was not evident because the effect of the photocatalytic oxidation was more important than that of the adsorption. The SEM images of TiO_2 mixed with CNTs indicated that TiO_2 and CNTs were orbicular and cylindrical. The main external diameters of TiO_2 and CNTs were 80–100 nm and 20–30 nm (Fig. 1), so the schematic mechanism of the photocatalytic activity of TiO_2/CNTs should be as shown in Fig. 2. Therefore, the crystal structure of the TC1 was analyzed using an X-ray diffractometer. The TC1 was first vacuum dried at 120 °C and then scanned from 20 to 80° at a voltage of 40 kV. The scan results revealed the anatase crystalline form of TiO_2 and an unknown form of CNTs (Fig. 3).

3.2. Preventive degradation mechanisms

Fig. 4 plots the photodegradation of T, TC1, TC2 and TC3 in UV-254 nm. According to this figure, the enhancements of photoactivity were significant in TC1, TC2 and TC3 processes, and especially in

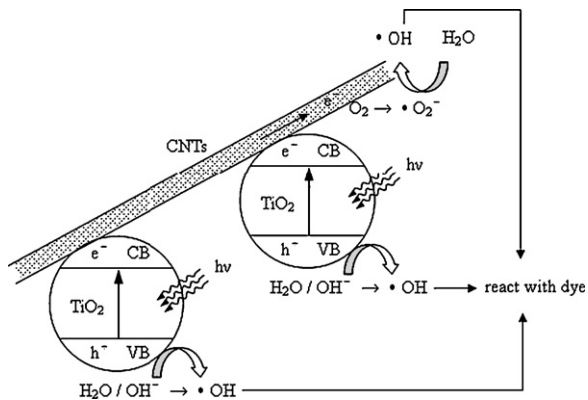


Fig. 2. Illustration of a preventive mechanism in TiO_2/CNTs .

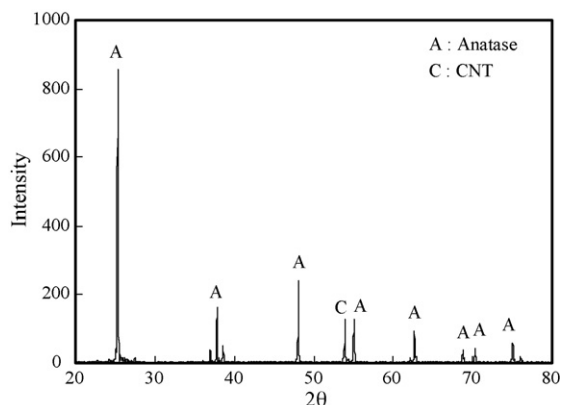


Fig. 3. XRD spectrum performed on TiO_2 photocatalysts mixing CNTs (TC1).

TC1. The photocatalytic degradation of RR2 left 2% residue after 150 min of photoreaction when TC1 was used, but 20% residues without CNTs. The e^- transport capacity CNTs has been extensively used for the composition with conjugated polymers in light-emitting diodes, field effect transistors and photovoltaic devices [19,20]. Photo-induced charge transfer occurs in the electronic interaction between polymer chains and CNTs [20]. Therefore, with the assistance of CNTs, the recombination of electron/hole excited by TiO_2 under UV light can be detrimental.

Since the effects of photodegradation in TC1, TC2 and TC3 were significant, a strong interaction occurred between TiO_2 and CNTs and they connected well with each other. Then, electron transfer occurs in the TiO_2/CNTs composites [19,20], reducing the electron/hole recombination and increasing the photon efficiency. The results concerning the effect of CNT concentration demonstrated that enhancements in photoactivity were most significant in the TC1 process because TC2 and TC3 obstructed the light. Although many CNTs can greatly inhibit electron/hole recombination, samples TC2 and TC3 cannot efficiently absorb UV light, reducing electrons and holes production. Hence, the photocatalytic activities of the TC2 and TC3 photocatalysts were lower.

Fig. 5, referring to various 410 nm/ TiO_2/CNTs processes, indicated that the effect of photoactivity in a TiO_2/CNTs process was stronger than that in the TiO_2 -only process. The electron transfer also happens in visible light with a wavelength of 410 nm, such that solar light is useable. In visible light with a wavelength of 410 nm,

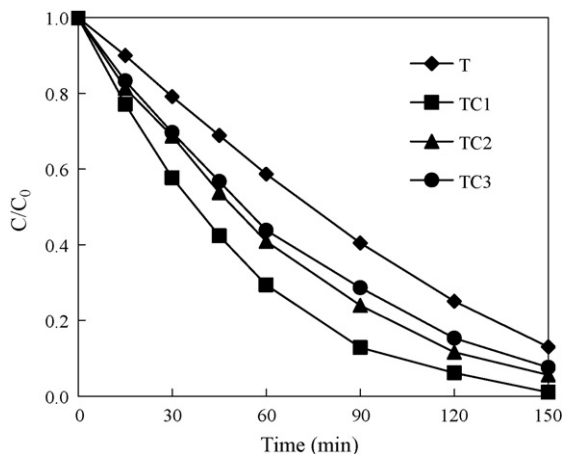


Fig. 4. The effect of TiO_2/CNT different weight ratios in the ultraviolet 254 nm (RR2 = 20 mg/L, TiO_2 = 0.5 g/L, pH 6.0–6.2, temperature = 25 ± 2 °C, O_2 = 7.8–8.2 mg/L).

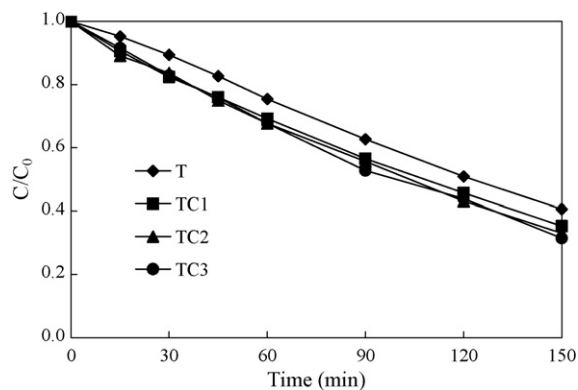
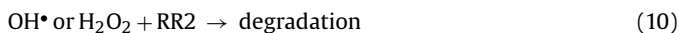


Fig. 5. The effect of TiO₂/CNT different weight ratios in the ultraviolet 410 nm (the same as Fig. 4).

the photocatalytic degradation of RR2 left 40% residue after 150 min of photoreaction when TC1, TC2 and TC3 were used. Accordingly, the results demonstrate that the duration of photocatalytic degradation must exceed 150 min and the effects of e^- transfer did not vary among TC1, TC2 and TC3 when visible light with a wavelength of 410 nm was used.

The adequate mechanism of photodegradation by UV/TiO₂/CNTs is given by the following equations. When an electron is transferred from TiO₂ to CNTs, Eqs. (5)–(7) apply. As more electrons are transferred from TiO₂ to CNTs, the e^-/h^+ recombination is reduced further. Furthermore, when hydrogen ions or water molecules are present, Eqs. (9) and (10) happen. In Eq. (6) more oxygen reacted with electrons in CNT to yield excited oxyhydrogen radicals (OH[•]). If oxygen is limited, recombination of photoproduced electrons and holes in TiO₂ substantially reduced the efficiency of photocatalytic reactions.



Meanwhile, when CNTs are composite with TiO₂, the absorption edge shifts to a shorter wavelength, and the band gaps, as determined by Yu et al. [20] for TiO₂ and TiO₂/CNTs are 3.17 and 3.54 eV, respectively. A larger band gap corresponds to more powerful redox ability [23] because the increase in the band gap increases the oxidation–reduction potential [24]. Moreover, Yu et al. [20] revealed that chemisorbed water on the surface of TiO₂/CNTs composite provides more hydroxyl groups, increasing photocatalytic activity. This increase of photocatalytic activity was also observed herein. Fig. 2 schematically depicts a convenient mechanism of photocatalytic activity of TiO₂/CNTs.

3.3. Intermediate formation and mineralization

Fig. 6 plots the treatment efficiencies of T and TC1 photocatalysts in the formation of sulfate and the degradation of TOC. RR2, of molecular formula C₁₉H₁₀Cl₂N₆Na₂O₇S₂, contains function groups of sulfite, and photocatalytic oxidation broke the bonds between sulfite and RR2. The experimental results show that the photodegradation of aqueous RR2 using T photocatalyst did not affect photocatalytic activity, because the removal of TOC was less

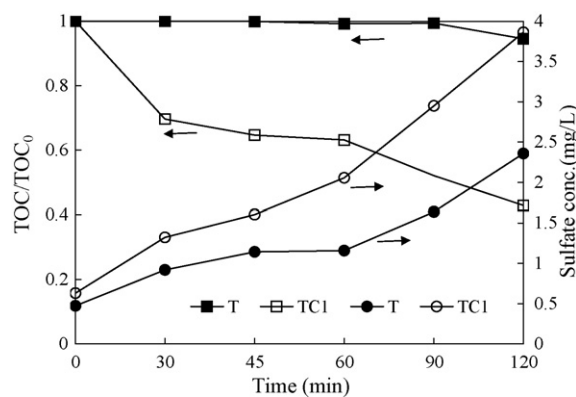


Fig. 6. Comparison of formation of sulfate and degradation of TOC with photocatalysts in the ultraviolet 254 nm (the same as Fig. 4).

than 10% over a reaction time of 120 min. However, the degradation efficiency of aqueous RR2 using TC1 photocatalyst revealed significant photocatalytic activity in TOC degradation over a reaction time of 120 min. In TC1 photocatalyst, more electrons were transferred to CNTs, yielding excited OH[•] radicals. The formation of sulfate using TC1 photocatalyst with a reaction time of 120 min was markedly higher than that using T photocatalyst. Therefore, the newly modified titanium dioxide with added CNTs exhibited increased photocatalytic activity, especially at a weight ratio of 10:1.

The UV/TiO₂/CNTs process destroyed organic pollutants and generated intermediates. In this study, the mass balance of the reactant is determined from the growth of the intermediate. The amount of intermediate carbon was calculated using:

$$\text{Int}_{\text{asC}} = \text{TOC}_{\text{asC}} - \text{RR2}_{\text{asC}} \quad (11)$$

$$\text{TIC}_{\text{asC}} = \text{C}_T - \text{TOC}_{\text{asC}} \quad (12)$$

where Int_{asC} denotes the intermediate carbon quantity; RR2_{asC} represents the quantity of azo dyes of RR2 as carbon, TIC_{asC} represents the amount of carbon in the form of total inorganic carbon, and C_T is the theoretical amount of total carbon.

In Fig. 7, the mass balance using carbon in the UV-254 nm/TC1 system indicated that the intermediate was formed late after 30 min of irradiation, but that the concentration of RR2 rapidly declined because the degradation of RR2 was more than 20% within initial 30 min and total inorganic carbon rapidly increased in the same time. Although the amounts of intermediate increased after 30 min of irradiation and the results indicated that some interme-

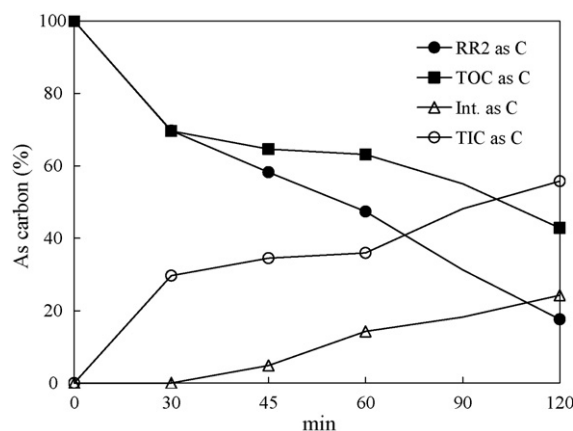


Fig. 7. Calculating the formation of intermediate products as carbon percentage with TC1 photocatalyst in the ultraviolet 254 nm (the same as Fig. 4).

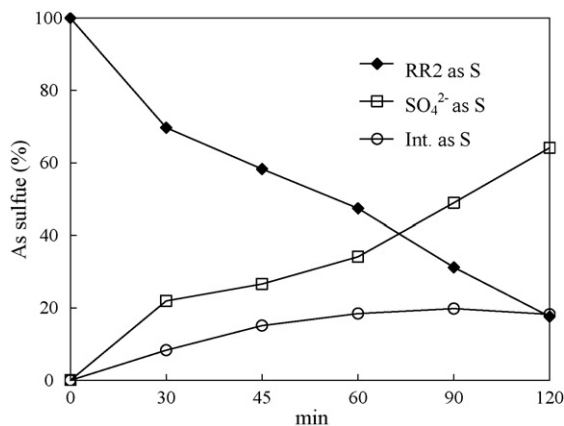


Fig. 8. Mass balance of intermediate products as total sulfur percentage with TC1 photocatalyst in the ultraviolet 254 nm (the same as Fig. 4).

diates needed more time to react, total inorganic carbon increase was more than 20% over a reaction time of 120 min. Hence, the photodegradation reaction in a UV-254 nm/TC1 system degraded not only the carbon functional group but also destroyed the RR2 to generate inorganic carbon. Therefore, the photodegradation reaction can be extended to over 120 min, reducing the amount of intermediate as inorganic carbon is formed.

In this study, the mass balance as sulfur in the reactant is determined from the increase in sulfate concentration. The amount of sulfuric intermediate was calculated using:

$$\text{Int}_{\text{asS}} = \text{RR2}_{\text{asS}} - \text{SO}_4^{2-}_{\text{asS}} \quad (13)$$

where Int_{asS} denotes the intermediate sulfuric quantity; RR2_{asS} represents the quantity of azo dyes of RR2 as sulfur. In Fig. 8, the mass balance using sulfur in the UV-254 nm/TC1 system demonstrated that the intermediate was formed slowly, less than 20%, during irradiation, but that the RR2 in the form of sulfur rapidly decreased, more than 80%, during the reaction time. In addition, formation of sulfate was shown to be rapid, more than 60%, over a reaction time of 120 min. The results indicated that the photocatalytic oxidation in a UV-254 nm/TC1 system easily degraded the sulfite functional group, destroying RR2 molecular structure and thereby forming sulfate.

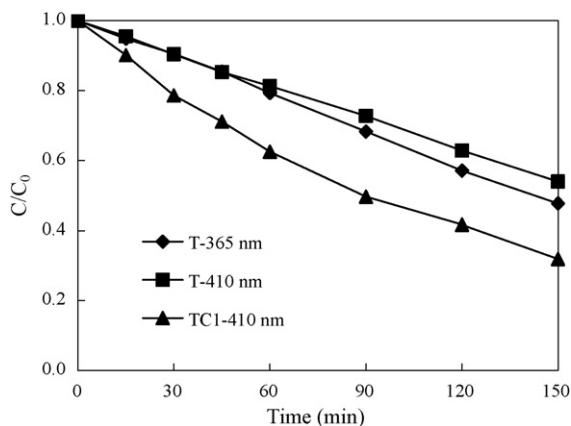


Fig. 9. The effect of photocatalytic activity in the different ultraviolet wavelengths (the same as Fig. 4).

Table 2

The reaction rate constants in the different parameters condition

Ultraviolet wavelength (nm)	Materials abbreviations	Doses (g/L)		k (min^{-1})	R^2
		TiO ₂	CNT		
254	T	0.5	0	0.0133	0.9694
	TC1	0.5	0.05	0.0169	0.986
365	T	0.5	0	0.0050	0.9849
	TC1	0.5	0.05	0.0082	0.9768
410	T	0.5	0	0.0066	0.9974
	TC1	0.5	0.05	0.0075	0.9981

3.4. Comparison effect of UV and visible light and determination of reaction rate

In Fig. 9, with respect to the T and TC1 processes in 365 and 410 nm irradiation, the effect of photoactivity in TC1-410 nm process was the better than that of the T-365 nm process. Electron transfer is higher for 410 nm irradiation than for 365 nm. Irradiating at 410 nm leads to TC1 degrading 60% of the dye than the TiO₂ irradiated at 365 nm which was only able to degrade 40% of the dye. Therefore, the results reveal that the e^- was transferred in visible light with a wavelength of 410 nm. Fig. 2 schematically depicts a proposal for photocatalytic activity of TiO₂/CNTs.

The photodegradation experiments that involve UV irradiation of the azo dye solutions exhibit pseudo-first-order kinetics with respect to the concentration of dyestuff in the bulk solution C ,

$$\frac{dC}{dt} = -k_{\text{app}}C \quad (14)$$

where k_{app} is the apparent reaction rate constant. Integrating this equation under the constraint $C=C_0$ at $t=0$, where C_0 is the initial concentration of RR2, yields a relation from which the value of k_{app} can be calculated. Comparing the k_{app} values of the photodegradation of RR2 with T and TC1 in Table 2 indicates that the photolysis of RR2 using a T photocatalyst in 254, 365 and 410 nm irradiation was lower than that using a TC1 photocatalyst.

4. Conclusion

In this study, the effects of photodegradation in TiO₂ combined with CNTs were significant; an electron transfer occurs in the TiO₂/CNTs composites, reducing the electron/hole recombination and increasing photon efficiency. The prevention mechanism of photodegradation by UV/TiO₂/CNTs was established in this study. Electron transfer is higher for 410 nm irradiation than for 365 nm. Therefore, the results revealed that the electron was transferred in visible light with a wavelength of 410 nm, and established the usability of the solar light. The results of mass balance concerning the amount of sulfur in the reactant, determined from the increase in the sulfate concentration, show that the photocatalytic oxidation in a UV-254 nm/TC1 system degraded the sulfite functional group easily because it destroyed RR2 molecular structure. Based on all of these results, CNTs not only prevent the recombination of electron/hole pairs, but also may increase the surface area, increasing the number of hydroxyl groups on the surface of the TiO₂/CNTs. Therefore, adding a suitable amount of CNTs can greatly improve the photocatalytic activity of TiO₂.

Acknowledgements

The author would like to thank Ms. Wong, Liao and Mr. Ying for helping in some experiments and the National Science Council of the Republic of China for financially supporting this research under Contract no. NSC 96-2622-E-224-006-CC3.

References

- [1] C.Y. Kuo, Desorption and re-adsorption of carbon nanotubes: comparisons of sodium hydroxide and microwave irradiation processes, *J. Hazard. Mater.* 152 (2008) 949–954.
- [2] C.H. Wu, C.L. Chang, C.Y. Kuo, Decolorization of Procion Red MX-5B in electrocoagulation (EC), UV/TiO₂ and ozone related systems, *Dyes Pig.* 76 (2008) 187–194.
- [3] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂, *Sol. Energy Mater. Sol. Cells* 77 (2003) 65–82.
- [4] C.H. Wu, C.Y. Kuo, C.L. Chang, Decolorization of azo dyes using catalytic ozonation, *React. Kinet. Catal. Lett.* 91 (2007) 161–168.
- [5] I.K. Konstantinou, T.A. Albanis, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—a review, *Appl. Catal. B* 49 (2004) 1–14.
- [6] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti, H. Hidaka, Exploiting the interparticle electron transfer process in the photocatalysed oxidation of phenol, 2-chlorophenol and pentachlorophenol: chemical evidence for electron and hole transfer between coupled semiconductors, *J. Photochem. Photobiol. A* 85 (1995) 247–255.
- [7] J.C. Yu, L.Z. Zhang, J.G. Yu, Rapid synthesis of mesoporous TiO₂ with high photocatalytic activity by ultrasound-induced agglomeration, *New J. Chem.* 26 (2002) 416–420.
- [8] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar/UV-induced photocatalytic degradation of three commercial textile dyes, *J. Hazard. Mater.* 89 (2002) 303–317.
- [9] C.Y. Kuo, H.U. Lin, Effect of coupled semiconductor system treating aqueous 4-nitrophenol, *J. Environ. Sci. Health: Part A* 39 (2004) 2113–2127.
- [10] C.Y. Kuo, Enhancement of photocatalytic activity in UV-illuminated tin dioxide/aluminum dioxide system in aqueous 4-nitrophenol, *React. Kinet. Catal. Lett.* 92 (2007) 337–343.
- [11] H. Yahiro, T. Miyamoto, N. Watanabe, H. Yamaura, Photocatalytic partial oxidation of *a*-methylstyrene over TiO₂ supported on zeolites, *Catal. Today* 120 (2007) 158–216.
- [12] H.H. Patterson, R.S. Gomez, H. Lu, R.L. Yson, Nanoclusters of silver doped in zeolites as photocatalysts, *Catal. Today* 120 (2007) 168–173.
- [13] A. Kuleyin, Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite, *J. Hazard. Mater.* 144 (2007) 307–315.
- [14] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56–58.
- [15] T.W. Ebbesen, H.J. Lezee, H. Hiura, J.W. Neentt, H.F. Ghaemi, T. Thio, *Nature* 382 (1996) 54.
- [16] X. Peng, Y. Li, Z. Luan, Z. Di, H. Wang, B. Tian, Z. Jia, Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes, *Chem. Phys. Lett.* 376 (2003) 154–158.
- [17] Y.H. Li, Y. Zhu, Y. Zhao, D. Wu, Z. Luan, Different morphologies of carbon nanotubes effect on the lead removal from aqueous solution, *Diamond Relat. Mater.* 15 (2006) 90–94.
- [18] C.H. Wu, Studies of the equilibrium and thermodynamics of the adsorption of Cu²⁺ onto as-produced and modified carbon nanotubes, *J. Colloid Interface Sci.* 311 (2007) 338–346.
- [19] Y. Yu, J.C. Yu, C.Y. Chan, Y.K. Che, J.C. Zhao, L. Ding, W.K. Ge, P.K. Wong, Enhancement of adsorption and photocatalytic activity of TiO₂ by using carbon nanotubes for the treatment of azo dye, *Appl. Catal. B* 61 (2005) 1–11.
- [20] Y. Yu, J.C. Yu, C.Y. Chan, Y.K. Che, J.C. Zhao, L. Ding, W.K. Ge, P.K. Wong, Enhancement of photocatalytic activity of mesoporous TiO₂ by using carbon nanotubes, *Appl. Catal. A* 289 (2005) 186–196.
- [21] J.C. Charlier, Defects in carbon nanotubes, *Acc. Chem. Res.* 35 (2002) 1063–1069.
- [22] X.Z. Li, F.B. Li, C.L. Yang, W.K. Ge, Photocatalytic activity of WO_x-TiO₂ under visible light irradiation, *J. Photochem. Photobiol. A: Chem.* 141 (2001) 209–217.
- [23] J.C. Yu, L.Z. Zhang, J.G. Yu, Direct sonochemical preparation and characterization of highly active mesoporous TiO₂ with a bicrystalline framework, *Chem. Mater.* 14 (2002) 4647–4653.
- [24] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.