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Preparation and photocatalytic degradation of CNT/TiO_2 composites using MWCNT and various titanium alkoxide precursors

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MWCNT와 여러가지 티탄알콕사이드 전구체를 사용하여 CNT/TiO_2 복합체의 제조와 광촉매분해

진명량[1] · 장봉군[1, 2] · 오원춘[1, ★]

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Abstract: CNT/TiO_2 composites were prepared by using multiwall carbon nanotubes (MWCNT) and various titanium alkoxide precursors. The composites were comprehensively characterized by scanning electron microscopy (SEM), field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX) and UV-vis absorption spectroscopy. The photoactivity of the prepared materials under UV irradiation, was tested using the conversion of MB from model aqueous solution. Finally, according to the results of methylene blue (MB) removal experiment, we could see that sample CTOS have better MB removal effect than samples CTIP and CTPP.

요 약: MWCNT 와 여러 가지 티탄 알콕사이드 전구체를 사용하여 CNT/TiO_2 복합제를 제조하였다. 이들 복합체들은 SEM, FE-SEM, XRD, EDX 및 UV-vis 분광기를 사용하여 종합적으로 분석하였다. UV 조사하에서 MB모델 수용액의 변이에 대한결과로부터 제조된 물질에 대한 광활성을 시험하였다. 마지막으로 MB 제거 실험의 결과에 따르면, 시료 CTOS의 경우 시료 CTIP 및 CTPP의 경우보다 우수한 MB제거 효과를 나타내었다.

Key words : CNT, TNB, FE-SEM, XRD, UV, photocatalytic decomposition

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1. Introduction

Multiwall carbon nanotubes (MWCNTs) are a new class of materials which have attracted the interest of scientists especially due to their electronic, mechanical properties[1] and their chemical stability[2] related with their nanometric size. Taking into account the carbon nanotubes characteristics, they could be used with success as support for thin layer deposition and also for reinforcement of nanocomposites materials. The first studies which reported the coating process of oxides thin layers on MWNTs by alkoxidic way were realized by Seeger *et al.*[3], who coated the nanotubes surface with SiO_2 and Hernadi *et al.*[4] who covered the MWNTs surface with Al_2O_3. Using the sol-gel method, Vincent *et al.*[5] obtained TiO_2-MWNTs thin film nanocomposites, where MWNTs (about 1 wt%) act as reinforcement for the thin films. Moreover, in our work,[6,7] we have been prepared CNT/TiO_2 composites which have excellent activity for organic dye and also explain the combination effects between TiO_2 and MWCNTs with plausible photodegradation mechanism.

Titanium (IV) oxide (TiO_2) has attracted much attention mainly in expectation of being applied to environmental photocatalytic processes such as deodorization, prevention of stains, sterilization,[8] and removal of pollutants from air and water.[9-11] For the realization of their practical application, development of highly active TiO_2 photo- catalyst is keenly desired. Based on the kinetic investi- gation of photocatalytic reactions, Ohtani *et al.* has pointed out that TiO_2 particles having both large surface area and high crystallinity must exhibit higher photocatalytic activity.[12] The former property should increase the amount of surface-adsorbed substrate (s) to enhance the capture of photogenerated electron (e^-) and positive hole (h^+), and the latter, i.e., less defects acting as the recombination center, should suppress mutual e^-–h^+ recombination.

In present paper, we use MWCNT and different titanium alkoxide precursors to prepare CNT/TiO_2 composites. Three titanium alkoxides were compared: titanium (IV) isopropoxide (TIP, $Ti\{OCH(CH_3)_2\}_4$), titanium (IV) propoxide (TPP, $Ti(OCH_2CH_2CH_3)_4$) and titanium (IV) oxysulfate (TOS, $TiOSO_4$). To compare the property, the corresponding composites were characterized by SEM, FE-SEM, XRD and EDX. To compare the photocatalytic decomposition, the CNT/TiO_2 composites were also determined by the methylene blue (MB, $C_{16}H_{18}N_3S{\cdot}Cl{\cdot}3H_2O$) in an aqueous solution under UV irradiation.

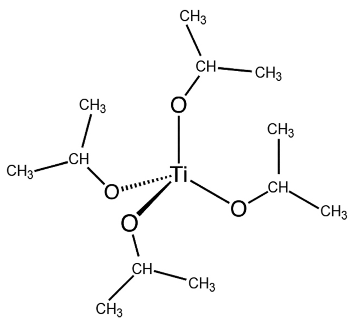
2. Experimental

2.1 Materials

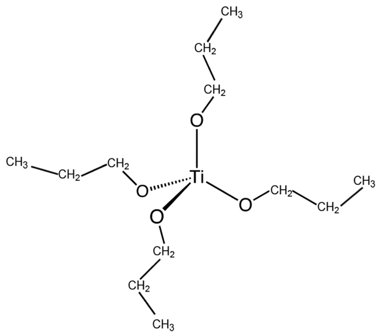
Crystalline MWCNT powder of 95.9 wt.% purity from Carbon Nano-material Technology Co., Ltd, Korea (diameter: ~20 nm, length: ~5 mm) was used as a starting material. The TIP, TPP and TOS as a titanium source for the preparation of CNT/TiO_2 composites were purchased from Kanto Chemical. Co., Inc (TOKYO, Japan), Aldrich Chemical Company and Sigma-Aldrich, respectively. For the oxidization the surface of MWCNT, *m*-chloroperbenzoic acid (MCPBA) was used as an oxidized reagent which was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%) and H_2SO_4 (98%) was used as an organic solvent which was purchased from Samchun Pure Chemical Co., Ltd, Korea. The MB was used as analytical grade which was purchased from Dukan Pure Chemical Co., Ltd. It was selected because it can be readily under anaerobic conditions to produce potentially more hazardous aromatic amines. The structures of TIP, TPP, TOS and MB are displayed in *Scheme* 1.

2.2. Synthesis and characterizations of CNT/TiO_2 composites

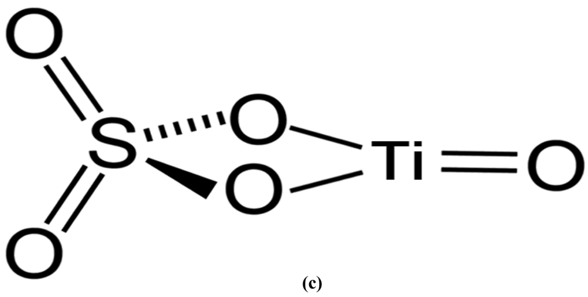
In this experimental, at first, for preparing the oxidizing agent, 0.96 g MCPBA was melted in 60 mL benzene. And then, 0.2 g MWCNT was put into the oxidizing agent, refluxed at 353 K for 6 h until the solid precipitates were formed and dried at 363 K. On the other hand, 0.7 g TOS was melted in 100 mL of 0.1 mol/L H_2SO_4 to prepare the TOS solution. The oxidized CNT was mixed into 20 mL of TIP, TPP and TOS solution and then the solutions were



(a)



(b)



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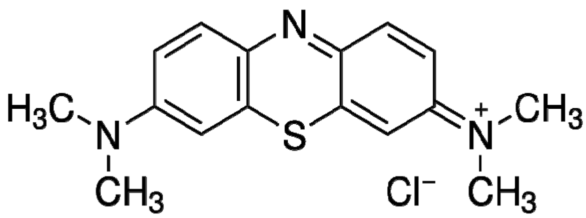


(d)

Scheme 1. The structures of (a) TIP, (b) TPP, (c) TOS and (d) MB.

Table 1. Nomenclature of samples prepared with MWCNT and various titanium alkoxide precursors

Samples	Nomenclatures
0.2 g MWCNT + 20 mL Titanium(IV) isopropoxide (TIP)	CTIP
0.2 g MWCNT + 20 mL Titanium(IV) propoxide (TPP)	CTPP
0.2 g MWCNT + 20 mL Titanium(IV) oxysulfate (TOS)	CTOS

homogenized under reflux at 343 K for 5 h using a magnetic stirrer in a vial. After the stirring the solutions were transformed to the CNT/TiO_2 gels, and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. The preparation condition and code of samples were listed in *Table* 1.

Synthesized powders were characterized by various techniques. SEM was used to observe the surface state and structure of the CNT/TiO_2 composites were carried out by using a JSM-5200 JOEL electron microscope (Japan). XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were obtained at room temperature with a Shimata XD-D1 (Japan) using CuKα radiation. EDX was used to measure the elemental analysis of the CNT/TiO_2 composites. UV-vis spectra for the MB solution degraded by CNT/TiO_2 composites under UV ray irradiation were recorded using a Genspec III

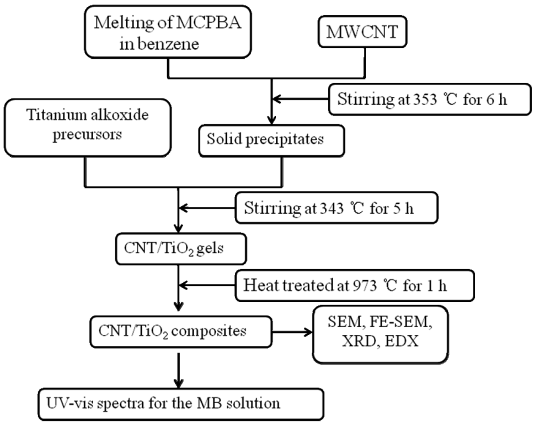


Fig. 1. Schematic diagram showing the procedure for the preparation of CNT/TiO_2 composites.

(Hitachi, Japan) spectrometer. The flow chart in *Fig.* 1 provides a summary of the route to prepare CNT/TiO_2 composites and their characterization.

2.3. Photocatalytic decomposition

The photocatalytic effect of CNT/TiO_2 composites was determined using MB decomposition in aqueous solution under an UV lamp (356 nm, 1.2 mW/cm^2). Because the characteristic dyes concentrations in wastewater from textile industry were in the range of 3.0×10^{-5} to 1.5×10^{-4} mol/L,[13] so the initial MB concentration was chosen 1.0×10^{-5} mol/L. The amount of suspended composites was kept at 1 g/L in 50 mL MB solution. Before turning on UV lamp, the solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. Then, the solution was irradiated with UV. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on), in order to determine the MB concentration in solution, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Samples were then withdrawn regularly from the reactor by an order of 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, and immediately centrifuged to separate any suspended solid.

The clean transparent solution was analyzed by using a UV-vis spectrophotometer (250~750 nm).[14,15] The spectra (550-750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for the each MB solution degraded.

3. Results and Discussion

3.1. Characteristics of CNT/TiO_2 composites

A low-magnification SEM images and a high-magnification FE-SEM images of CNT/TiO_2 composites prepared with MWCNT and different titanium alkoxide precursors were showed in *Fig.* 2. It seems that MWCNT introduced into TiO_2 can prevent TiO_2 particles from agglomerating, consequently increasing its surface area of the composite materials. Meanwhile, the absence of MWCNT aggregated pores in the composite catalysts suggests a homogeneous coverage of TiO_2 over MWCNT. This effect is just supported by FE-SEM observation of sample CTOS (*Fig.* 2(f)). The morphologies of sample CTOS feature relatively homogeneous TiO_2 supported on MWCNT without apparent agglomeration of TiO_2 particles. But on the other hand, from the FE-SEM observations of samples CTIP and CTPP (*Fig.* 2(b) and (d)), we can observe the agglomeration of TiO_2 particles with a little existence of MWCNT on the TiO_2 surface and the MWCNTs may be embedded into these aggregates. So it can be considered that the photocatalytic effect of sample CTOS will be better than that of samples CTIP and CTPP.

The X-Ray diffractograms of CNT/TiO_2 composites prepared with CNT and different titanium alkoxide precursors after heat treatment at 973 K for 1 h are presented in *Fig.* 3. As we known, the anatase phase formed below 773 K starts to transform to rutile-type structure above 873 K and changed into single phase of rutile at 973 K-1173 K.[15,16] But in the case of the samples CTIP and CTPP, the patterns indicate that both anatase and rutile structures presented when they annealed at 973 K. It was agree with the previous works[13,17,18] which evidenced that CNT/TiO_2 composites had a mixing structure of anatase and rutile crystals by crystallization when the temperature reached 973

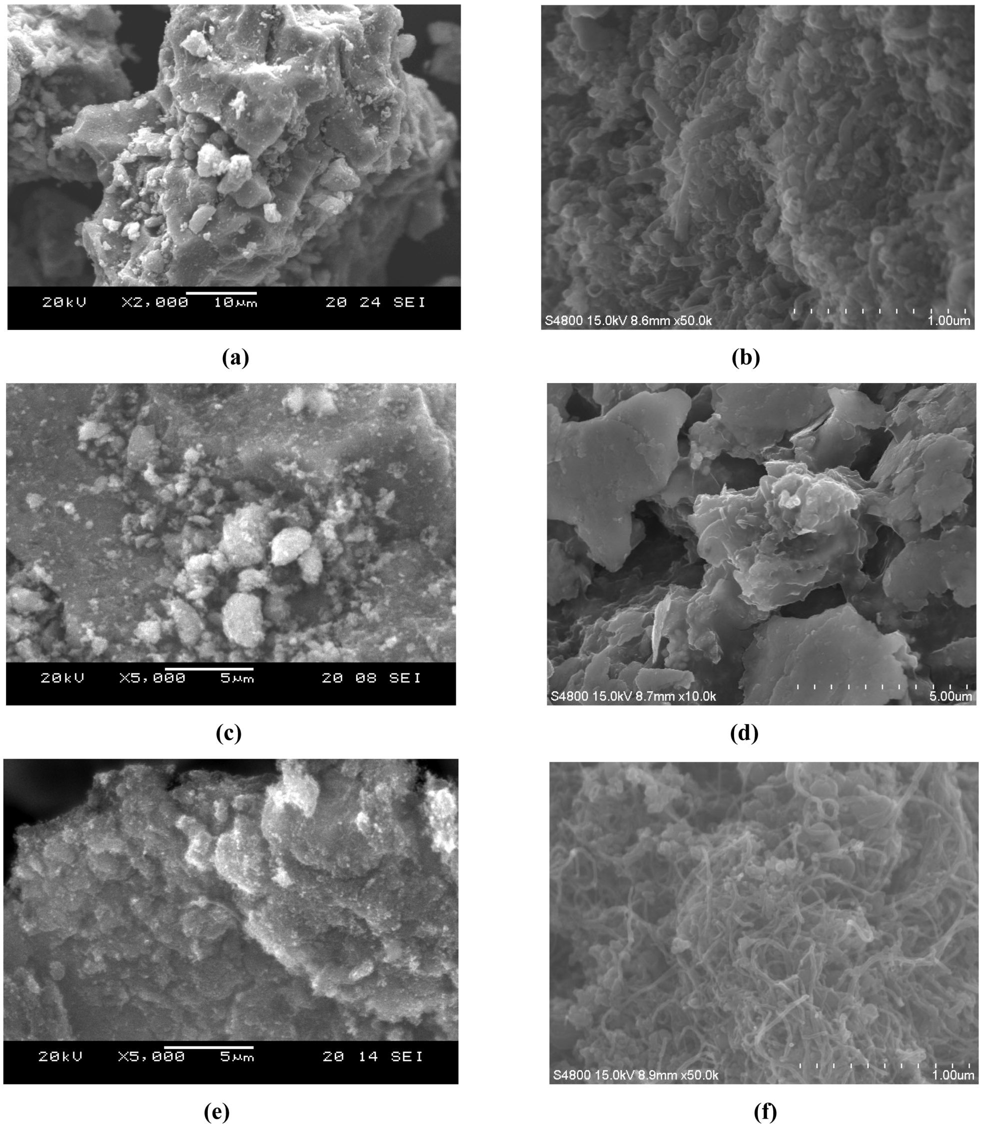
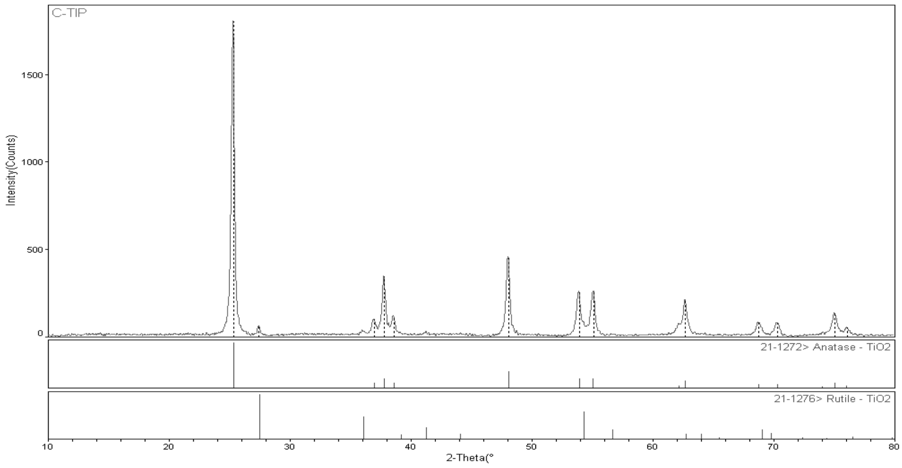


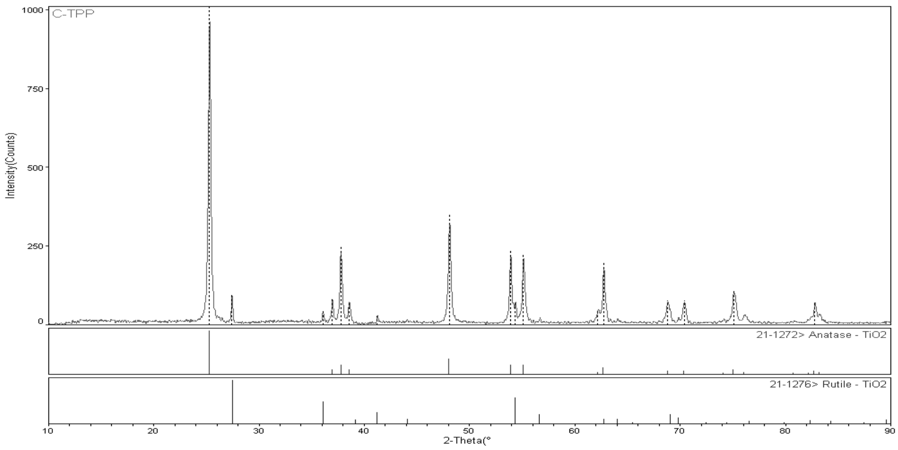
Fig. 2. SEM and FE-SEM images of CNT/TiO_2 composites; CTIP: (a) and (b); CTPP: (c) and (d); CTOS: (e) and (f).

K. However, in the case of CTOS, it is not only anatase (TiO_2) structure kept up without any rutile structure, but also some new peaks appeared, which belong to $ZnTiO_3$. Chai *et al.*[19] indicated that the $ZnTiO_3$ powders begin to crystallize at 773 K. And the $ZnTiO_3$ is an attractive material for applications in microwave dielectrics, catalysts and phosphors.[20] So we can be considered that the CTOS would show an excellence MB degradation effect.

The EDX spectra of CNT/TiO_2 composites prepared with MWCNT and different titanium alkoxide precursors are shown in *Fig.* 4. From the spectra, it is confirmed that the presence of main elements such as C, O and Ti in all of the samples. But some impure elements such as Fe, Zn, Cu, Au and V are existed only in samples CTIP and CTOS, which may be derived from the titanium alkoxide precursors TIP and TOS. The EDX elemental microanalysis (wt. %) of CNT/TiO_2 composites is listed in *Table* 2. From the data, we can also see that the samples CTIP and CTPP



(a)



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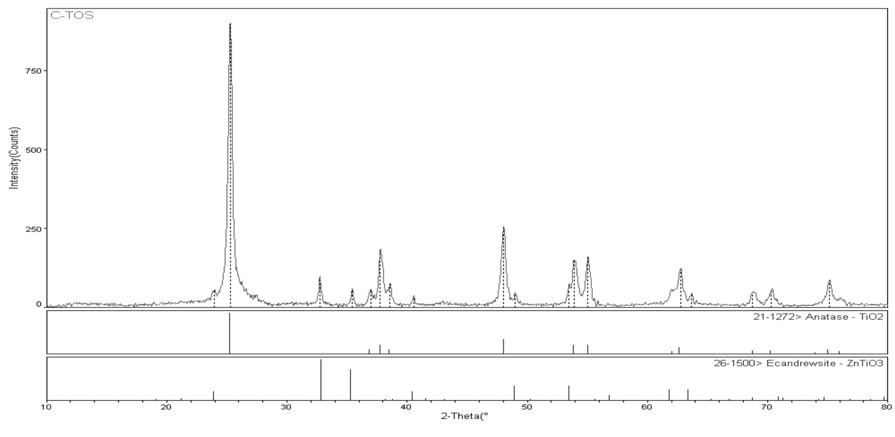

(c)

Fig. 3. The XRD patterns of CNT/TiO_2 composites which were heat treated at 973 K. (a) CTIP, (b) CTPP and (c) CTOS.

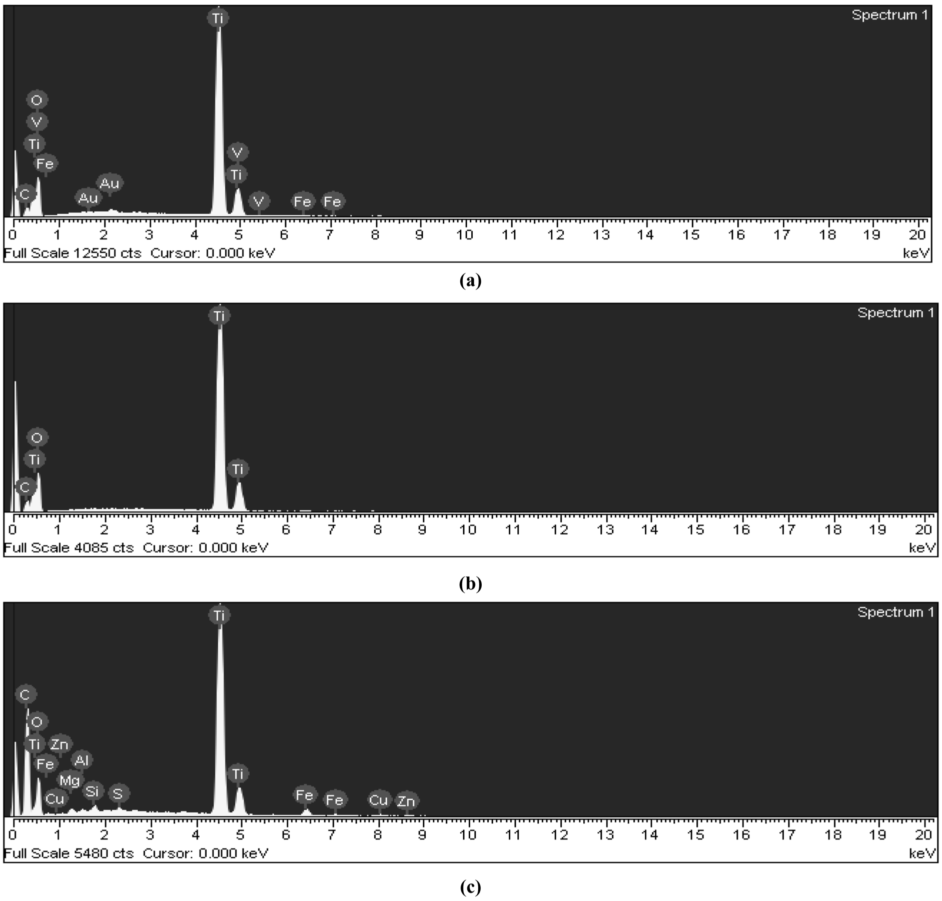

Fig. 4. EDX elemental microanalysis of CNT/TiO_2 composites, (a) CTIP, (b) CTPP and (c) CTOS.

are very rich in O and Ti metals with very poor in C element. However, the sample CTOS have almost same amount of C, O and Ti elements. So it can be explained the appearance of their FE-SEM observations as mentioned above.

Table 2. EDX elemental microanalysis (wt%) of CNT/TiO_2 composites

Samples	Elements			
	C	O	Ti	Others
CTIP	5.35	43.02	50.85	0.78
CTPP	6.21	43.93	49.86	-
CTOS	34.36	28.46	32.37	4.81

3.2. Photocatalytic activity of CNT/TiO_2 composites

The absorption spectra of MB were recorded with an UV-vis spectrophotometer for determination of concentration of dye in the wavelength range from 250 to 750 nm. *Fig.* 5 shows the absorption spectra of MB solution under UV irradiation as function of various time conditions for CNT/TiO_2 composites prepared with MWCNT and different titanium alkoxide precursors. The absorbance of MB solution showed only one maximum, which was observed at 660 nm. There existed a linear relationship between the absorbance and irradiation time, so the 660 nm was used to monitor the photocatalytic efficiency on the degradation of MB. From the spectra of *Fig.* 5, we can also observe that the absorbance maxima for all samples decrease with an increase of UV irradiation time. This result suggests that the color of MB solution is removed, so it can be considered that the concentration of MB solution may be decreased.

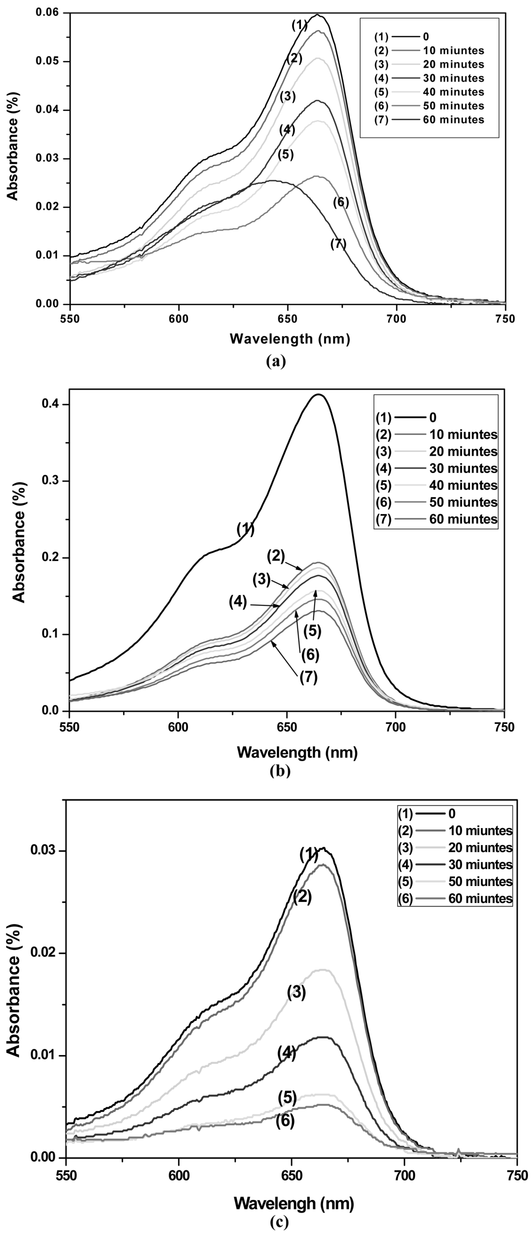

Fig. 5. UV/VIS spectra of MB concentration against the CNT/TiO_2 composites under various time conditions; (a) CTIP, (b) CTPP and (c) CTOS.

Furthermore, the absorbance maxima of the sample CTOS is much more decreased than that of the samples CTIP and CTPP in the same irradiation time. So we can consider that the CTOS will have better photocatalytic degradation of MB solution than that of the CTIP and CTPP. On the other hand, it is noted

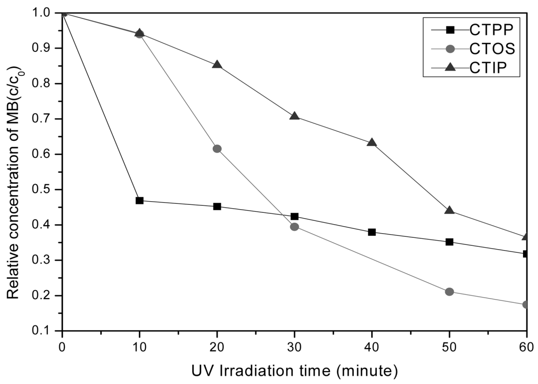

Fig. 6. Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of UV irradiation for the CNT/TiO_2 composites; MB : 1.0×10^{-5} mol/L.

that the absorbance of the CTPP shown a suddenly decrease from 0 min to 10 min and a gradually decrease from 10 min to 60 min, it can be considered that the degradation of MB solution should be expressed mainly in range of 0 min to 10 min (it can be ascertained in the further results).

The photocatalytic removal of MB from model aqueous solutions was investigated using UV light irradiation source. The changes in relative concentration (c/c_0) of MB in the aqueous solution on time of UV irradiation time for the CNT/TiO_2 composites were shown in *Fig.* 6. After 60 min, the highest degradation of MB solution was achieved with the sample CTOS, which was almost removed 95%. And the MB degradation of samples CTIP and CTPP were also achieved at 64% and 68%, respectively. As mentioned above, the sample photocatalytic removal of MB for the sample CTPP shown a suddenly decrease from 0 min to 10 min and a gradually decrease from 10 min to 60 min, which means the photodegradation of MB was mainly occurred at initial 10 min. Meanwhile, the samples CTIP and CTOS had the same photocatalytic removal of MB at initial 10 min. But from 10 min to 60 min, the slope of CTOS was almost two times as that of CTIP, which means that the photodegradation rate of MB using sample CTOS as catalyst is two times as that using sample CTIP as catalyst. On the other hand, as have been indicated in our earlier works, the TiO_2 particles with anatase structure have a better photocatalytic activity.[18,21] However, the present results shown that the samples CTIP and CTPP contained both anatase and rutile structures. But the sample CTOS had not only anatase structure (TiO_2), but also $ZnTiO_3$ structure, which was also a catalyst. So the sample CTOS had a better photocatalytic effect than the samples CTIP and CTPP.

4. Conclusions

CNT/TiO_2 composites were prepared by using MWCNT and different titanium alkoxide precursors. In case of sample CTOS, there is a homogeneous coverage of TiO_2 over MWCNT and less agglomeration of TiO_2 nanoparticles on MWCNT surface. However, in case of samples CTIP and CTPP, there is a large amount of TiO_2 particle aggregates and small amount of CNT particles, and the MWCNTs were embedded into these aggregates. It can be also observed that samples CTIP and CTPP have a mixture structures anatase and rutile when they heat treated at 973 K. However, in the case of CTOS, it is not only anatase (TiO_2) structure kept up without any rutile structure, but also some new peaks appeared, which belong to $ZnTiO_3$. From the EDX data, the main elements such as C, O and Ti were existed in all of the samples and other impure elements were also existed only in samples CTIP and CTOS. Finally, according to the results of MB removal experiment, we could see that sample CTOS have better MB removal effect than samples CTIP and CTPP.

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References

1. M. S. Dresselhaus, G. Dresselhaus and P. Avouris (Eds.), Topics in Applied Physics, Springer-Verlag, Berlin-Heidelberg, **80**, 147(2001).
2. T. Saito, K. Matsushige and K. Tanaka, *Physica B*, **323,** 280-283(2002).
3. T. Seeger, Ph. Redlich, N. Grobert, M. Terrones, D.R.M.Walton and H.W. Kroto, et al., *Chem. Phys. Lett.*, **339,** 41-46(2001).
4. K. Hernadi, E. Ljubbovic, J.W. Seo and L. Forro, *Acta Mat.*, **51,** 1447- 1452(2003).
5. P. Vincent, A. Brioude, C. Journet, S. Rabaste, S.T. Purcell and J. Le Brusq, et al., *J. Non-Cryst. Solids*, **311,** 130-137 (2002).
6. W. C. Oh and M. L. Chen, *Bull. Korean Chem. Soc.*, **29**, 159-164(2008).
7. M. L. Chen and W. C. Oh, *Analytical Science & Technology*, **21**, 229-236(2008).
8. T. Wakanabe, A. Kitamura, E. Kojima, C. Nakayama, K. Hashimoto, A. Fujishima, in: D. E. Olis, H. Al-Ekabi(Eds.), *Elsevier*, 747 (1993).
9. M. A. Fox and M. T. Dulay, *Chem. Rev.* **93,** 341-357(1993).
10. M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.* **95,** 69-96(1995).
11. T. Ibusuki and K. Takeuchi, *J. Mol. Catal.* **88,** 93-102(1994).
12. B. Ohtani and S. I. Nishimoto, *J. Phys. Chem.* **97,** 920-926(1993).
13. Z. H. Zhang, Y. Yuan, L. H. Liang, Y. J. Fang, Y. X. Cheng and H. C. Ding, *et al.*, *Ultrason. Sonochem.*, **15,** 370-375(2008).
14. M. L. Chen and W. C. Oh, *Carbon Science*, **8,** 108-114(2007).
15. M. L. Chen, J. S. Bae, Y. S. Ko and W. C. Oh, *Analytical Science & Technology*, **19**, 376-382(2006).
16. M. Inagaki, Y. Hirose, T. Matsunaga, T. Tsumura and M. Toyoda, *Carbon*, **41,** 2619-2624(2003).
17. M. L. Chen, J. S. Bae and W. C. Oh, *Carbon Science*, **7,** 259-265(2006).
18. M. L. Chen, J. S. Bae and W. C. Oh, *Analytical Science & Technology*, **19**, 460-467(2006).
19. Y. L. Chai, Y. S. Chang, G. J. Chen and Y. J. Hsiao, *Mater. Res. Bull.*, **43,** 1066-1073(2008).
20. M. Z. Zheng, X. R. Xing, J. X. Deng, L. Li, J. Zhao, L. J. Qiao and C. Y. Fang, *J. Alloys Compd.*, **456,** 353-357(2008).
21. M. L. Chen, C. S. Lim and W. C. Oh, *J. Ceramic Processing Research*, **8**, 119-124(2007).