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# Preparation and photocatalytic effect of MWCNT/$TiO_2$ composites

**Ming-Liang Chen and Won-Chun Oh**[1]★
*Department of Advanced Materials & Science Engineering, Hanseo University, Chungnam 356-706, Korea*

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# MWCNT/$TiO_2$ 복합체의 제조 및 광촉매 특성

**진명량 · 오원춘**★
한서대학교, 신소재공학과

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**Abstract:** C/$TiO_2$ composites were prepared with surface modified MWCNT sequentially after HCl treatment and TNB as titanium source. There is a single crystal structure which is anatase in all of the samples from the data of XRD. The SEM microphotographs of C/$TiO_2$ composites show that the $TiO_2$ particles were well mixed with the CNT. There are C, O and Al with strong Ti peaks in all samples from EDX results, and it also shows that the sample CT has much more amount of C and Ti content than that of sample HCT. Finally, the photocatalytic activities for the C/$TiO_2$ composites have more effective than that of pristine $TiO_2$.

**요 약**: 본 연구에서 HCl을 처리하지 않고 혹은 HCl 처리한 표면 처리된 MWCNT 및 TNB를 이용하여 C/$TiO_2$ 복합체를 제조하였다. XRD 결과 값으로부터 모두 시료에 한 가지 결정 구조 즉 anatase형을 존재하고 있음을 알 수 있었다. SEM 사진으로부터 $TiO_2$ 입자와 CNT는 균일하게 분포하고 있음을 알 수 있었다. EDX 결과에서, 모두 시료에 C, O, Al와 Ti 피크를 볼 수 있으며, 특히 시료 CT에 있는 C와 Ti의 함량은 시료 HCT에 있는 것보다 많게 나타났다. 마지막으로, C/TiO2 복합체는 $TiO_2$보다 더 좋은 광촉매 특성을 가지고 있음을 알 수 있었다.

**Key words :** Titanium (IV) n-butoxide (TNB), MWCNT, XRD, SEM, EDX, photoactivity

## 1. Introduction

Titanium (IV) dioxide or titania ($TiO_2$) is one of the most common metal-oxides recognized in various industries. Due to its good physical and chemical properties, such as catalytic activity,[1] photocatalytic activity,[2] good stability toward adverse environment,[3] sensitivity to humidity and gas,[4] dielectric character,[5] nonlinear optical characteristic[6] and photo-luminescence,[7] titania has been used in many fields of application including the use as catalysts, catalyst supports, electronics, cosmetics, pigments and filler coating. Nevertheless, photocatalyst is one of the most important applications of titania. Although titania is known to have three natural polymorphs, i.e. rutile, anatase, and brookite, only anatase is

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★ Corresponding author
Phone : +82-(0)41-660-1337 Fax : +82+(0)41-688-3352
E-mail : wc_oh@hanseo.ac.kr

generally accepted to have significant photocatalytic activity.[8-10]

Carbon nanotubes (CNTs) are one of the most actively studied materials for nanoscal building blocks in nanotechnology. The unique properties and one-dimensional nature of carbon nanotubes make them potential nanoelectronic devices, chemical and biological sensing elements. Carbon nanotubes could be considered as a good support for materials with photocatalytic properties due to their high mechanical[11] and chemical[12] stability and their mesoporous character which favors the diffusion of reacting species. On the other hand, a dispersion of $TiO_2$ on the MWCNTs surface could create many active sites for the photocatalytic degradation. Different techniques have already been used to coat carbon supports for specific applications. The first $TiO_2$ coating by hydrolysis of $TiCl_4$ was realized on activated carbon fibers[13] in order to obtain absorptive materials for $NH_3$. $TiO_2$ has been also deposited by sol-gel method on carbonfibers in order to increase their thermal stability.[14] By electrodeposition, Zhithomirsky *et al*.[15] succeeded to deposite a $TiO_2$ thin layer on a graphite support which is an important component of PZT soild solutions. Activated carbon spheres coated with $TiO_2$ by hydrothermal treatment demonstrated very good performance in the photocatalytic degradation of methylene blue.[16,17]

In this paper, we prepared C/$TiO_2$ composites with MWCNT, which was surface modified by MCPBA sequentially after HCl treatment, and Titanium (IV) n-butoxide (TNB) as titanium source. The synthesized composites were characterized by various techniques, i.e. X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray (EDX). The catalytic efficiency of the developed composites was evaluated by the photodegradation of an azo compound, methyl blue (MB, $C_{16}H_{18}N_3S\cdot Cl\cdot 3H_2O$).

## 2. Experimental

### 2.1. Materials

Titanium (IV) n-butoxide (TNB, 99%) was used as started material for titania synthesis which was purchased from Acros organics Co., Ltd, USA. CNT was purchased from nanokarbon Co., Ltd, Korea. M-chlorperbenzoic acid (MCPBA, purchased from Acros Organics, New Jersey, USA.) and Benzene (99.5%, purchased from Samchun Pure Chemical Co., Ltd.) were used as oxidizing agent. The Methylene Blue (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.

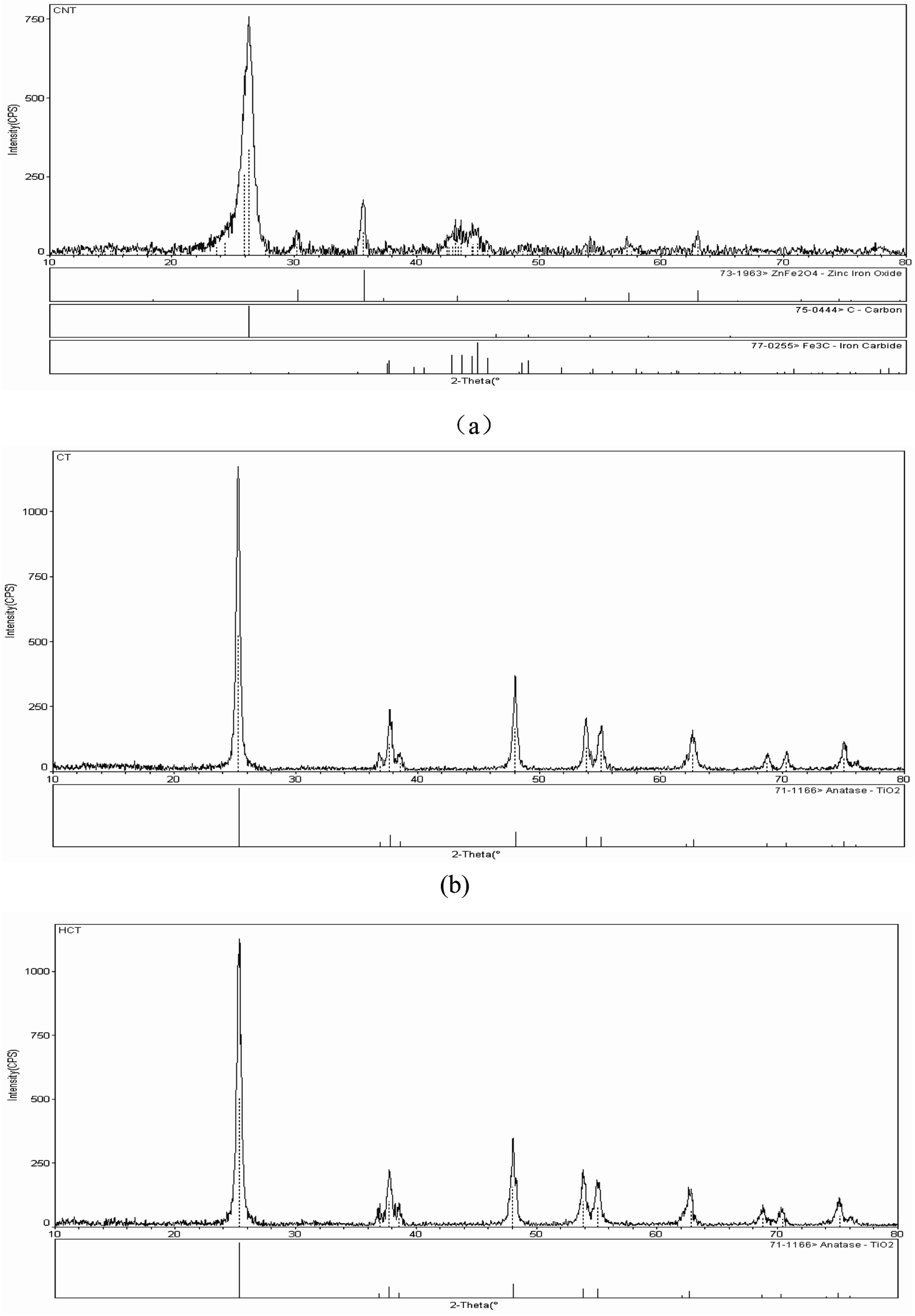
### 2.2. Samples preparation

In this experimental, at first, for preparing the oxidizing agent, 0.9 g MCPBA was melted in 60 mL Benzene. And then 0.2 g CNT was put into the oxidizing agent, refluxed for 6 h, filter anddry. Some of the oxidized CNT was treated with 0.05 mol/L HCl. The oxidized CNT and HCl-treated CNT were mixed with 20mL TNB by stirring at 343 K for 5 h. The obtained products were heat treated at 973 K for 1 h with a heating rate of 279 K/min. The samples prepared with the Non-HCl and HCl treatment were named as sample CT and sample HCT, respectively.

### 2.3. Characterization

X-ray diffraction (XRD) was used for crystal phase identification and estimation of the anastase-to-rutile ratio. XRD patterns were obtained at room temperature with a diffractometer Shimata XD-D1 (Japan) using CuKα radiation. Scanning electron microscope (SEM) which was used to observe the surface state and pore structure of the C/$TiO_2$ composites were carried out using a JSM-5200 JOEL electron microscope (Japan). Energy dispersive X-ray (EDX) was used to measure the elemental analysis of the C/$TiO_2$ composites. UV-VIS spectra for the MB solution obtained from degradation by C/$TiO_2$ composites dispersion under UV ray irradiation were recorded using a Genspec (Hitachi, Japan) spectrometer.

### 2.4. Photocatalytic degradation of Methylene blue (MB)



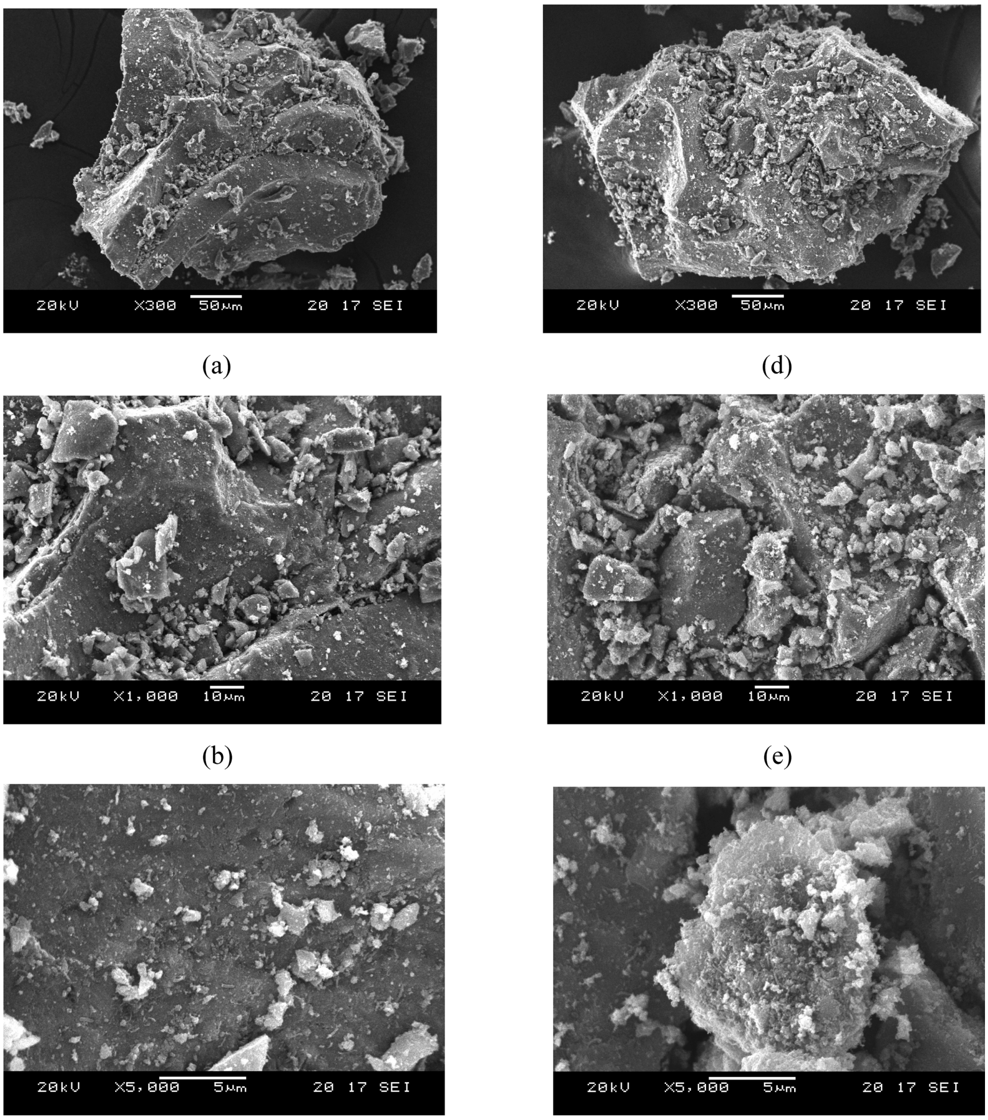
（a）

(b)

(c)

*Fig.* 1. XRD patterns of C/$TiO_2$ composites prepared by heat-treatment at 973 K for 1 h.

The photocatalytic effectiveness of C/$TiO_2$ composite was determined using MB degradation in aqueous solution under an ultraviolet (UV) lamp (356 nm, 1.2 mW/$cm^2$). The initial concentration of MB was $1.0\times10^{-6}$ mol/L. At this time the concentration of MB in the solution was denoted as $c_0$. The amount of the composite which put into the MB solution was 0.05 g. After the composite put into the MB solution, the UV light was turned on. And then the solution was irradiated for 10 min, 30 min, 40 min, and 50 min. Obtained MB solution should removal the minute particles of C/$TiO_2$ composite in the solution by centrifuging. The concentration of MB after photodegradation by $TiO_2$ reaction was determined by using a UV/VIS spectrophotometer (250~600 nm, Genspec III (Hitachi), Japan).[18]



(a) (d)

(b) (e)

(c) (f)

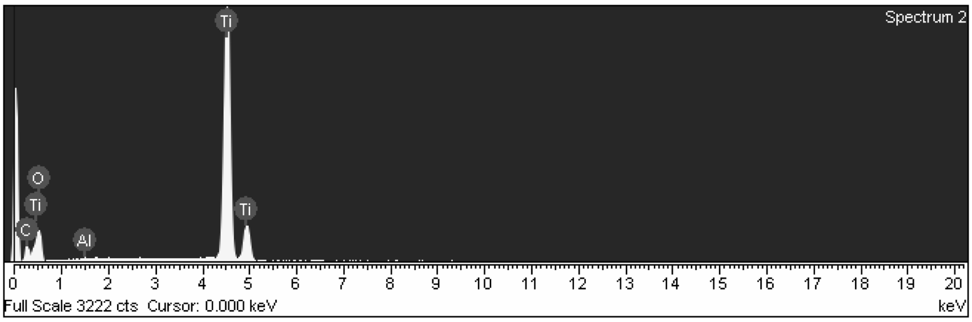
*Fig.* 2. SEM micrographs of the C/$TiO_2$ composites; (a) CT (×300), (b) CT (×1000), (c) CT (×5000), (d) HCT (×300), (e) HCT (×1000), (f) HCT (×5000).

## 3. Results and Discussion

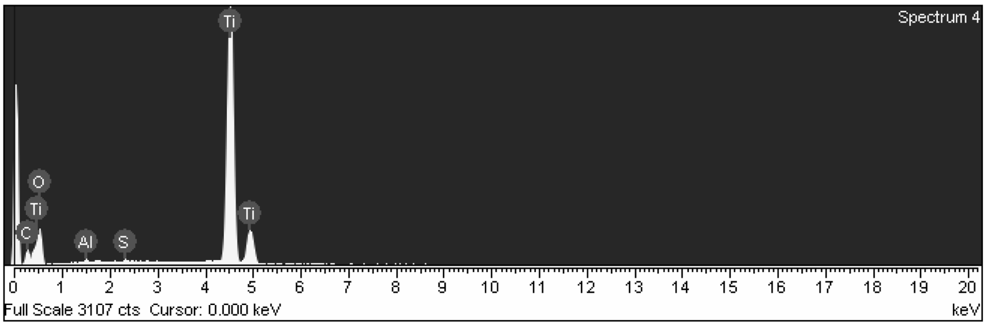
### 3.1. Physical properties of C/$TiO_2$ composites

The XRD patterns of C/$TiO_2$ composites were prepared with surface modified MWCNT sequentially after HCl treatment and TNB as titanium source, which were heat-treated at 973°K for 1 h were displayed in *Fig.* 1. The patterns demonstrate the highly crystalline nature of the composites. The peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 were the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, respectively, which indicating the developed two C/$TiO_2$ composites, just CT and HCT, existed in anatase state. This result was in agreement with the results from our previous work that anatase crystals were formed by crystallization when the temperature reached 973 °K,[18,19] This also indicates that the precursor, titanium (IV) n-butoxide, was converted to anatase, which deposited on the MWCNTs under the experimental conditions.

The SEM micrphotographs of C/$TiO_2$ composites were prepared with surface modified MWCNT sequentially after HCl treatment and TNB as titanium source were shown in *Fig.* 2. It was seen that the synthesized powder was an irregular aggregates of particles with large amount of Ti particles and small amount of C particles (ascertained in the EDX microanalysis). According to Park *et al.*,[20] agglomeration of the precipitates is influenced by dielectric constant of the reaction medium. A large amount of $TiO_2$ particle aggregates were observed during the SEM observation, and the MWCNTs were embedded into these aggregates. Careful SEM examination exhibited that almost every MWCNT was enwrapped with a $TiO_2$ layer. Based on the assumption that the titanium precursor TNB was completely converted to $TiO_2$ and all the formed particles were surrounded by the MWCNTs under experimental conditions. It was also observed that almost all MWCNTs particles deposited on the $TiO_2$, and almost every MWCNT was decorated with $TiO_2$ particles. So it was considered that C/$TiO_2$ composites could have much more activity and



(a)



(b)

*Fig.* 3. EDX elemental microanalysis of the C/$TiO_2$ composites; (a) CT, (b) HCT.

*Table* 1. EDX Elemental Microanalysis of C/$TiO_2$ Composites Prepared with Non-HCl-treatment and HCl-treatment

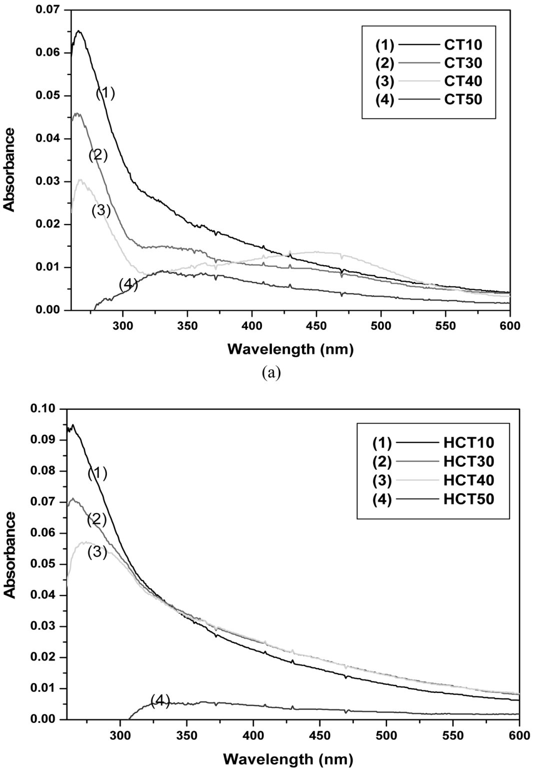
| Sample | Elements | | | | |
|---|---|---|---|---|---|
| | C | O | Ti | Al | S |
| CT | 8.73 | 38.32 | 53.67 | 0.22 | - |
| HCT | 7.89 | 40.06 | 52.60 | 0.33 | 0.22 |

would show an excellent photocatalytic activity.

*Fig.* 3 shown the EDX spectra of C/$TiO_2$ composites were prepared with surface modified MWCNT sequentially after HCl treatment and TNB as titanium source. These spectra show the presence of C, O, and Al with strong Ti peaks (as seen in SEM microphotographs). The results of EDX elemental microanalysis of C/$TiO_2$ composites were listed in *Table* 1, all of the composites were richer in Ti metal than any other elements, as the same as the results of EDX spectra. So it can be considered that C/$TiO_2$ composites would show excellent photocatalytic decomposition mainly. It should be also note that the C and Ti content of CT was more than that of HCT, so it could considered that CT should have much more activity than HCT.

### 3.2. Photocatalytic activity of C/$TiO_2$ composites

*Fig.* 4, absorbance of MB solution under UV irradiation was shown on the samples under various time conditions. As can be seen from the figure, the absorbance maxima for all samples slowly decrease with increase of UV irradiation time. This indicates that the characters of the $TiO_2$ and MWCNTs have been changed due to the indubitable interaction of $TiO_2$ particles with the MWCNTs, which may modify the process of the electron/hole pair formation under UV light irradiation.[21] So it may be the unique structure of the C/$TiO_2$ composites that led to the high catalytic activity for MB solution. It is also considered that C/$TiO_2$ composites show photocatalytic performance mainly due to MWCNTs have very small surface area. *Fig.* 5 showed the changes in relative concentration ($c/c_0$) of MB in the aqueous solution on time of UV irradiation for the C/$TiO_2$ composites. It has been reported that negligible photocatalytic activity of amorphous titania is attributable to the facilitated recombination of photoexcited electrons and holes in the amorphous structure. Therefore, the result in *Fig.* 5 suggested that titania synthesized by TNB has structure with high crystallinity that prevents electron-hole recombination. Kamat and co-workers investigated the photochemical behavior of $C_{60}$ and $C_{70}$ adsorbed on $TiO_2$ particles.[22] Because the band gap of $C_{60}$ is smaller than that of $TiO_2$, it can be excited under irradiation of UV light, and the photo-induced electrons transferred between $TiO_2$ and $C_{60}$. Since MWCNTs have similar structure and characters to $C_{60}$, we can deduce the possible role of MWCNTs in the photocatalytic process as follows. MWCNTs were induced to generate electron ($e^-$) by UV light irradiation, and the photo-induced electrons transferred



(a)

(b)

*Fig.* 4. UV/VIS spectra of MB concentration against the C/$TiO_2$ composites for various Times; (a) CT and (b) HCT.

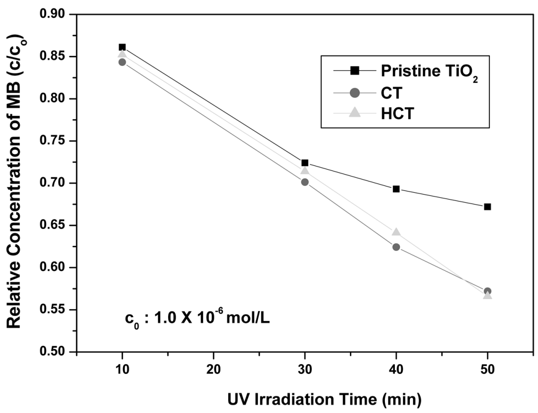


*Fig.* 5. Dependence of relative concentration ($1.0\times10^{-6}$ mol/L) of MB in the aqueous solution $c/c_0$ on time of UV irradiation for the C/$TiO_2$ composites.

to conduction band of $TiO_2$ and electrons of valance band (VB) of $TiO_2$ transferred to MWCNTs simultaneously. In other word, the positive charged holes ($h^+$) formed while the induced electrons migrated from MWCNTs to $TiO_2$. The injecting electrons from MWCNTs to $TiO_2$ could catch the $O_2$ adsorbed on the surface of $TiO_2$ to yield very active radicals, superoxide radical ions, and the positive charged hole could catch $OH^-$ to yield hydroxyl radicals. Both superoxide radical ions and hydroxyl radicals were responsible for the degradation of MB solution. Therefore, the connection between MWCNTs and $TiO_2$ particles may play a key important role in the electron transfer. In this study, the MWCNT particles firmly combined with the surface of $TiO_2$ as described above. For all the C/$TiO_2$ composites prepared with surface modified MWCNT sequentially after HCl treatment and TNB as titanium source, slope relationship between $c/c_0$ of MB and t were observed at $1.0\times10^{-6}$ mol/L of MB concentration. At slope relationship between $c/c_0$ of MB and t, it was obtained that removal effect of MB for the C/$TiO_2$ composite was better excellent than that of pristine $TiO_2$ for all samples.

## 4. Conclusion

In this study, C/$TiO_2$ composites were prepared with surface modified MWCNT sequentially after HCl treatment and TNB as titanium source, and the properties of C/$TiO_2$ composites were investigated. There is a single crystal structure which is anatase in all of the samples which were heat treated at 973 K from the data of XRD. By the SEM observation, the synthesized powder was an irregular aggregate of particles with a large amount of $TiO_2$ particle aggregates and small amount of C particles, and the MWCNTs were embedded into these aggregates. There are C, O and Al with strong Ti peaks in all samples from EDX results. It was also observed all of the samples have a large amount of Ti contents in the EDX elemental analysis. Finally, the C/$TiO_2$ composites have much more photoactivity than pristine $TiO_2$, and it also could be attributed to the $TiO_2$ derived from TNB on the structural anatase phase.

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