

Synthesis and Characterization of CNT/TiO₂ Composites Thermally Derived from MWCNT and Titanium(IV) *n*-Butoxide

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Two kinds of CNT/TiO₂ composite photocatalysts were synthesized with multi-walled carbon nanotubes (MWCNTs) and titanium(IV) *n*-butoxide (TNB) by a MCPBA oxidation method. Since MWCNTs had charge transfer and semiconducting, the CNT/TiO₂ composite shows a good photo-degradation activity. The XRD patterns reveal that only anatase phase can be identified for MCT composite, but the HMCT composite synthesized with HCl treatment was observed the mixed phase of anatase and rutile. The EDX spectra were shown the presence as major elements of Ti with strong peaks. From the SEM results, the sample MCT and HMCT synthesized by the thermal decomposition with TNB show a homogenous sample with only individual MWCNTs covered with TiO₂ without any jam-like aggregates between CNTs and TiO₂. From the photocatalytic results, we could be suggested that the excellent activity of the CNT/TiO₂ composites for organic dye and UV irradiation time could be attributed to combination effects between TiO₂ and MWCNTs with plausible photodegradation mechanism.

Key Words : Carbon nanotube, Titanium(IV) *n*-butoxide, XRD, SEM, Photocatalysis

Introduction

Carbon based TiO₂ composites have attracted much attention and become a very active field of research due to their unique properties and promising applications for the big problem of pollutions.¹⁻⁵ Especially, carbon nanotubes (CNTs) have attracted considerable attention in recent years owing to their remarkable photoelectrical and mechanical properties.⁶ As well these composites have intrinsic properties as the materials exhibit cooperative or synergistic effects. Titania is an important semiconducting material, which has been applied as photocatalysis and photosensitive active materials due to its excellent physical and chemical properties.^{7,8} One of its most important applications is to behave as photocatalyst for some chemical reaction for the water contaminated with organic pollutants such as dyes and aromatic or cyclic compounds.^{9,10} Multi-walled carbon nanotubes (MWCNTs) could be considered as a good support for materials with field emission displays and photocatalytic properties. On the other hand, a combination of TiO₂ and MWCNT could create many active sites for the photocatalytic degradation. Different research techniques have already been used to coat carbon supports for the special usages. The titanium(IV) *n*-butoxide (TNB) treated carbon composite was synthesized with activated carbon fiber¹¹ in order to obtain adsorptive materials for pollutant gas and photocatalysis for the degradation of dyes.¹² Activated carbon materials and TiO₂ composites by mechanical and hydrothermal treatment demonstrated very good performance in the photocatalytic degradation of methylene blue.^{13,14} For the number of applications, however, the practical use of TiO₂ in powder shows some drawbacks like the immobilization of TiO₂ on fixed supports, which was

found to reduce the functional efficiency of the material. The first trial of CNT coating on the oxide layers was studied by Seeger *et al.*¹⁵ and Hernandi *et al.*¹⁶ CNT are attractive and comparative catalyst supports when compared to activated carbon due to the combination of their electronic, adsorption, mechanical and thermal properties. The characteristic electronic properties of CNT are that they can be metallic as well as semiconducting depending on their geometry.¹⁷ Composites containing CNT are believed to provide many applications and exhibit combination effects between carbon phases and metal oxides.

In this study, we present the synthesis and characterization of CNT/TiO₂ composites synthesized by an improved oxidation method. The structural variations, surface state and elemental compositions were investigated through preparation of two kinds of CNT/TiO₂ composites. X-ray diffraction (XRD), energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM) and UV/VIS spectroscopy were characterized for these new photocatalysts.

Experimental

Materials. Crystalline MWCNT powder of 95.9 wt.% purity from Nanokarbon (Nanokarbon Co., Ltd, Korea) was used as a starting material. The XRD pattern for the pristine MWCNT was shown in Figure 1. Reagents (benzene and ethyl alcohol) were purchased as reagent-grade from Duksan chemical Co and Daejung chemical Co. and used without further purification unless otherwise stated. Evaporation and concentration in vacuum were done at a water aspirator pressure and compounds were dried at 1.33 Pa. For the comparison, the TiO₂ photocatalysts used were the commer-

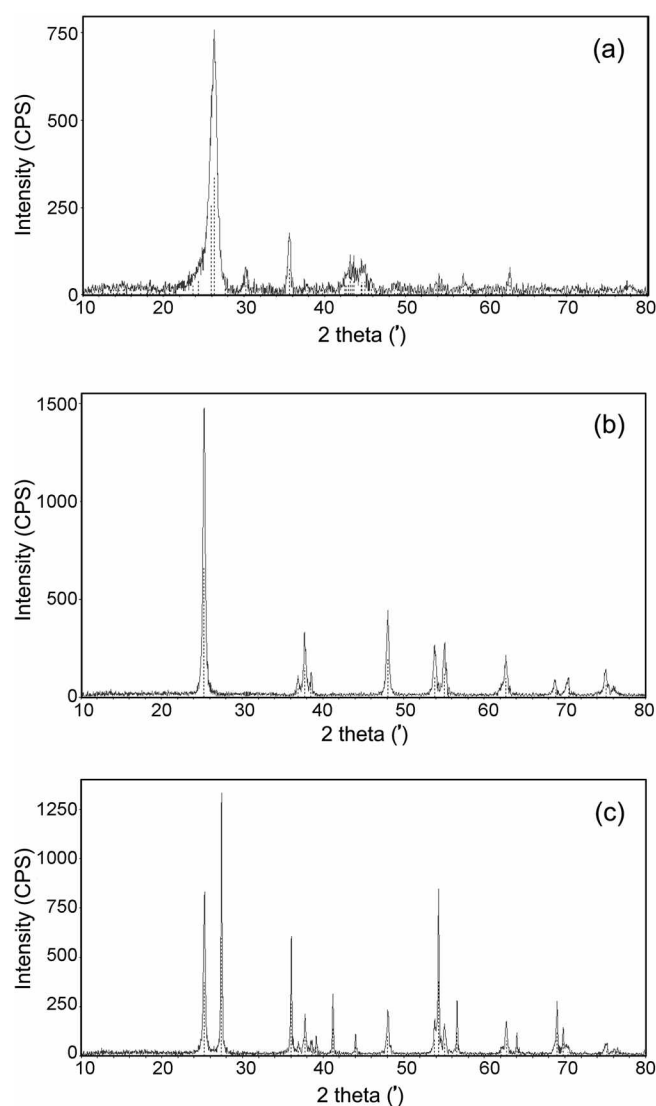


Figure 1. XRD patterns of CNT/TiO₂ composites; (a) Pristine MWCNT, (b) MCT composite catalyst and (c) HMCT composite catalyst.

cially available (Duk-San Pure Chemical Co., Korea), which were used of a single phase of anatase with secondary particles of about 80-150 μm aggregated from the primary particles of about 30-50 μm with BET surface area of about 83 m^2/g . The titanium(IV) *n*-butoxide (TNB, C₁₆H₃₆O₄Ti) as a titanium source for the synthesis of CNT/TiO₂ composites

were purchased as reagent-grade from Acros Organics, USA.

Chemical oxidation on the MWCNT surface. *m*-chloroperbenzoic acid (ca. 0.96 g) was suspended in 60 mL benzene as a solvent, and MWCNT (ca. 40 mg) was added, the mixture was refluxed in an air atmosphere for 6 h. Then the solvent was dried at the boiling point (353.13 K) of benzene. The solid precipitates were transformed to a dark brown color. After completion, dark brown precipitates were washed with ethyl alcohol and then dried at 363 K. Before the TNB treatment for the oxidized MWCNT, we prepared to two kinds of samples of non and HCl treatment to the oxidized MWCNT.

Preparation of CNT/TiO₂ composite. We prepared two kinds of oxidized MWCNT (non and HCl treated) slurry solutions with pristine concentrations of 20 mL of TNB for the synthesis of CNT/TiO₂ composites. For the synthesis, 0.5 g of powdered two kinds of oxidized MWCNT were mixed into 20 mL of TNB aqueous solution and stirred for 5 hours at 333 K. Then, the powder mixtures of TNB with two kinds of oxidized MWCNT were heated at 973 K for 1 h for the thermal decomposition. Before heat treatment, the solvent in the mixtures was vaporized at 343 K for 1 hour. Finally, these samples were dried at 368 K for 72 hours in an air atmosphere. The summary of synthesis procedure and nomenclatures for the CNT/TiO₂ composites listed in Table 1.

Characterization of CNT/TiO₂ composites. For the determination of the crystallographic structure of the inorganic constituent of the composites, XRD patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with Cu K α radiation. EDX spectra were also used for the elemental analysis of the samples. SEM (JSM-5200 JOEL, Japan) was used to observe the surface state and structure of two kinds of CNT/TiO₂ composites. For the analysis of photo-degradation effects, UV-VIS spectra for the CNT/TiO₂ composites were recorded using a Genspec (Hitachi, Japan) spectrometer.

Photocatalytic effect. Photocatalytic activities were evaluated by MB degradation in aqueous media under ultraviolet light irradiation. For UV irradiation, the reaction tube was located axially and held in UV lamp (20 W, 365 nm) box. The lamp was used at the distance of 100 mm from the solution in darkness box. The initial MB concentration (c₀) was 1.0×10^{-6} mole/L. The amount of suspended CNT/

Table 1. Summary of Synthesis Procedure and Nomenclatures of Samples Prepared with Non and Hydrochloric Acid Treatment to MWCNT

Synthesis Procedure	Nomenclatures
1) MWCNT + MCPBA (<i>m</i> -chloroperbenzoic acid) : Oxidation of MWCNT surface 2) 1) + TNB (Titanium <i>n</i> -butoxide, 99.99%) 3) Thermal decomposition (at 973K)	MCT
1) MWCNT + MCPBA (<i>m</i> -chloroperbenzoic acid) : Oxidation of MWCNT surface 2) 1) compound + 0.01 M HCl treatment : Formation of surface group 3) 2) + TNB (Titanium <i>n</i> -butoxide, 99.99%) 4) Thermal decomposition (at 973 K)	HMCT

TiO₂ composites was kept at 0.005 g/mL. Before turning on illumination, the suspension containing MB and CNT/TiO₂ composites was stirred with ultrasonicator in the dark condition for 3 minutes to establish an adsorption-desorption equilibrium. The suspension was irradiated with ultraviolet light as a function of irradiation time. Samples were then withdrawn regularly from the reactor and removal of dispersed powders through centrifuge. The clean transparent solution was analyzed by UV/VIS spectroscopy. The concentration of MB in the solution was determined as a function of irradiation time from the absorbance region at a UV wavelength line of 256 nm.

Results and Discussion

Structural and elemental analysis. XRD technique was used to determine the crystallographic structure of the inorganic constituent of the composite. The components profile of carbon and TiO₂ for the composite catalysts determined by XRD was shown in Figure 1. In case of sample MCT (Fig. 1(b)) synthesized without HCl treatment procedure, the XRD patterns reveal that only anatase phase can be identified for CNT/TiO₂ composite. But, the sample HMCT (Fig. 1(c)) synthesized with HCl treatment was observed the mixed phase of anatase and rutile. In the former studies for the TiO₂ formation from TNB,^{18,19} the XRD results were shown that the anatase phase has disappeared with the increasing temperature process and the rutile phase has occurred at relatively high temperature. In this study, it was worthy of notice that the characteristic peaks of MWCNT can hardly be identified from all the patterns of composite catalysts. It is considered that the peak widths broaden slightly and gradually with a decrease with peak intensity of MWCNT for the composite catalysts. The absence of MWCNT aggregated in the composite catalysts proves a homogeneous dispersion of MWCNT in TiO₂ matrix, which was also supported by the disappearance of MWCNT characteristic peaks in their XRD patterns. In case of another study,³ however, the XRD lines for the anatase type structure of MWNT-TiO₂ derived from MWCNT and Ti(OC₃H₇)₄ at 673 K were observed the sharpened peaks and the separation of these diffraction peaks becomes clear. The XRD patterns of TiO₂/carbon composites by the study of Maldonado-Hodar *et al.*²⁰ showed the very similar results for the formation of anatase crystallites at low temperatures. The increase in the pyrolysis temperature, however, the patterns were shown the results in mixtures of anatase and rutile structures. This means that the increase in the heat treated temperature is include to phase transition from pure anatase phase to mixture phase of anatase and rutile or to rutile phase. In this study for the CNT/TiO₂ composite, the TiO₂ structure shown was the anatase phase for the sample MCT. It was observed that the major peaks are diffractions from (101), (004), (200) and (204) planes of anatase. In case of sample HMCT, the main crystalline phase had presented the rutile plans of (101), (103), (112), (105), (211), (204), (116) and (220) with anatase plans, indicating the TiO₂ prepared

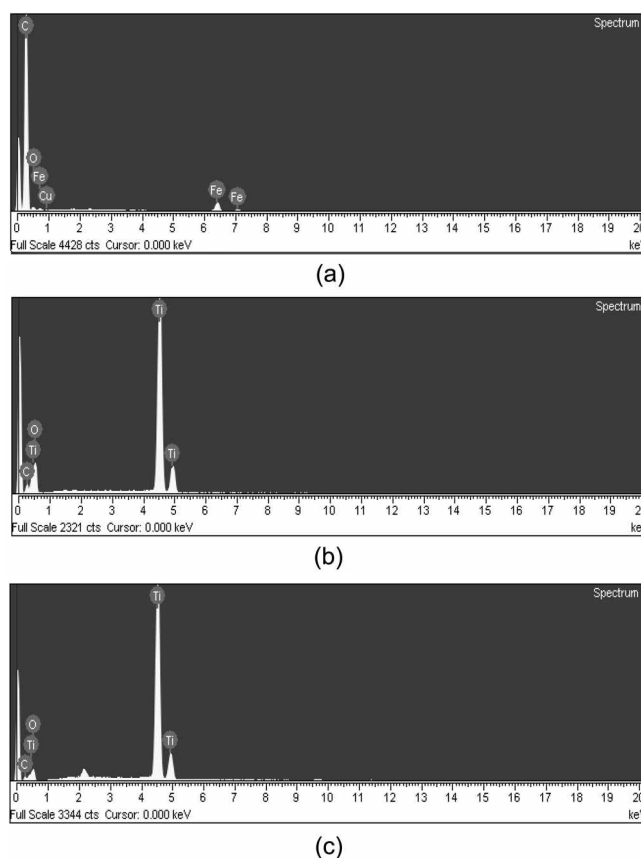


Figure 2. EDX elemental microanalysis for the CNT/TiO₂ composites; (a) Pristine TiO₂, (b) MCT composite catalyst and (c) HMCT composite catalyst.

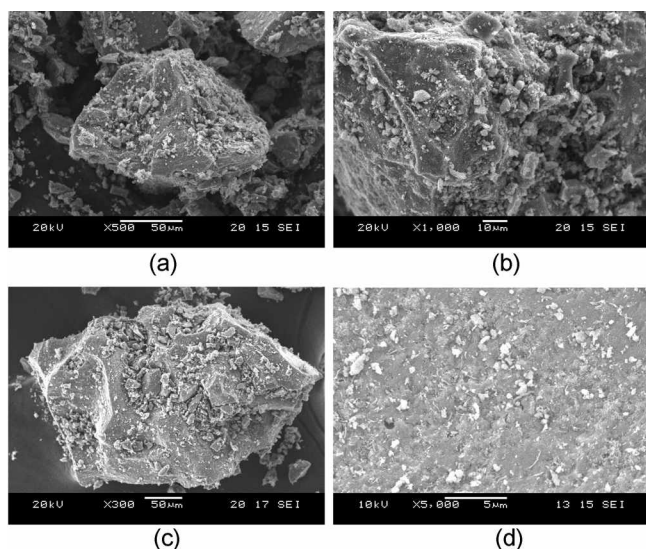
existed in anatase and rutile mixture state.

The quantitative microanalysis of C and Ti as major elements for the CNT/TiO₂ composite was performed by EDX. The EDX spectra of CNT/TiO₂ composites were shown in Figure 2. The carbon coated solid particles and composite typed carbon for the elemental analyses has been reported on the various typed titania.^{21,22} In this study, the spectra were shown the presence as major elements of C and O with strong Ti peaks. However, it could be considered that the spectrum for the pristine MWCNT is shown the presence as impurity element of Fe, due to MWCNTs are synthesized by a catalytic chemical vapor deposition method in fluidized bed reactor on a Fe catalyst. The numerical result of EDX quantitative microanalysis of the CNT/TiO₂ composite was presented the 5.44:42, 7:51.9 for the sample MCT and 3.09:26.2:70.68 for the sample HMCT as components ratio of C:Ti:O. In the case of most of the samples, oxygen and titanium were present as major elements with small quantities of carbon element in the CNT/TiO₂ composites. The results of EDX elemental microanalysis (wt.%) of CNT/TiO₂ composites prepared with non and hydrochloric acid treatment to MWCNT listed in Table 2.

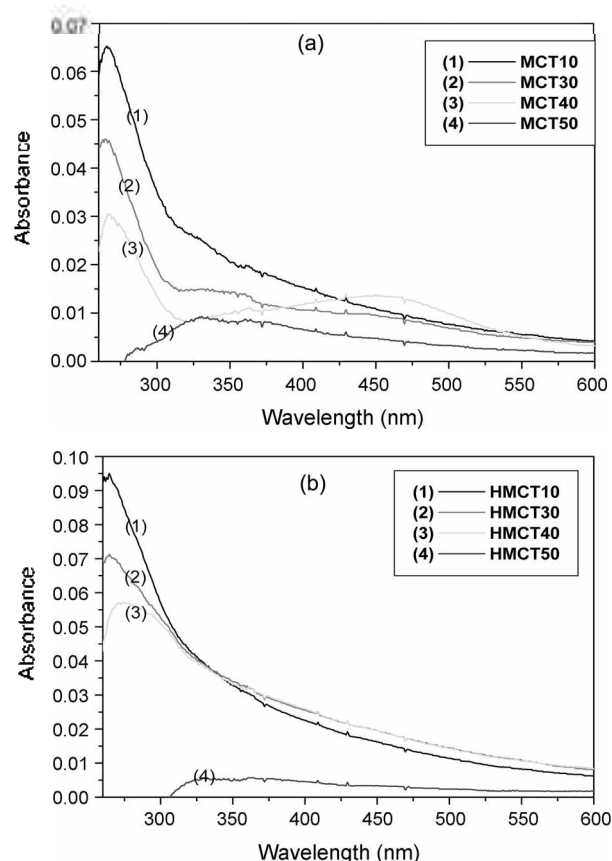
Surface morphology. The morphology and microstructure of the products prepared with or without acid were examined by SEM. The changes in the morphology for the MWCNT based composites obtained from our unique

Table 2. EDX Elemental Microanalysis (Weight %) of CNT/TiO₂ Samples Prepared with Non and Hydrochloric Acid Treatment to MWCNT

Sample	C (%)	O (%)	Ti (%)	Others (%)
Pristine CNT	87.9	5.75	-	6.26
MCT	5.44	42.7	51.9	-
HMCT	3.09	26.2	70.68	-

**Figure 3.** SEM micrographs for the CNT/TiO₂ composites; (a) MCT composite catalyst (over-all scale), (b) MCT composite catalyst (close-up), (c) HMCT composite catalyst (over-all scale) and (d) HMCT composite catalyst (close-up).

experimental condition were shown in Figure 3. In Figure 3, (a) and (b) showed a representative SEM images of the sample prepared without procedure of hydrochloric acid treatment (named as sample MCT), which clearly illustrates that the MWCNTs were homogeneously decorated with well-dispersed particles. It can be seen that the composites reveals the crystalline feature and well-resolved aligned lattice fringes of anatase. The low magnification images of the sample MCT (a) and sample HMCT (c) prepared by the thermal decomposition with TNB showed a homogenous sample with only individual MWCNTs covered with TiO₂ without any jam-like aggregates between CNTs and TiO₂. Higher magnifications (Fig. 3(b) and (d)) showed that all the MWCNTs are homogeneously covered in the wall of TiO₂ and TiO₂ aggregates are not observed. These materials were shown microscopically compact and uniformly distribution and aggregates linked the MWCNTs resulting in a dense material. It was well explained that the good dispersion of small MWCNT particles into the TiO₂ aggregates could provide the information on the existence of more reactive sites, due to a considerable portion of TiO₂ would be enclosed in the three-dimensional matrix. Accordingly, a high photocatalytic yield was expected for a homogenous distribution of small MWCNT particles into the TiO₂ aggregates. The higher photocatalytic activity of the CNT/TiO₂ composites might be attributed to the homogenous distri-

**Figure 4.** UV/VIS spectra of MB concentration against the CNT/TiO₂ composites under various irradiation time conditions; (a) MCT composite catalysts and (b) HMCT composite catalysts.

bution of CNT complexes and play important role as an energy sensitizer for improving the quantum efficiency and a charge transfer of the CNTs.

Photocatalytic effect of MB. Figure 4 showed changes by color disappearance in relative MB degradation concentration under UV light irradiation in the solution as a function of time. The MB degradation with CNT/TiO₂ composite was carried out to observe the UV photolysis effect. As shown in earlier study,^{11,14} if the MB concentration used is higher,¹¹ the intensity of absorbance maxima values could be estimate by photoproduct formed as a function of irradiation time. The formation of absorbance maxima was proportional to the concentration decreased of the transient formed after the UV light excitation. However, if the concentration is lower,¹⁴ the maxima values could not be certainly estimated, but absorbance at tried region decreased with an increase of degradation time. In this study, the measurement of absorbance from 220 nm to 600 nm region with MB products was tried as the function of photodegradation time by CNT/TiO₂ composites. It was shown that the maxima values were moved into long wavelength with a decrease to lower absorbance region with increasing irradiation time. It is considered that the light transparent of the MB solution highly increase by photocatalytic degradation effect.

The photocatalytic degradation of MB in aqueous solution containing CNT/TiO₂ composite photocatalyst under ultra-

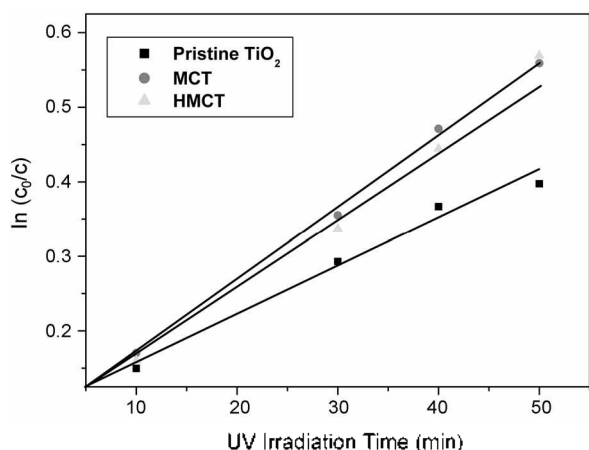


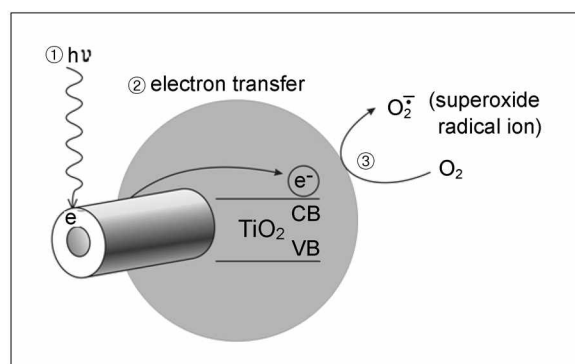
Figure 5. Apparent first-order linear transform $\ln(c_0/c)$ against $f(t)$ of MB degradation kinetic plots for TiO₂, MCT composite and HMCT composite.

violet light irradiation follows pseudo-first-order kinetics. The kinetic plots were shown by apparent first-order linear transform $\ln(c_0/c)$ against time function ($f(t)$) in Figure 5. The changes by color removal were presented on the logarithm scale of relative concentration $\ln(c_0/c)$ of MB degraded in the aqueous solution as a function of UV irradiation time. The appearance photodegradation effect might be due to the combination of the presence of UV light and an oxidation effect by dissolved oxygen in the suspension. The MB solution is quite unstable with variation of concentration when it was irradiated under UV light with CNT/TiO₂ composites. The relationship on the $\ln(c_0/c)$ of MB solution products as a time function under UV irradiation was shown linearity properties depending on kinetic first-order. As above mentioned, MWCNT had an energy sensitizer for improving the quantum efficiency with an increase of charge transfer. It is believed that the degradation of MB concentration in the aqueous solution can be occurred in two physical phenomena such as quantum efficiency by CNT and photocatalytic decomposition by TiO₂. As a MB molecules absorbed energy from irradiation, therefore their delocalized electrons can be shift from bonding to anti-bonding orbital. Since MB adsorption likely occurs *via* π - π interactions between its delocalized electrons and the CNT's graphene layers, it is reasonable that shifts in its electron orbital would alter adsorption. The activity of the synthesized catalysts evaluated by comparing the apparent first-order rate constants (k_{app}) listed in Table 3. A combination factor (R) was defined as $R = k_{app}(\text{CNT}/\text{TiO}_2)/k_{app}(\text{TiO}_2)$ to quantify the combination effect. TiO₂ and CNT/TiO₂ composite photocatalyst (CT) give apparent rate constant of $6.8 (\pm 0.1) \times 10^{-3}$ and $1.1 (\pm 0.1) \times 10^{-2}$, respectively. The introduction of MWCNT into matrix obviously creates kinetic combination effect in MB degradation with an increase in the rate constant by the combination factor of 1.62. In this paper, the photocatalytic effect of CNT/TiO₂ composites could be attributed to the homogeneous aggregation of MWCNT in the TiO₂ aggregates. The combination effect between MWCNT and TiO₂ could be ascribed the enhanced

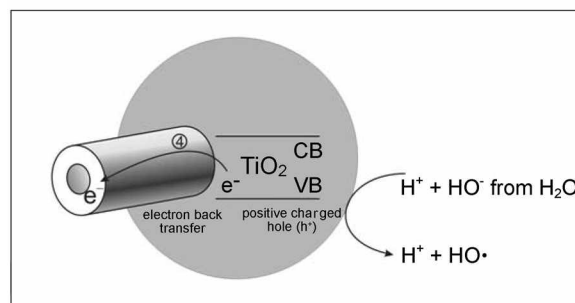
Table 3. The Apparent Kinetic Constant (k_{app}) of CNT/TiO₂ Samples Prepared with Non and Hydrochloric Acid Treatment to MWCNT

Sample	$k_{app} (\text{min}^{-1})$	R
Pristine TiO ₂	$6.8 (\pm 0.1) \times 10^{-3}$	1
MCT	$1.1 (\pm 0.1) \times 10^{-2}$	1.62
HMCT	$9.1 (\pm 0.1) \times 10^{-3}$	1.33

degradation of the MB as a pollutants on CNT/TiO₂ composite followed by a transfer through an interphase to titania where it is photo-degraded. According to earlier studies,^{21,24} the combination effects for the MB degradation should be attributed to the both effects between photocatalysis of the supported TiO₂ and adsorptivity of the carbons. From the results of MB solution degraded during 50 minutes at 1.0×10^{-6} mol/L of initial MB concentration, it was shown that the kinetics for the CNT/TiO₂ composites results in a more significant degradation effect with increase of $\ln(c_0/c)$ values than that of original TiO₂. In the photocatalytic performance, it is suggested that the shade of MB concentration should be considered to the both effects between photocatalysis of the supported TiO₂ and charge transfer on the MWCNT layers. The photocatalytic decomposition of pollutants occurs on TiO₂ particles, even on those coated it on the carbon or aggregated it in the carbon, and that light absorption was actives on carbon particles. But, it is considered that carbon deep inside TiO₂ is not easily



- 1) CNT/TiO₂ → CNT⁺/TiO₂⁻
- 2) CNT⁺/TiO₂⁻ + O₂ → CNT⁺/TiO₂ + O₂⁻



- 3) CNT⁺/TiO₂⁻ → CNT/TiO₂⁺
- 4) CNT/TiO₂⁺ + (H⁺ + OH⁻ from H₂O) → CNT/TiO₂ + H⁺ + HO[·]

Figure 6. Schematic diagram of mechanism to describe the combination effect to MWCNT acting as electron sensitizer and donor in the composite photocatalysts.

accessible to light with excitation due to the long traveling distance and reflection and scattering by the support.

As plausible mechanism, it is quite reasonable to describe the combination effect to MWCNT acting as electron sensitizer and donator in the composite photocatalysts. The schematic diagram for the mechanism was shown in Figure 6. According to the semiconducting properties of CNT, MWCNT may accept the photo-induced electron (e^-) by UV irradiation. It is considered that the electrons in MWCNT transfer into the conduction band in the TiO_2 particles. In this time, these electrons in conduction band may react with O_2 , which can be trigger the formation of very reactive superoxide radical ion ($O_2^{\cdot-}$). Simultaneously, a positive charged hole (h^+) might be formed with electron transfer from valence bond in TiO_2 to MWCNT. The positive charged hole (h^+) may react with the OH^- derived from H_2O , which can be trigger the formation of hydroxyl radical (HO^{\cdot}). Consequently, these radical groups are responsible for the decomposition of the organic compounds.

Conclusions

In this study, we present the synthesis and characterization of CNT/ TiO_2 composites thermally derived from MWCNTs and TNB by an improved oxidation method. The structural variations, elemental analysis and surface morphology are investigated through preparation of two kinds of CNT/ TiO_2 composites. In the XRD patterns for the CNT/ TiO_2 composites, the patterns reveal that only anatase phase can be identified for MCT composite, but the HMCT composite synthesized with HCl treatment was observed the mixed phase of anatase and rutile. The EDX spectra were shown the presence as major elements of Ti with strong peaks. From the SEM results, the sample MCT and HMCT synthesized by the thermal decomposition with TNB were shown a homogenous sample with only individual MWCNTs covered with TiO_2 without any jam-like aggregates between CNTs and TiO_2 . According to the photocatalytic results, the relationship on the $\ln(c_0/c)$ of MB solution products as a time function under UV irradiation was shown linearity properties depending on kinetic first-order. From the results, it could be suggested the plausible photocatalytic mechanism between MWCNTs and TiO_2 .

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