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# Fabrication of Carbon Nanotube/$TiO_2$ Composite Photocatalysts and Their Electro-photolysis for Organic Dye

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In present work, the improved performance of carbon nanotube/$TiO_2$ structure electrode for organic dye has been studied. The composite electrodes consisting of carbon nanotubes (CNTs) and a titanium oxide matrix with phenol resin binder was fabricated by means of mixture method. The chemical and morphological structure of CNT/$TiO_2$ composites were characterized by means of BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), Raman spectroscopy and energy dispersive X-ray (EDX). The electrode showed a remarkably enhanced performance for methylene blue oxidation under UV illumination with or without electro-chemical reaction. Such a remarkably improved performance of the CNT/$TiO_2$ structure electrode might be due to the enhanced methylene blue oxidation by electro- and photo-generated electrons and holes in the CNT and $TiO_2$ under UV illumination with or without electro-chemical reaction.

**Key Words: Carbon nanotubes, Titanium dioxide, SEM, XRD, EDX, Elctrolysis, Photorolysis.**

## INTRODUCTION

In recent years carbon nanotube have been widely explored in electrochemical studies[1,2], mainly for microelectrode construction[3]. Microelectrodes prepared with carbon nanotubes (CNTs) material have good advantage due to their efficient radial mass transport properties leading to high sensitivity and short response time allowing for scanning. Another important advantages displayed by CNTs as electrodes is their high surface area containing acidic functional groups, which allow modification possibilities[4,5]. Titanium dioxide, a large-band-gap semiconductor, is an excellent candidate as photocatalysts in the electro-oxidation of a wide variety of organic and inorganic substances[6]. Titanium dioxide shows high adsorption ability to organic dye, corresponding with a high photocatalytic activity. $TiO_2$, as one of the semi

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conductive oxide, has been widely studied for its special photoelectric properties. In addition, $TiO_2$ is very stable in acidic solution and it is reported that $TiO_2$ electrode has high catalytic activity and CO-tolerance for alcohol electro-oxidation[7]. Several modified methods have been reported to improve the photocataytic efficiency. These include increasing the surface area and efficiency of photocatalysts[8], the generation of defect structures to induce space-charge separation[9] and the modification of $TiO_2$ with metals[10,11] or other semiconductors and carbon materials[12-15]. Another method that might possibly increase the photocatalytic efficiency of $TiO_2$ is to add a co-sorbent such as silica, alumina, zeolites or clay and activated carbon[16-19]. The development of new materials for modifying $TiO_2$ system is urgently needed to increase the photocatalytic activity of $TiO_2$ for organic pollutant treatment. Carbon nanotube based electrodes attract considerable attention due to their special structure, extraordinary mechanical and unique electronic properties and potential applications. Their high mechanical strength makes them to be good candidates for advanced composites. They have either semiconducting, semimetallic or metallic, depending on the helicity and the diameter of the tube[20]. Such various properties open a promising field in nanoscale electrodevice applications. Thus, CNTs based electrode can be used as a promising system in the environmental cleaning. The application of CNTs electrode to enhance the photocatalytic activity of $TiO_2$ is proposed due to its superior photocatalytic ability compared with other photocataysts. The purpose of this study is to propose synergetic effects of photolysis and electrolysis with CNT/$TiO_2$ electrode system by an electro-chemical method and to develop a new method to regenerate CNT/$TiO_2$ composite electrodes. The electrical driving force may play role in the sorption and decomposition of nonpolar molecules and metallic ions by creating obstacles for physical adsorption and prevent molecules from occupying the most energetically favourable positions on the carbon surface[21,22].

In this study, we have focused on the characterization of the CNT/$TiO_2$ composite electrodes prepared with weight ratio among CNT, anatase typed $TiO_2$ and phenol resin binder. Moreover, the adsorption effects, structural variations, surface state and elemental compositions were investigated through preparation of three kinds of CNT/$TiO_2$ composites. We have studied the chemical and morphological structure of CNT/$TiO_2$ composites by means of BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), Raman spectroscopy and energy dispersive X-ray (EDX). Finally, methylene blue solutions obtained from photolysis and electrolysis with CNT/$TiO_2$ electrode system by an electrochemical method were characterized by UV/Vis spectrophotometer.

## EXPERIMENTAL

Crystalline multiwalled carbon nanotube (MWCNT) powder of 95.9 wt. % purity from Carbonnano (Carbonnano Co., Ltd, Korea) was used as a starting material. Reagents (benzene, tetrahydrofuran and ethyl alcohol) were purchased as reagent-grade from Duksan Pure Chemical Co and Daejung Chemical Co. and used without further purification unless otherwise stated. Methylene blue ($C_{16}H_{18}N_3SCl\cdot 3H_2O$) was analytical grade and also purchased from Duksan Pure Chemical Co., Ltd. The novolac typed phenol resin was supplied from Kangnam Chemical Co. (Korea). The $TiO_2$ photocatalysts was commercially available (Duk-San Pure Chemical Co., Korea), which was composed of a single phase of anatase with secondary particles of about 80-150 μm aggregated from the primary particles of about 30-50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area of about 8.319 $m^2/g$.

**Fabrication of electrodes:** For the melting of phenol resin, ethyl alcohol was used as solvent. After dissolving of phenol resin in the alcohol solution, $TiO_2$ powder and CNT were mixed with resin-alcohol solution. And then, the mixtures were pressed into 9.95 mm × 39.5 mm × 5.95 mm hexagonal pellets in a mould. The curing temperature of the pelletized CNT/$TiO_2$ matrix was about 423 K. The cured samples were then pyrolyzed at 673 K for 1 h in order to completely cure the binder. The nomenclatures of prepared samples were listed in Table-1.

TABLE-1
NOMENCLATURES OF CNT/$TiO_2$ COMPOSITES PREPARED AS FUNCTION OF PREPARATION CONDITION

| Preparation method | Nomenclatures |
|---|---|
| Carbon Nanotube (50) + Titanium Dioxide [$TiO_2$ (99.99 %), Anatase] (10) + Phenol Resin (Binder) (40) | CTP |
| Carbon Nanotube (30) + Titanium Dioxide [$TiO_2$ (99.99 %), Anatase] (30) + Phenol Resin (Binder) (40) | CTP1 |
| Carbon Nanotube (10) + Titanium Dioxide [$TiO_2$ (99.99 %), Anatase] (50) + Phenol Resin (Binder) (40) | CTP2 |

*(Numerical Quantitiy): Weight Ratio (wt. %).

**Electrochemical characteristics:** The CNT/$TiO_2$ composite matrix of test electrode was consisting of the size of 9.95 mm × 39.5 mm × 5.95 mm. The counter electrode of same size was artificial graphite (TCK, Korea). The initial methylene blue solutions of $1.0 \times 10^{-5}$ mol/L ($c_0$) were used as an electrolyte. The condition of electrochemical reaction (ECR) for the measurements was 0.5 $mA/cm^2$ with 3 V at room temperature.

**Characterization of CNT/$TiO_2$ composites:** For the characterization of CNT/$TiO_2$ composites, $N_2$ adsorption isotherm was measured at 77 K using a BEL sorp Analyzer (BEL, Japan). Then the BET surface area was calculated by nitrogen adsorption. SEM (JSM-5200 Jeol, Japan) was employed to observe the surface state and structure of the three kinds of CNT/$TiO_2$ composites. For the determination of the crystallographic structure of the composites, XRD patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with CuKα radiation. EDX spectra were also used for elemental analysis of the samples. For the analysis of the electrophotodegradation effects, UV-Vis spectra of the CNT/$TiO_2$ composites were recorded using a Genspec (Hitachi, Japan) spectrometer.

**Elclectrophotocatalytic (EPC) effect:** The elclectrophotocatalytic decomposition was performed with CNT/$TiO_2$ electrode and an aqueous solution of methylene blue in a 100 mL glass container with ultraviolet (UV) light and with or without electro-chemical reaction. For UV irradiation, the electro-chemical reaction container was located axially and held in the UV lamp (20 W, 365 nm) box. The lamp was used at a distance of 100 mm from the solution in the darkness box. The $c_0$ was $1.0 \times 10^{-5}$ mol/L. The container was irradiated with UV light and operated with or without electro-chemical reaction as a function of irradiation time. Methylene blue solution degraded was then withdrawn regularly from the reactor. The clean transparent solution was analyzed by UV/Vis spectroscopy. The concentration of methylene blue in the solution was determined as a function of irradiation time from the absorbance region at a wavelength line of 660 nm.

## RESULTS AND DISCUSSION

**Adsorption and surface properties:** The CNT/$TiO_2$ composite catalysts fabricated with anatase, CNTs and phenol resin binder were noted as CTP, CTP1 and CTP2. Nitrogen adsorption isotherms for the pristine CNTs and three kinds of CNT/$TiO_2$ composites are shown in Fig. 1. The formation of type II adsorption isotherms in these samples confirmed, which can be ascribed to one kind of reason for the containing of the majorly micropores and minorly mesopores on the surface of the composites. The adsorption volumes of CNT/$TiO_2$ composites studied decreased with an increase of $TiO_2$, which were mainly micro- and mesoporous in character with pore blocking and a minor presence of wider pores where capillary condensation occurred. Table-2 shows the textural properties with microstructure changes of CNT/$TiO_2$ samples compared with pristine CNT and $TiO_2$. The BET surface areas of pristine $TiO_2$ and CNTs are 8.319 and 299.2 $m^2/g$, respectively, while those of composite catalysts decreased from 135.1 to 28.86 $m^2/g$ with an increase of $TiO_2$ components. It is observed that the surface areas of composite catalysts are catastrophically reduced due to decreasing of CNTs components. Average pore diameter of different solids obtained from $N_2$ isotherm are also given in Table-2. Pores in multi walled CNT (MWCNT) include narrowly distributed inner hollow cavities of 3.4 nm and widely distributed aggregated pores of 20 nm formed by interaction of isolated MWCNT[23]. In this study, $TiO_2$ presents the average pore size at 5.831 nm. Average pore diameter of the MWCNT was 7.114 nm, which decreased greatly to about 4.432 and 2.946 nm

TABLE-2
TEXTURAL PROPERTIES OF CNT/$TiO_2$ COMPOSITE SAMPLES

| Sample | Parameter | | |
|---|---|---|---|
| | $S_{BET}$ ($m^2/g$) | Micropore volume ($cm^3/g$) | Average pore diameter (nm) |
| $TiO_2$ | 8.319 | 0.0121 | 5.831 |
| CNT | 299.2 | 0.3496 | 7.114 |
| CTP | 135.1 | 0.2437 | 7.218 |
| CTP1 | 100.4 | 0.1112 | 4.432 |
| CTP2 | 28.86 | 0.0112 | 2.946 |

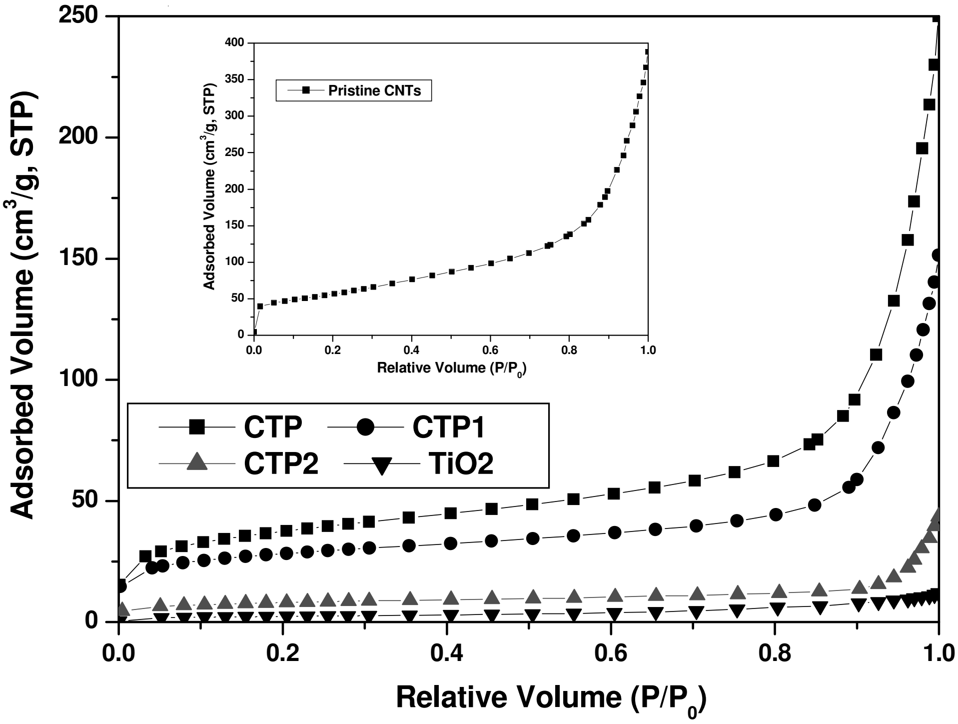
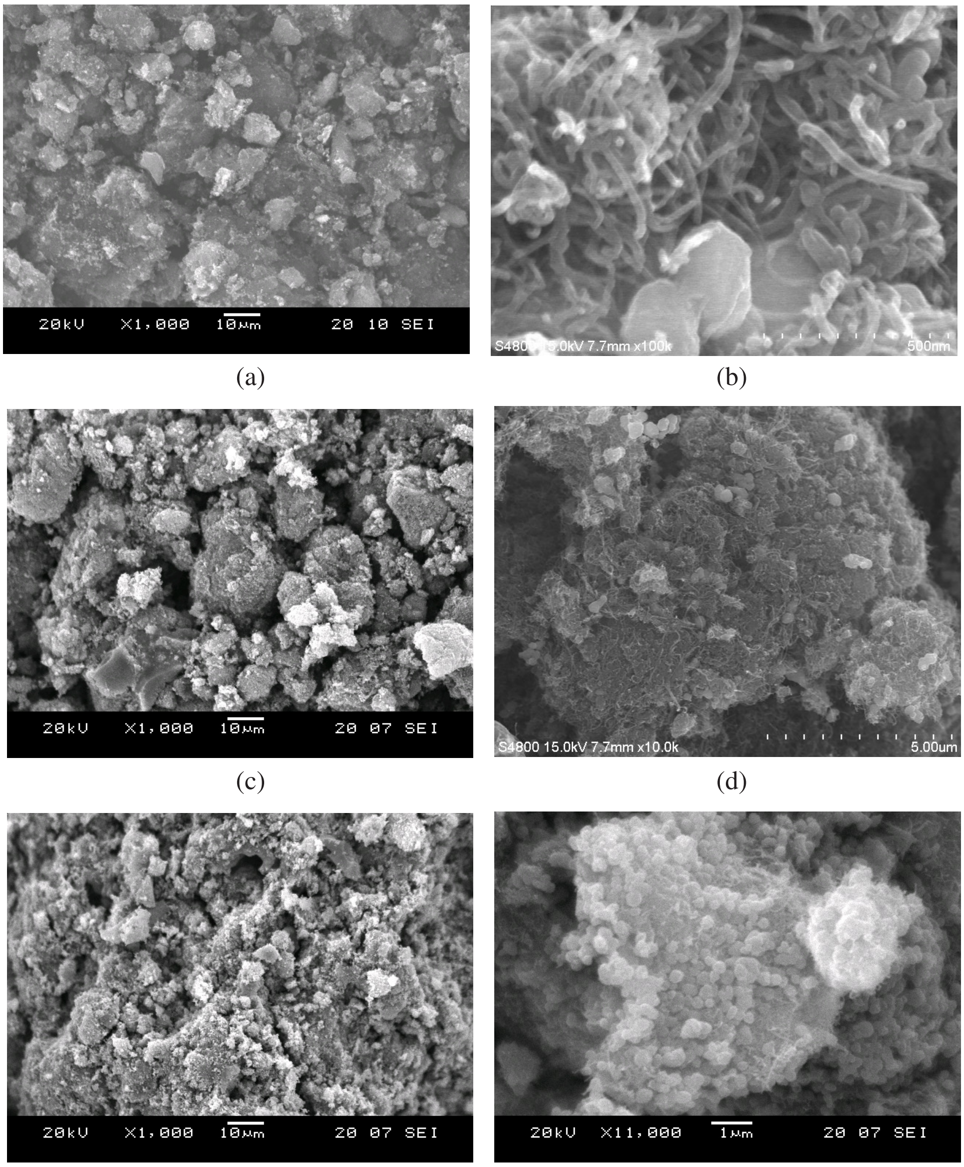


Fig. 1. Nitrogen adsorption isotherms obtained from the pristine TiO$_2$, CNTs and CNT/TiO$_2$ composites

when CTP1 and CTP2 composites were formed. It is considered that the average pore diameter is decreased a lot and it indicated that CNTs particles are homogenously distributed with TiO$_2$ particles. All of surface textural parameters for these composites were considerably more decrease than that of pristine materials due to surface structural modification by an increase of TiO$_2$ components.

The micro-surface structures and morphology of the CNT/TiO$_2$ composites fabricated with anatase, CNTs and phenol resin binder were characterized by SEM and FE-SEM. The changes in the morphology for the CNT/TiO$_2$ composites obtained from present experimental condition are presented in Fig. 2. In case of CTP, it seems that a small amount of TiO$_2$ introduced into CNTs is distributed with TiO$_2$ particles from agglomerating. The particles of TiO$_2$ among the CNTs aggregated to be small clusters and the aggregation was more evident of binding effect by phenol resin. This result (Fig. 2b) as well confirmed by FE-SEM inspection of CNT/TiO$_2$ composite materials. The image presents a close-up scale view of TiO$_2$ introduced from composite with external diameters ranging from 1.0 to 1.5 μm. In case of CTP1 and CTP2, it seems that a large amount of TiO$_2$ particles introduced into composites are distributed with a decrease of CNTs from agglomerating. It is observed that the pores for the composite matrix together with the interphases between the agglomerates resulted in the appearance of meso or macropores. All samples have pores in their structures, which are connected randomly and lack discernible long-range order in the pore arrangement. It is also found that, with the increase of the amount of CNTs, the morphology of $TiO_2$ changes from spherical particles (Fig. 2b, d and f), big agglomerated particles to bulk and there are more and more CNTs observed in the composites.



(a) (b)

(c) (d)

(e) (f)

Fig. 2. SEM and FE-SEM micrographs for the CNT/$TiO_2$ composites ; (a) CTP (over-all scale), (b) CTP (close-up), (c) CTP1 (over-all scale), (d) CTP1 (close-up), (e) CTP2 (over-all scale) and (f) CTP2 (close-up)

By virtue of the composites with phenol resin being sintered, CNTs and $TiO_2$ particles were coherent each other, which formed the agglomerates with compact framework over the whole composites. However, the distribution of $TiO_2$ in the composites was not very uniform due to the control of amount of CNTs or $TiO_2$ in fabrication process. Adding a few CNTs to the polymer matrix may significantly enhance the mechanical properties[24]. However, the morphology state and mechanical properties of CNT/$TiO_2$ composites depend on the affinity of the filler to the phenol resin matrix.

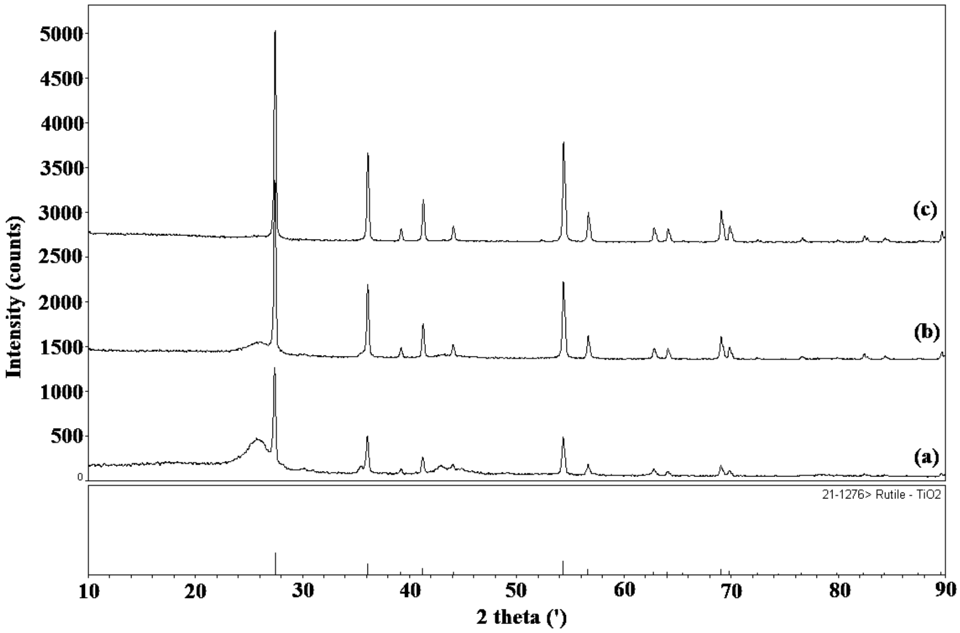
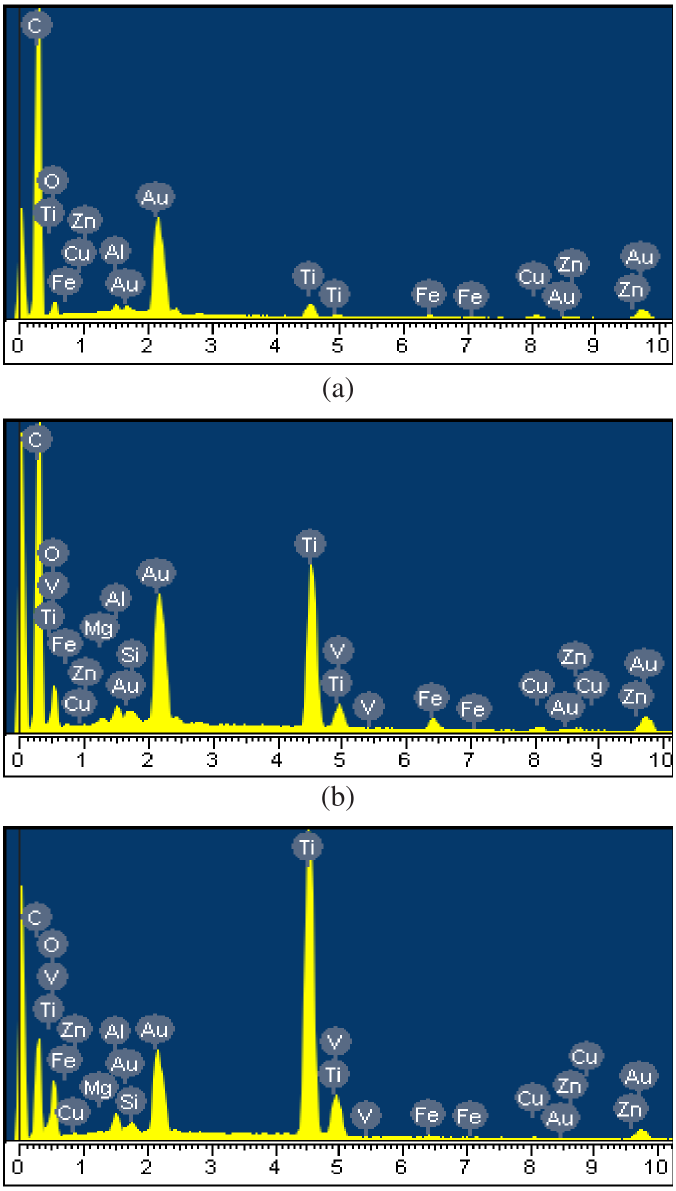


Fig. 3. XRD patterns of the CNT/$TiO_2$ composites prepared with pristine CNTs and titanium dioxide; (a) CTP, (b) CTP1 and (c) CTP2

**Structural and chemical components:** Fig. 3 showed the XRD patterns of three kinds of samples fabricated with CNTs, anatase and phenol resin binder. These results are presented the highly crystalline nature of the composites. X-ray diffraction results indicate that the phase transition from anatase phase to rutile phase has taken place at heat treated temperature (673 K). The most intense peaks of $TiO_2$ correspond to the rutile phases of (110), (101), (200), (211), (220), (311) and (112) at 28.1, 37.0, 89.1, 53.2, 55.2, 67.8 and 69.2 peaks. In case of CTP1 and CTP2, one kind of intense peak of MWCNTs had presented to the (002) reflection. It is worth to notice that the intensity of CNTs diffraction peak increase from CTP to CTP2 and the width at half height of the peaks increases. This is consistent with the increasing amount of CNTs from CTP to CTP2. However, the diffraction peaks of MWCNTs were not clearly observed due to the relatively high intensity of $TiO_2$. Of the two crystal forms of $TiO_2$ catalysts, the anatase invariably exhibits a higher photoactivity than the rutile dose[25,26]. In contrast to present results, the results from Kominami *et al.*[27], showed that the XRD patterns of $TiO_2$ derived from titanium alkoxide in organic solvents consistently presented the formation of anatase crystallites at low temperatures.



(a)

(b)

(c)

Fig. 4. EDX elemental microanalysis for the CNT/$TiO_2$ composites; (a) CTP, (b) CTP1 and (c) CTP2

Elemental analyses of CNT/$TiO_2$ composites fabricated with CNTs, titanium dioxide and phenol resin binder were confirmed using energy disperse X-ray. Fig. 4 showed the spectra obtained from the CNT/$TiO_2$ composites. The spectra indicate the presence of C, O and Ti as major elements with small impurity metallic components. Additionally, the numerical result of quantitative EDX microanalysis of the CTP yielded a component ratio of 81.3: 10.4: 2.68 for C: O: Ti. However, the results of the other case increased for the Ti component with a decrease of the C component. In the case of most of the samples, C, Ti and O components were present as major elements in the CNT/$TiO_2$ composites. The results of the EDX elemental microanalysis (wt. %) of CNT/$TiO_2$ composites are listed in Table-3.

TABLE-3
EDX ELEMENTAL MICROANALYSES OF CNT/$TiO_2$ COMPOSITES

| Sample | C | O | Ti | Others | Total |
|---|---|---|---|---|---|
| CTP | 81.3 | 10.4 | 2.68 | 5.67 | 100.0 |
| CTP1 | 56. 9 | 18.9 | 17.3 | 6.82 | 100.0 |
| CTP2 | 26.6 | 33.5 | 36.8 | 3.10 | 100.0 |

Raman spectroscopy had been commonly applied discriminate the local order characteristics of CNTs. Fig. 5 showed the comparison of the Raman spectra of CPT series in the wavenumber range between 1000 and 2000 $cm^{-1}$. There are three strong peaks at about 1134, 1330 and 1590 $cm^{-1}$ in the samples of CNT/$TiO_2$ electrodes. The peak at 1330 $cm^{-1}$ is assigned to the ill-organized graphite, the so-called D-line in CNTs[28]. The peak at around 1590 $cm^{-1}$ is an unresolved Raman triplet identified with tangential carbon atom displacement modes, which is related to the $E_{2g}$ mode in graphite[29]. The spectra of CNT/$TiO_2$ electrodes prepared are shown two strong peaks corresponding to the characteristic modes of MWCNTs. Another peak assigned at 1134 $cm^{-1}$ can be attributed to the $TiO_2$ compound derived from titanium sources.

**Electrophotocatalytic effects for the methylene blue (MB):** The dye degradation studies in aqueous solution installed CNT/$TiO_2$ composite electrode showed that three kinds of samples could photocatalyzed with or without electolysis for the MB. The changes of the absorbance after a colour removal process in the relative MB degraded concentration using the CNT/$TiO_2$ composites under photolysis with or without electrolysis are shown in Fig. 6. These changes of the absorbance for the MB degradation with CNT/$TiO_2$ photocatalysts were used to measure the differences of decomposition effect under the photolysis with or without electrolysis. In UV/Vis spectra, the absorbance maxima ($\lambda_{max}$) values for the decomposed MB products were remarkable distinguished as a function of the degradation time against the CNT/$TiO_2$ photocatalysts with or without electro-oxidation. As general tendency, the $\lambda_{max}$ values moved a lower absorbance region with an increase of the ECR time for all of samples. In previous studies[30-32], it is consistent that the intensity of the $\lambda_{max}$ values measured as a function of the irradiation time depends on the concentration

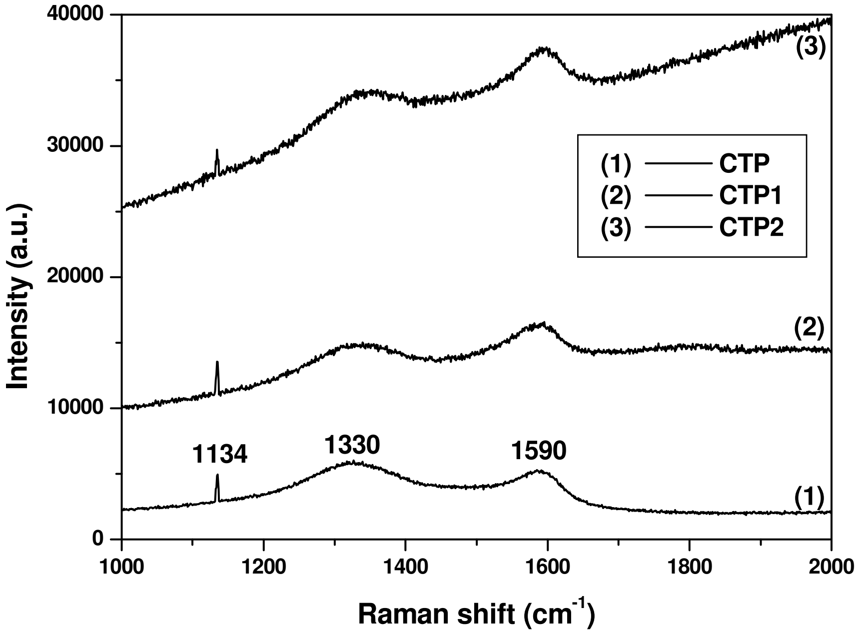
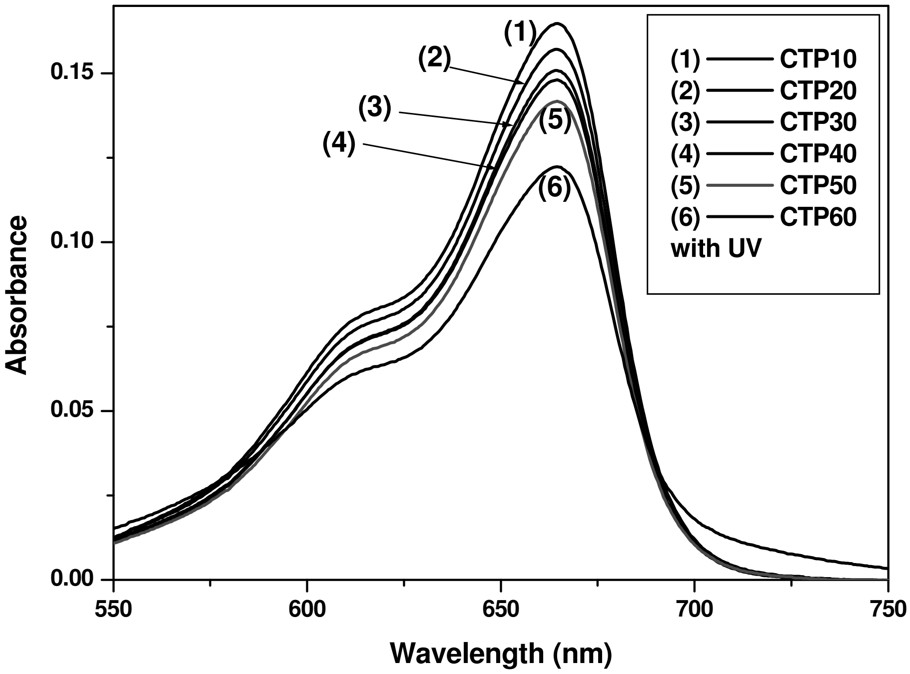
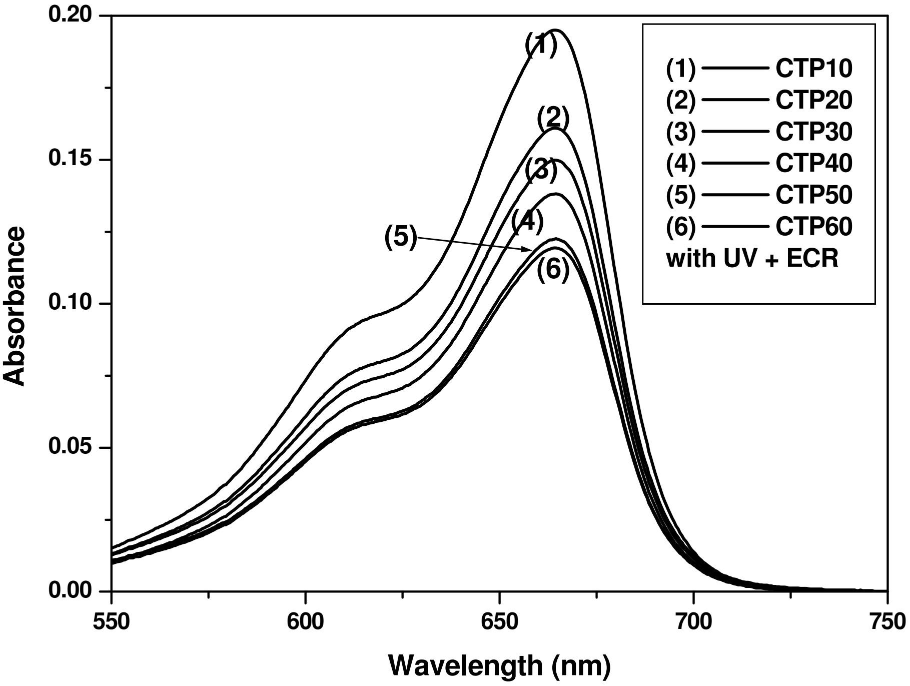


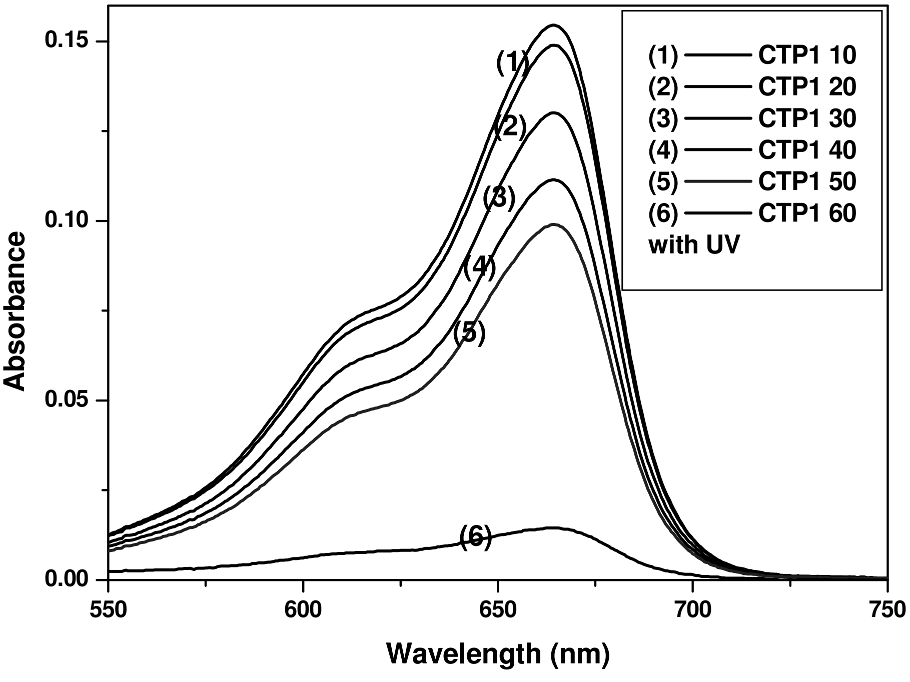
Fig. 5. Raman spectra of the CNT/TiO$_2$ composites prepared with pristine MWCNTs and titanium dioxide



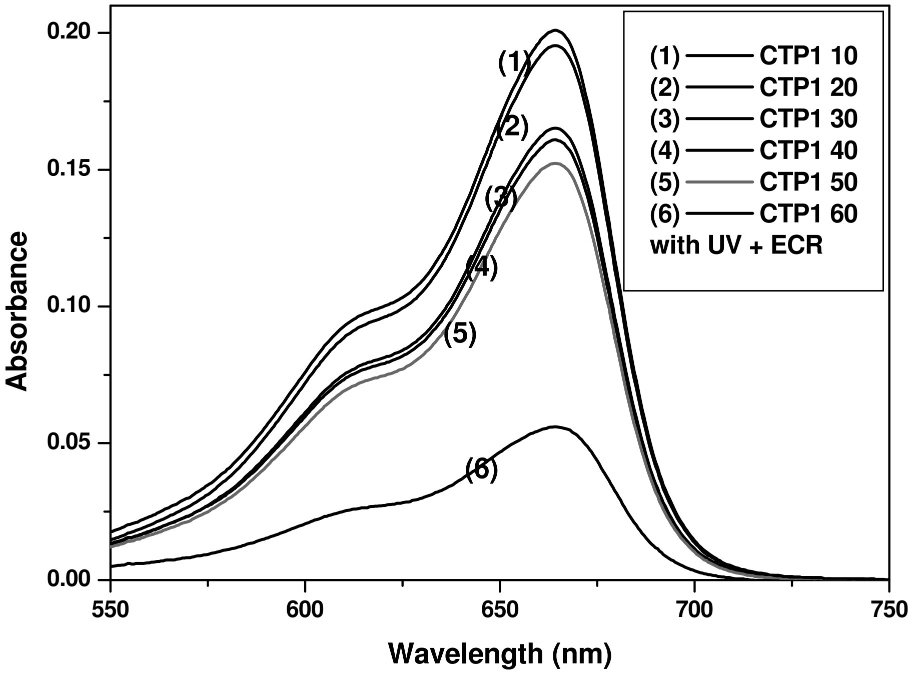
(a)


Absorbance
0.20
0.15
0.10
0.05
0.00
550
600
650
700
750
Wavelength (nm)
(1)
(2)
(3)
(4)
(5)
(6)
(1) CTP10
(2) CTP20
(3) CTP30
(4) CTP40
(5) CTP50
(6) CTP60
with UV + ECR

(b)


Absorbance
0.15
0.10
0.05
0.00
550
600
650
700
750
Wavelength (nm)
(1)
(2)
(3)
(4)
(5)
(6)
(1) CTP1 10
(2) CTP1 20
(3) CTP1 30
(4) CTP1 40
(5) CTP1 50
(6) CTP1 60
with UV

(c)


Absorbance
0.00
0.05
0.10
0.15
0.20
Wavelength (nm)
550
600
650
700
750
(1) CTP1 10
(2) CTP1 20
(3) CTP1 30
(4) CTP1 40
(5) CTP1 50
(6) CTP1 60
with UV + ECR
(1)
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(3)
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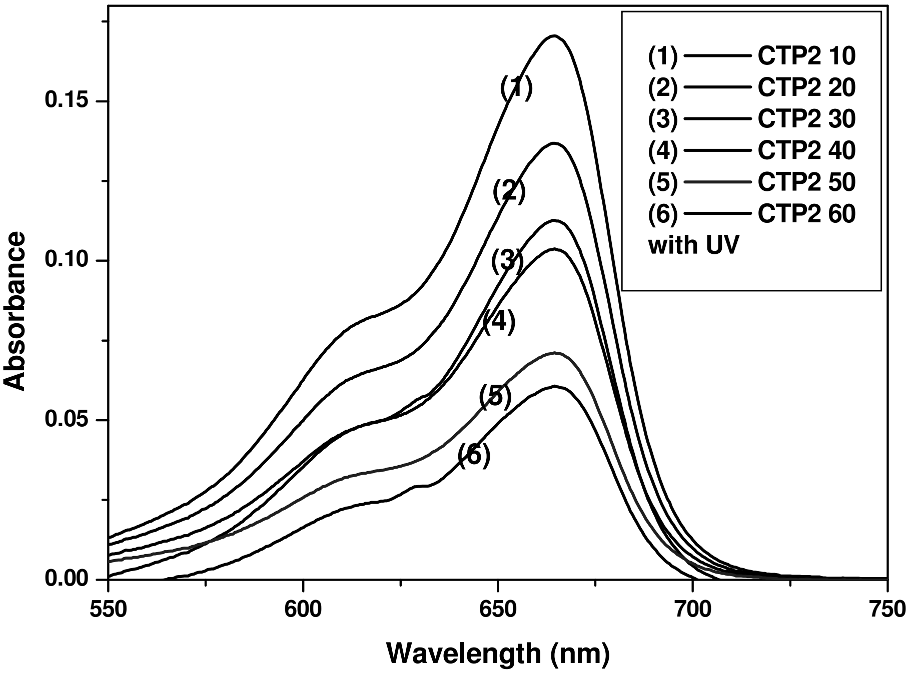
(d)


Absorbance
0.00
0.05
0.10
0.15
Wavelength (nm)
550
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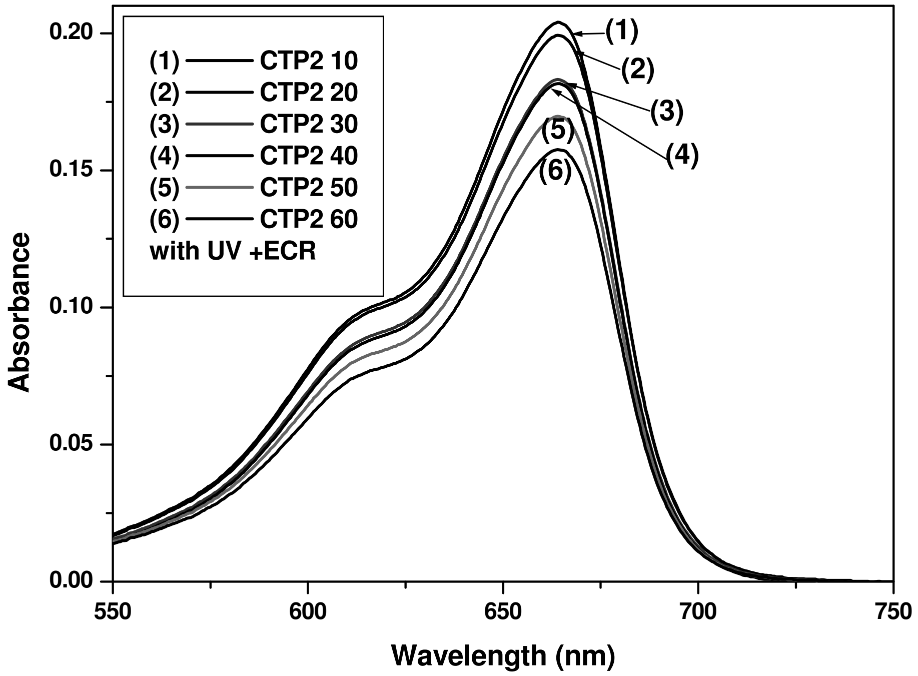
650
700
750
(1) CTP2 10
(2) CTP2 20
(3) CTP2 30
(4) CTP2 40
(5) CTP2 50
(6) CTP2 60
with UV
(1)
(2)
(3)
(4)
(5)
(6)

(e)



(f)

Fig. 6. UV/Vis spectra of methylene blue concentration against the CNT/TiO$_2$ composites after electrolysis and photolysis as time function

of organic dyes. The values were proportional to the concentration decrease of the transient formed after UV light excitation with or without electro-chemical reaction (ECR), due to the sharp decrease in the $\lambda_{max}$ values of absorbance by a degradative reaction.

Fig. 7 showed the changes of relative concentration ($c/c_0$) against time function [f(t)] by the photocatalytic degradation of MB solution installed with CNT/TiO$_2$ composite photocatalysts under UV light irradiation with or without ECR. In case of all samples, it was shown that the MB solution is quite unstable against CNT/TiO$_2$ composites under UV light irradiation without ECR. Especially, the solution decomposed with the sample CTP with UV and ECR appeared an excellent degradation effect with reaction time, due to the increase of electrical conductivity and electro-oxidation activity. It is expected that the operation of CTP with UV and ECR is good candidate for the degradation of organic materials in pollutants. Generally, MWCNTs had a semi-conducting with an increase of charge transfer. It is considered that the decomposition of organic dye in the aqueous solution occur in two synergetic effects such as photodecomposition and quantum efficiency. Carbon nanotubes have 1D carbon-based ideal molecule with the nanocylinder structures, which can conduct electricity at room temperature with essentially no resistance. This phenomenon is known as ballistic transport[20], where the electrons can be considered as moving freely

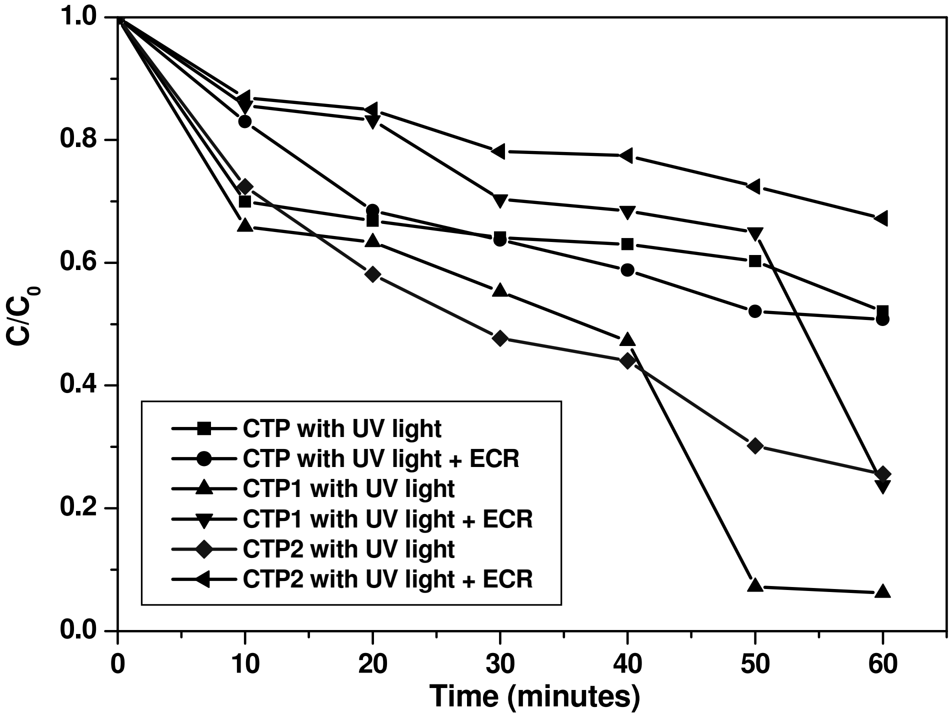


Fig. 7. Dependence of relative concentration of methylene blue in the aqueous solution $C/C_0$ after electrolysis and photolysis as time function with the CNT/$TiO_2$ composites electrodes

through the structure, without any scattering from atoms and defects. While the electron formed by the UV irradiation and electrical power migrate to the surface of $TiO_2$, it is easy for the electrons to transport in CNTs which are bound with $TiO_2$. The semiconducting properties of MWCNTs have been introduced the indubitable interaction between MWCNT and $TiO_2$[32], which may led to the higher catalytic activity by the process of the electron/hole pair formation under light irradiation. Multi walled carbon nanotubes acting as electron sensitizer and donator in the composite photocatalysts may accept the electron ($e^-$) induced by light irradiation or ECR. The electrons in MWCNTs may be transfer into the conduction band in the $TiO_2$ particles. It is considered that photo-induced charge transfer occurs in the electronic interaction between the carbon layers or walls of MWCNT and $TiO_2$. The electrons formed by the light irradiation or ECR on the surface of MWCNTs migrate to the surface of $TiO_2$ and thus they lead to the higher rate of the reduction of the $e/h^+$ pair recombination and the increase of the photon efficiency, which reduces the quantum yield of the $TiO_2$ catalyst. It has been confirmed that photo- or electro-induced charge transfer occurs in the electronic interaction between polymer chain and CNTs[4]. Since they connect well with each other and there is a strong interaction between CNTs and $TiO_2$, it is proposed that $e^-$ transfer also happens in the CNT/$TiO_2$ composites, leading to the $e^-/h^+$ recombination and the increase of the photon efficiency. The light absorption capability of photocatalyst and separation of photo-generated $e^-/h^+$ pairs are crucial factors influencing the photoactivity. Accordingly, it is more reasonable to ascribe that the electron absorptionability of CNT/$TiO_2$ composites greatly increases due to the more active sites available on the CNTs surface. Considering the semiconducting property of CNTs, it may absorb the irradiation and inject the photo- or electro-induced electrons into $TiO_2$ conduction band. These electrons in conduction band may react with $O_2$, which can be trigger the formation of very reactive superoxide radical ion ($O_2^{\bullet -}$). Simultaneously, a positive charged hole ($h^+$) might be formed with electron transfer from valence bond in $TiO_2$ to CNTs. The positive charged hole ($h^+$) may react with the $OH^-$ derived from $H_2O$, which can be produced the hydroxyl radical ($HO^\bullet$). The more hydroxyl groups on the surface of photocatalysts, the more hydroxyl radical ($HO^\bullet$) will be produced by the oxidation of $h^+$.

## Conclusion

In this study, we present the fabrication and characterization of CNT/$TiO_2$ composite electrodes consisting of CNTs and a titanium oxide matrix with phenol resin binder. The adsorption and surface properties, structural and chemical composition were investigated through preparation of the CNT/$TiO_2$ composites. Surface areas and pore volumes of CNT/$TiO_2$ samples were catastrophically reduced due to increasing of $TiO_2$ components. From the SEM results, all samples have pores in their structures, which are connected randomly and lack discernible long-rang order in the pore arrangement. In the XRD patterns, the diffraction patterns were certainly observed the transformed peaks from anatase to rutile phase. The electron disperse X-ray spectra revealed the presence of major elements such as C and O with strong Ti peaks. According to the photocatalytic results, the solution decomposed with the sample CTP with UV and ECR appeared an excellent degradation effect with reaction time, due to the increase of electrical conductivity and electro-oxidation activity. It is considered that the decomposition of organic dye in the aqueous solution occur in synergetic effects such as photodecomposition and quantum efficiency by photo- and electro-induced electrons.

## REFERENCES

1. T. Maiyalagan, *Appl. Catal. B. Environ.*, **80**, 286 (2008).
2. L. Li, G. Wu and B.Q. Xu, *Carbon*, **44**, 2973 (2006).
3. H. Yadegari, A. Jabbari, H. Heli, A.A. Mosavi-Movahedi, K. Karimian and A. Khodadadi, *Electrochim. Acta*, **53**, 2907 (2008).
4. Y. Yu, J.C. Yu, J.G. Yu, Y.C. Kwok, Y.K. Che, J.C. Zhao, L. Ding, W.K. Ge and P.K. Wang, *Appl. Catal. A. Gen.*, **289**, 186 (2005).
5. H. Song, X. Qiu, F. Li, W. Zhu and L. Chen, *Electrochem. Commun.*, **9**, 1416 (2007).
6. S. Si, K. Huang, X. Wang, M. Huang and H. Chen, *Thin. Solid Films*, **422**, 205 (2002).
7. H. Song, X. Qiu and F. Li, *Electrochim. Acta*, **53**, 3708 (2008).
8. N. Lakshminarasimhan, E. Bae and W. Choi, *J. Phys. Chem. C*, **111**, 15244 (2007).
9. M.C. Thurnauer, T. Rajh and D.M. Tiede, *Acta Chem. Scand.*, **51**, 610 (1997).

10. H. Yamashita, M. Harada, J. Misaka, T.M. Akeuchi and M. Anpo, *J. Photochem. Photobiol. A. Chem.*, **148**, 257 (2002).
11. A.W. Xu, Y. Gao and H.Q. Liu, *J. Catal.*, **207**, 151 (2002).
12. W.C. Oh, J.S. Bae and M.L. Chen, *Anal. Sci. Technol.*, **19**, 301 (2006).
13. W.C. Oh, J.S. Bae and M.L. Chen, *Bull. Korean Chem. Soc.*, **27**, 1423 (2006).
14. W.C. Oh and M.L. Chen, *Bull. Korean Chem. Soc.*, **29**, 159 (2008).
15. W.C. Oh and J.S. Bae, *J. Ceram. Korean. Soc.*, **45**, 196 (2008).
16. H.K. Matrails, M. Ciardelli, M. Ruwet and P. Grange, *J. Catal.*, **157**, 368 (1995).
17. J. Chen, L. Eberlein and C.H. Langford, *J. Photochem. Photobiol. A Chem.*, **148**, 183 (2002).
18. W.C. Oh and M.L. Chen, *Carbon Sci.*, **8**, 108 (2007).
19. W.C. Oh, S.B. Han and J.S. Bae, *Anal. Sci. Technol.*, **20**, 279 (2007).
20. G. Cao, Nanostructures and Nanomaterials, Imperial College Press, pp. 344-360 (2004).
21. W.C. Oh and T.S. Park, *J. Ind. Eng. Chem.*, **11**, 671 (2005).
22. W.C. Oh and C.S. Lim, *J. Ceram. Process. Res.*, **5**, 301 (2004).
23. P. Ndungu, Z.G. Godongwana, L.F. Petrik, A. Nechaev, S. Liav and V. Linkkov, Synthesis of Carbon Nonostructured Materials Using LPG, Microus and Mesoporous Materials, Internet Ed, (2008).
24. S.M. Tuen, C.C. Ma, C.Y. Chung, Y.H. Hsiao, C.L. Chiang and A.D. Yu, *Composites*, **39A**, 119 (2008)
25. M.L. Chen, J.S. Bae and W.C. Oh, *Anal. Sci. Technol.*, **19**, 460 (2006).
26. W.C. Oh, J.S. Bae and M.L. Chen, *Carbon Sci.*, **7**, 259 (2006).
27. H. Kominami, J. Kato, Y. Takada, Y. Doushi, B. Ohtani, S. Nishimoto, M. Inoue, T. Inui and Y. Kera, *Catal. Latt.*, **46**, 235 (1997).
28. K. Tanaka, T. Yamabe and K. Fukui, The Science and Technology of Carbon Nanotubes, Elsevier, Oxford, pp. 51-61 (1999).
29. M.S. Dresselhous, G. Dresselhous and P. Avouris, Carbon Nonotubes: Synthesis, Structure, Properties and Applications, Springer, Berlin, pp. 213-246 (2001).
30. W.C. Oh and A.R. Jung, *J. Ceram. Korean Soc.*, **45**, 150 (2008).
31. W.C. Oh and Y.R. Na, *J. Ceram. Korean Soc.*, **45**, 36 (2008).
32. W.C. Oh and T.S. Park, *Eng. Res.*, **12**, 218 (2007).

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