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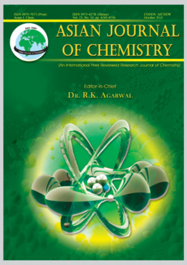

Photodegradation of Organic Dyes Over Nickel Distributed CNT/TiO_2 Composite Synthesized by a Simple Sol-Gel Method

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In this study, the multi-walled carbon nanotubes was oxidized by *m*-chlorperbenzoic acid at first and then reaction with titanium *n*-butoxide and nickel nitrate to prepare Ni distributed CNT/TiO_2 composite by a simple sol-gel method. The functional groups formed on the surface of MWCNTs were analyzed by Fourier transform infrared spectroscopy. The prepared Ni distributed CNT/TiO_2 composite was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray analysis. The photodegradation of methylene blue, methylene orange and rhodamine B solution under UV irradiation was employed to test the photocatalytic activity of the Ni distributed CNT/TiO_2 composite. According to the results, Ni distributed CNT/TiO_2 composite showed excellent photocatalytic activity for decomposing of methylene blue, methylene orange and rhodamine-B solution, due to the electron absorb effect of MWCNTs and electron trap effect of nickel could improve the photocatalytic activity of TiO_2.

Key Words: Multi-walled carbon nanotubes, Nickel, Organic dyes, Sol-gel, Photocatalytic activity.

INTRODUCTION

Semiconductor photocatalysis has attracted a lot of attention because it provides an ideal way to utilize solar energy or artificial light energy for decomposition of toxic gas and wastewater. The photocatalysis process commonly involves the following steps: (i) the semiconductors absorb photons and generate electron-hole pairs; (ii) the photoinduced electron/hole pairs are separated with electrons in the conduction band and holes in the valence band; (iii) then the electrons/holes migrate to the surface active sites of the particles; (iv) finally, the organic molecule are decomposed over the semiconductor surfaces. Among oxide photocatalysts, titanium dioxide (TiO_2) has been intensively used in photocatalysis and environmental pollutant clean up applications[1-4]. However, electron-hole recombination is generally in direct competition with the trapping process. The rate of the trapping and subsequent photocatalytic reaction on TiO_2 surface can be enhanced by retarding the electron-hole recombination. One of the principal methods of improving photocatalytic activity of TiO_2 is combining with carbon nanotubes to create a CNT/TiO_2 system. Carbon nanotubes outperform other carbon materials due to their exceptionally high mechanical strength, high thermal conductivity, medium to high specific surface areas and high external surface area, which render them interesting candidates for use as catalyst supports for preparing nanosized metal and metal oxide particle catalysts[5-8]. Recently, we reported the synthesis of multi-walled carbon nanotubes (MWCNTs)/TiO_2 composites by using a sol-gel method and determined their photocatalytic activity by decomposing different organic dyes under irradiation of ultraviolet or visible light[9-12]. The results indicated that the photocatalytic activity of TiO_2 for decomposing organic dyes could be improved by combining with carbon nanotubes under irradiation of UV or visible light. Because the MWCNTs could use its photo-absorption character to absorb a photo-induced electron (e^-), which could be introduced into the conduction band (CB) of TiO_2 particles and react with O_2 to trigger formation of the very reactive superoxide radical ion ($O_2^{-}\bullet$).

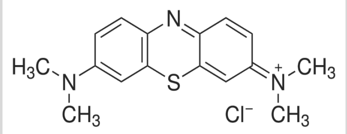
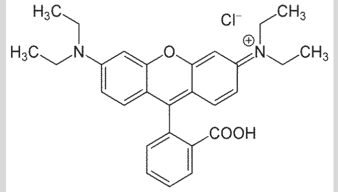
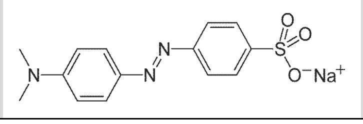
Reduction of the grain or doping of the transition metals (Fe, V, Mn, Co and Ni) and noble elements (Pt, Pd or Rh) has been investigated as methods to enhance the photocatalytic performance of TiO_2[13-16]. It is considered that the metal cocatalyst dispersed on the TiO_2 expedites the transportation of electrons produced by the photoexcitation to the outer system, *i.e.* photocatalytic reaction. Although precious metal cocatalyst, especially platinum (Pt), shows outstanding performance for photocatalytic activity[16,17], it is fairly costly. Therefore, another important base metal cocatalyst, *i.e.* nickel, is proposed to be more emphasized because of its much relative cost-effectiveness. Tseng *et al.*[18] reported the degradation of xylene vapour over Ni-doped TiO_2 photocatalysts prepared by polyol-mediated synthesis. Ren *et al.*[19] reported the improved photocatalytic properties of P-type NiO loaded porous TiO_2 sheets prepared *via* free tape-casting. It is known that the metallic nickel could enhance the photocatalytic activity of TiO_2.

In this study, the transition metallic Ni distributed CNT/TiO_2 composite was synthesized by a simple sol-gel method. Due to the MWCNTs is to oxidized by *m*-chloroperbenzoic acid, so the functional groups formed on the surface of MWCNTs were examined by a KBr method using Fourier transform infrared (FT-IR) spectroscopy. The prepared Ni distributed CNT/TiO_2 composite was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray analysis. The photocatalytic properties of Ni distributed CNT/TiO_2 composite were investigated by decomposing three kinds of organic dyes methylene blue, methylene orange and rhodamine B under UV light irradiation.

EXPERIMENTAL

Crystalline multi-walled carbon nanotubes (purity, 95.9 wt. %; diameter: *ca.* 20 nm; length: 5 µm) powder was used as support material, which obtained from Carbon Nano-material Technology Co., Ltd., Korea. *m*-Chlorperbenzoic acid (MCPBA) was used as the oxidizing agent to oxidize the surface of MWCNTs, which purchased from Acros Organics, New Jersey, USA. The titanium *n*-butoxide (TNB, $Ti\{OC(CH_3)_3\}_4$, 99 %) was used as titanium alkoxide precursor to form the TiO_2, which purchased from Acros Organics, New Jersey, USA. Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, 97 %) was used as a nickel ion source, which obtained from Duksan Pure Chemical Co., Ltd., Korea. Benzene (99.5 %) was used as the organic solvent purchased from Samchun Pure Chemical Co. Ltd., Korea. The methylene blue ($C_{16}H_{18}N_3S \cdot Cl$, 99.99 + %), methylene orange ($C_{14}H_{14}N_3O_3SNa$, 99.99 + %) and rhodamine-B ($C_{28}H_{31}N_2O_3Cl$, 99.99 + %) was used as analytical grades which purchased from Duksan Pure Chemical Co. Ltd., Korea, Daejung Chemicals & Metals Co. Ltd., Korea and Samchun Pure Chemical Co. Ltd., Korea, respectively. Table-1 shows the structure of methylene blue, methylene orange and rhodamine-B.

TABLE-1
MOLECULAR STRUCTURE AND λ_{MAX} OF ORGANIC DYES

Organic dyes	Molecular structure	λ_{max} (nm)
Methylene blue (MB)		665
Methylene orange (MO)		465
Rhodamine B (Rh.B)		554

For the synthesis of Ni distributed CNT/TiO_2 composite, three step procedure was used. In the first step, the MWCNTs were oxidized by *m*-chloroperbenzoic acid, which consequently allowed reacting with titanium *n*-butoxide in the second step to prepare CNT/TiO_2 composite. Then the nickel nitrate was introduced at last step.

Oxidization of multi-walled carbon nanotubes: Due to the stable nature of MWCNTs, it needs to be treated with strong acids to introduce active function groups on their surface. We took 1.0 g MCPBA melted in 60 mL benzene to prepare oxidizing agent. And then 0.5 g MWCNTs was put into the oxidizing agent. The mixture was stirred with a magnet for 6 h at 343 K. Then the MWCNTs was dried at 373 K.

Preparation of CNT/TiO_2 composite: 0.1 M titanium *n*-butoxide-benzene solution was prepared *via* dissolution of titanium *n*-butoxide in benzene solution. Subsequently, the pre-oxidized MWCNTs were put into 50 mL 0.1 M titanium *n*-butoxide-benzene solution. The mixtures were loosely covered and kept stirring by magnet at 343 K for 5 h, until a homogenous MWCNTs-contained gel formed. The gel was heat treated at 773 K for 1 h with a heating rate of 279 K/min to obtain CNT/TiO_2 composite.

Preparation of Ni distributed CNT/TiO_2 composite: 0.1 M $Ni(NO_3)_2$ solution was prepared *via* dissolution of $Ni(NO_3)_2$ in distilled water. Subsequently, the prepared CNT/TiO_2 composite was put into 50 mL 0.1 M $Ni(NO_3)_2$ solution. The mixtures were loosely covered and kept stirring by magnet at 343 K for 5 h. The temperature of the mixture was brought down to ambient temperature and the mixture was filtered through filter paper. Obtained solids were dried at 373 K for 1 h and heat treated at 773 K for 1 h with a heating rate of 279 K/min. Finally the Ni distributed CNT/TiO_2 composite was prepared.

Characterization: The functional groups formed on the surface of MWCNTs were examined by a KBr method using fourier transform infrared (FT-IR) spectroscopy (FTS 3000MX). Discs for the method were prepared by first mixing 1 mg of powdered oxidized MWCNTs with 600 mg of KBr (for FT-IR spectroscopy) in an agitate mortar and then pressing the resulting mixture successively under a pressure of 450 Pa for 3 min. The spectra of the samples were measured between 3000 and 500 cm^{-1}. For the physical parameter measurements, XRD (Shimadz XD-D1) result was used to identify the crystallinity with CuK_α radiation. SEM (JSM-5600) was used to observe the surface state and structure of Ni distributed CNT/TiO_2 composite using an electron microscope. TEM (JEM2000 -FX) at an acceleration voltage of 200 kV was used to investigate the size and distribution among the various metals. TEM specimens were prepared by placing a few drops of the sample solution on a carbon grid. The element mapping over the desired region of the Ni distributed CNT/TiO_2 composite was detected by an EDX analysis attached to SEM.

Photocatalytic activity measurement: The photocatalytic activity of Ni distributed CNT/TiO_2 composite was taken out by decomposition of methylene blue, methylene orange and rhodamine-B solution under irradiation of UV light (356 nm, 8 W, 1.2 mW/cm^2). In an ordinary photocatalytic test performed at room temperature, 0.05 g Ni distributed CNT/TiO_2 composite was added to 50 mL of 1.0×10^{-5} mol/L methylene blue, methylene orange and rhodamine-B solution, respectively. Before turning on the UV lamp, the solution mixed with composite 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 light. 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 methylene blue 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 0.5, 1, 1.5, 2 and 4 h and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-VIS spectrophotometer (Optisen POP) at wavelength from 250 to 800 nm. The maximum absorbance (λ_{max}) was determined at characteristic wavelength 665, 465 and 665 nm for the each methylene blue, methylene orange and rhodamine-B solution degraded, respectively.

RESULTS AND DISCUSSION

FT-IR analysis: FT-IR was conducted on as-received MWCNTs and functionalized MWCNTs and their corresponding spectra are shown in Fig. 1. For the as-received MWCNTs the IR spectra showed almost no functional groups on the surface. However, after oxidized by *m*-chloroperbenzoic acid, the MWCNTs have various kinds of functional groups on the surface. The band at 2910 and 2847 cm^{-1} ascribe to C-H stretching vibration. And the bands at 1695, 1303 and 2847 cm^{-1} ascribed to C=O, S=O and C-H stretching vibration, respectively. The above observations suggest that oxidation was promoted in all treatments and these formed functional groups could increase the active sites on the surface of MWCNTs. Moreover, the spectra of as-received MWCNTs and functionalized MWCNTs, some small absorption bands around 1500 cm^{-1} exist which ascribed to C=C stretching vibration. And some another peaks at 2350 cm^{-1}, which might be due to the ambient CO$_2$ in the spectrometer.

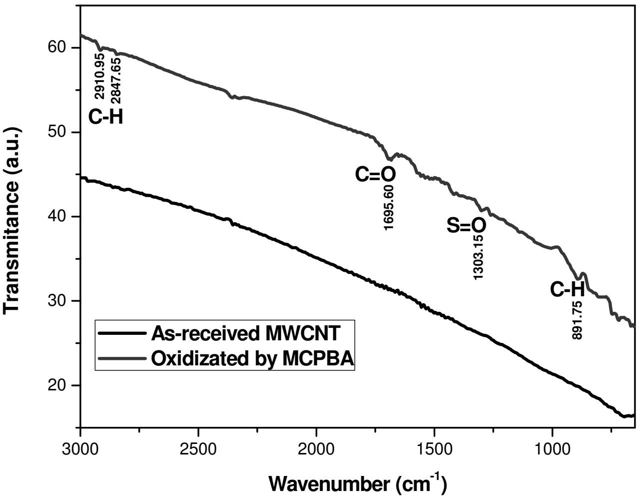


Fig. 1. FT-IR spectra of as-received MWCNTs and functionalized MWCNTs by MCPBA

XRD analysis: The XRD patterns of CNT/TiO$_2$ composite and Ni distributed CNT/TiO$_2$ composite heat treated at 773 K for 1 h is shown in Fig. 2. Diffraction peaks corresponding to anatase phases and nickel has been marked with A and Ni, respectively. The crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature, 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[20,21]. In our case, all of the composites were heat treated at 773 K for 1 h. Both of CNT/TiO$_2$ composite and Ni distributed CNT/TiO$_2$ composite have peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase (JCPDS: 21-1272) without any other peaks, indicating the TNB was transferred to TiO$_2$ with anatase structure. Moreover, for Ni distributed CNT/TiO$_2$ composite, apart from peaks of anatase, some other peaks at 44.4, 51.7 and 76.3 are the diffractions of (111), (200) and (220) planes of face-centered-cubil (fcc) nickel (JCPDS: 04-0850)[22]. In addition, there is no nickel carbide of the cementite phase and nickel oxides detected. In accordance with above results, one can believe that nickel ions originally distributed on CNT/TiO$_2$ composite and high purity of Ni distributed CNT/TiO$_2$ composite was prepared. However, the characteristic peaks of MWCNTs can hardly be identified from the XRD patterns of CNT/TiO$_2$ composite and Ni distributed CNT/TiO$_2$ composite. It can be considered that the peaks of MWCNTs were overlapped of diffraction peaks attributed to TiO$_2$, or the intensity of MWCNTs peaks was very weaker than that of nickel peaks.

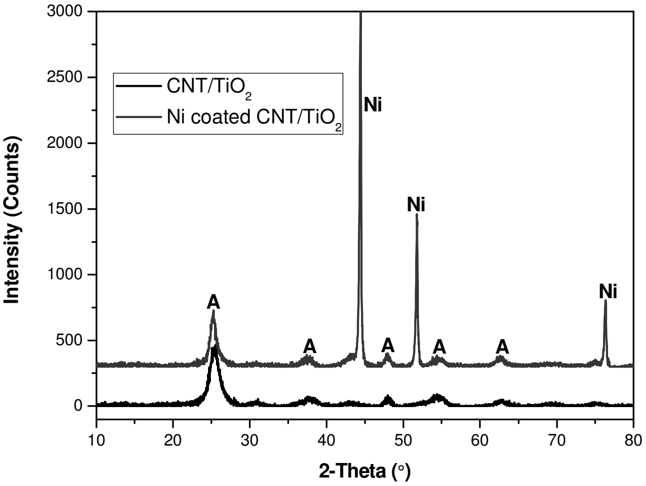


Fig. 2. XRD patterns of CNT/TiO$_2$ composite and Ni distributed CNT/TiO$_2$ composite

SEM, TEM and EDX analysis: Fig. 3 (a) and (b) show SEM micrograph and TEM image of Ni distributed CNT/TiO$_2$ composite. From Fig. 3 (a), after the deposition of titanium *n*-butoxide and nickel, the TiO$_2$ particles and Ni particles mixed with MWCNTs together. From Fig. 3 (b), it can be seen that the TiO$_2$ aggregates homogeneously dispersed on the surface of MWCNTs. However, the presence of Ni particles was not clearly observed. It can be considered that most of the Ni particles were expected to be present on the surface of the TiO$_2$ because the nickel precursor was added after the complete synthesis of CNT/TiO$_2$ composite during the preparation. The morphologies of particles and MWCNTs are clearly observed. The size of nanoparticles varies from 10 to 20 nm. Most particles are quasi-spherical in shape. The element analysis by EDX proves that the resulting product contains the elements C, Ti, O and Ni in Fig. 3 (c).

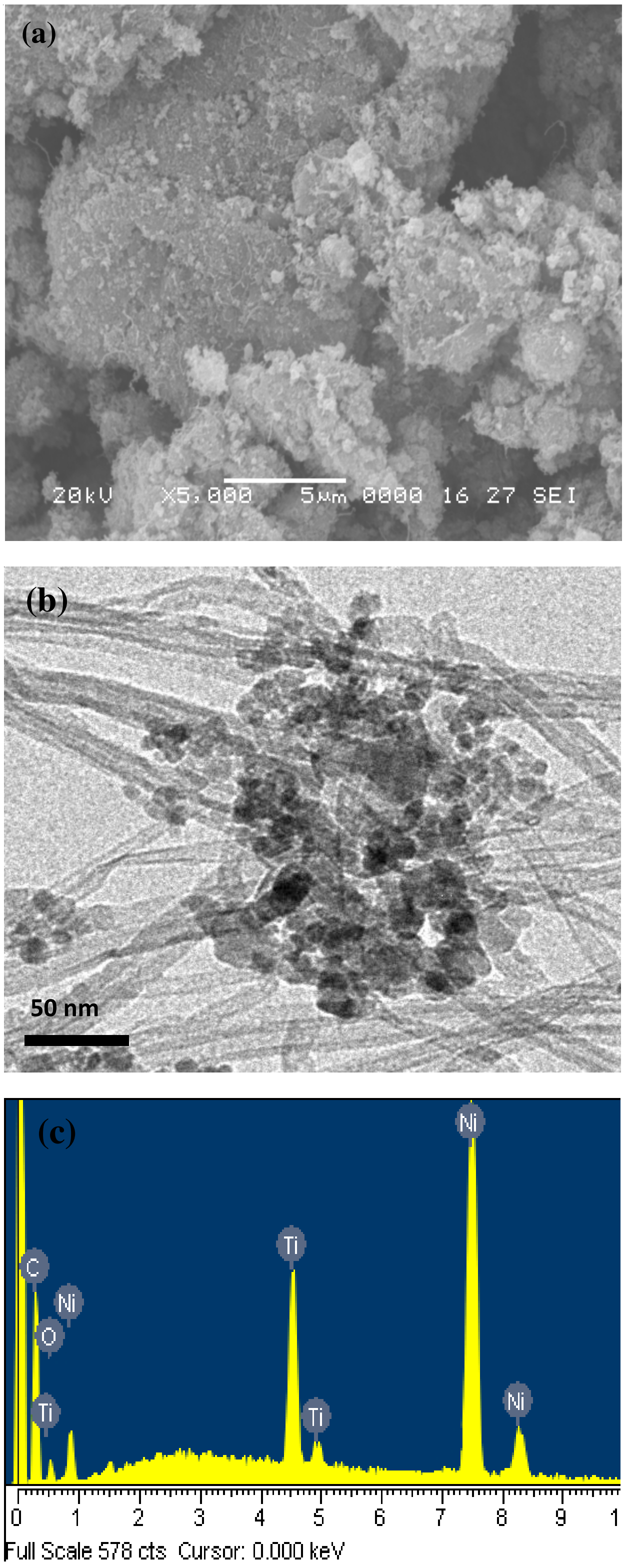


Fig. 3. SEM photo (a), TEM image (b) and EDX microanalysis (c) of Ni distributed CNT/TiO_2 composite

Photocatalytic activity: Fig. 4 shows the UV-VIS absorbance spectra of methylene blue, methylene orange and rhodamine-B solution decomposed by Ni distributed CNT/TiO_2 composite as time function. The absorbance of methylene blue, methylene orange and rhodamine-B solution show only one maximum and is observed at 665, 465 and 554 nm, respectively, which is same as showed in Table-1. It is observed that the absorbance maximum for all of organic dyes decrease with an increase of UV irradiation time. This results suggests the colour of organic dyes is removed by Ni distributed CNT/TiO_2 composite with an increasing of UV irradiation time. After irradiation under UV light for 4 h, the absorbance of the organic dyes is almost reached zero, indicating the colour of organic dyes is removed almost completely.

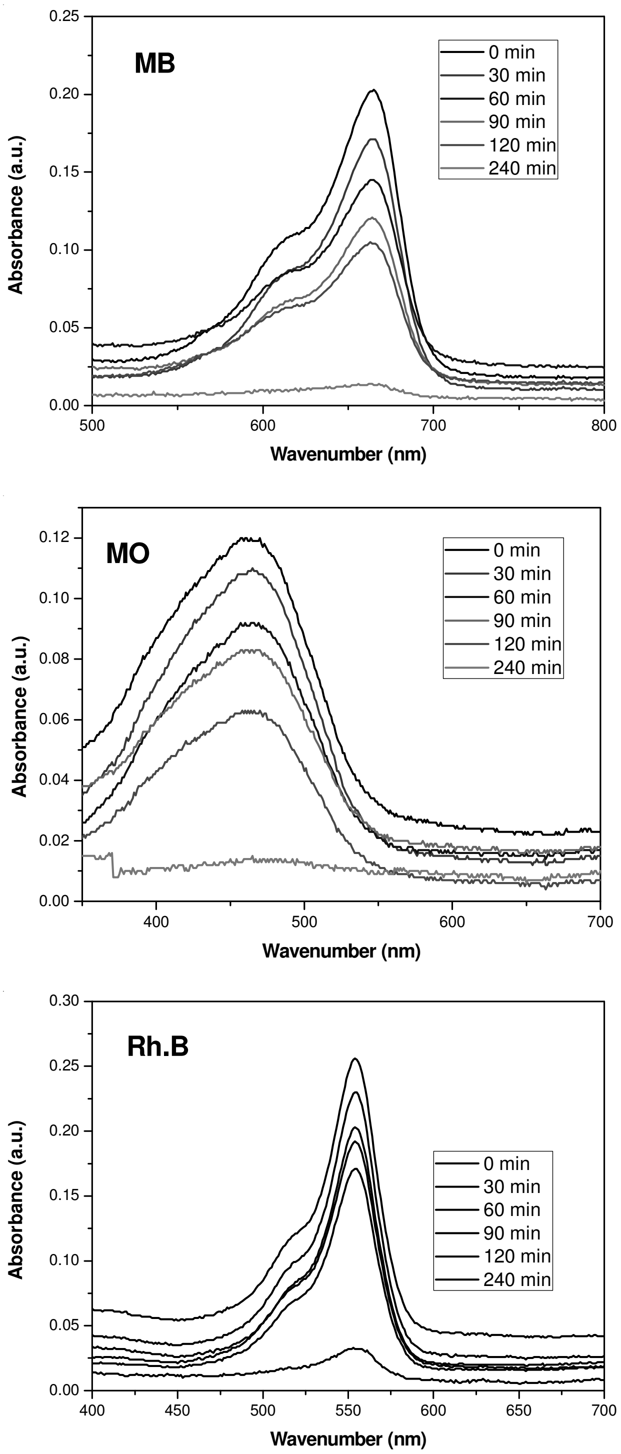


Fig. 4. UV-VIS absorbance spectra of different organic dyes photodegraded by Ni distributed CNT/TiO_2 composite under UV irradiaton as time function

Fig. 5 shows the changes in relative concentration (c/c_0) of methylene blue, methylene orange and rhodamine-B solution on time of UV irradiation for Ni distributed CNT/TiO_2 composite. Prior to the photocatalystic reaction, a blank test is performed without composite and irradiation. The concentration of methylene blue, methylene orange and rhodamine-B solution does not change with time under UV irradiation without composite (the data was not shown). However, when Ni distributed CNT/TiO_2 composite is used as a photocatalyst under UV light, a significant decreasing concentration of methylene blue, methylene orange and rhodamine-B solution is observed after an irradiation time of 2 h, namely about 50, 48 and 34 %, for methylene blue, methylene orange and rhodamine-B, respectively. When the UV irradiation time extends to 4 h, the concentration of methylene blue, methylene orange and rhodamine-B solution is almost decreased completely, namely *ca.* 94, 87.5 and 87.5 %, for methylene blue, methylene orange and rhodamine-B, respectively. Because the Ni distributed CNT/TiO_2 composite shows the most excellent photodegradation for methylene blue solution. So a plot of $-\ln(c/c_0)$ *versus* t for methylene blue degradation with Ni distributed CNT/TiO_2 composite and CNT/TiO_2 composite is presented in Fig. 5 (inset). The value of kinetic constant (k_{app}) of Ni distributed CNT/TiO_2 composite and CNT/TiO_2 composite can be obtained directly from the slopes of the respective linear curves in the plots, which is 5.66×10^{-3} and 3.81×10^{-3}, respectively. It can be indicated that the degradation rate of methylene blue solution degraded by Ni distributed CNT/TiO_2 composite is much faster than that of CNT/TiO_2 composite, almost 1.5 times.

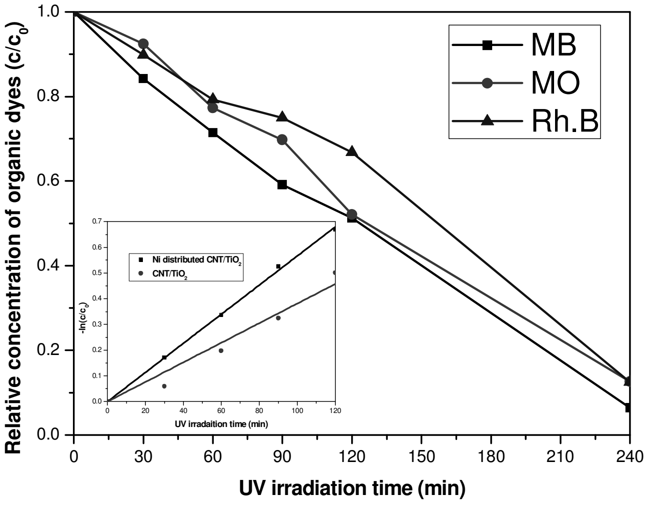


Fig. 5. Relative concentration (c/c_0) of organic dyes solution on time of UV irradiation for Ni distributed CNT/TiO_2 composite. The inset shows a plot of $-\ln(c/c_0)$ versus t for methylene blue degradation with Ni distributed CNT/TiO_2 composite and CNT/TiO_2 composite

Multi-walled carbon nanotubes could act an electron sensitizer and donor in the composite photocatalysts[23-25]. The nickel particle can also act a probable photogenerated electron trappers in TiO_2, thus ensuring a good separation effect on the electron-hole pairs[26]. When MWCNTs accept the photo-induced electrons (e^-) into the conduction band of the TiO_2 particles by UV irradiation, these photo-induced electrons (e^-) can be immediately transferred to Ni particles, thus avoiding the electron-hole recombination of TiO_2 particle. The electrons in Ni particles may react with O_2, which can be trigger the formation of very reactive superoxide radical ion ($O_2^{-}\bullet$). The positive charged hole (h^+) in the VB of TiO_2 may react with the OH• derived from H_2O. Consequently, both radical groups (superoxide radical ion $O_2^{-}\bullet$ and hydroxyl radical OH•) are responsible for the degradation of the organic compound. So the Ni distributed CNT/TiO_2 composite shows excellent photocatalytic activity for methylene blue, methylene orange and rhodamine-B solution.

Conclusion

In this study, the Ni distributed CNT/TiO_2 composite was successfully prepared by a simple sol-gel method. Comparisons with as-received MWCNTs, various functional groups were formed on the surface of MWCNTs after functionalized by *m*-chloroperbenzoic acid from FT-IR spectra. XRD result showed the anatase structure of TiO_2 and nickel structure in Ni distributed CNT/TiO_2 composite. From TEM image, the TiO_2 aggregates homogeneously dispersed on the surface of MWCNTs and most of Ni particles were expected to be present on the surface of the TiO_2. The elemental analysis by EDX proved that the Ni distributed CNT/TiO_2 composite contained the elements C, Ti, O and Ni. According to a decreasing absorbance of methylene blue, methylene orange and rhodamine-B solution with an increasing UV irradiation time, it could be indicated that the concentration of methylene blue, methylene orange and rhodamine-B solution was decreased by Ni distributed CNT/TiO_2 composite under UV irradiation. When the UV irradiation time extended to 4 h, the concentration of methylene blue, methylene orange and rhodamine-B solution was decreased almost completely. Because of the electron absorb effect of MWCNTs and electron trap effect of nickel, thus Ni distributed CNT/TiO_2 composite showed very excellent photocatalytic activity for decomposing of methylene blue, methylene orange and rhodamine-B solution.

REFERENCES

1. A.L. Linsebigler, G. Lu and J.T. Yates Jr, *Chem. Rev.*, **95**, 735 (1995).
2. A. Mills and S. Le Hunte, *J. Photochem. Photobiol. A: Chem.*, **108**, 1 (1997).
3. O. Legrini, E. Oliveros and A.M. Braun, *Chem. Rev.*, **93**, 671 (1993).
4. M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
5. W.Z. Li, C.H. Liang, J.S. Qiu, W.J. Zhou, H.M. Han and Z.B. Wei, *Carbon*, **40**, 787 (2002).
6. Y.H. Li, S.G. Wang, A.Y. Cao, D. Zhao, X.F. Zhang, C.L. Xu, Z.K. Luan, D.B. Ruan, J. Liang, D.H. Wu and B.Q. Wei, *Chem. Phys. Lett.*, **350**, 412 (2001).
7. Y.H. Li, J. Ding, J.F. Chen, C.L. Xu, B.Q. Wei, J. Liang and D.H. Wu, *Mater. Res. Bull.*, **37**, 313 (2002).
8. L.M. Ang, T.S.A. Hor, G.Q. Xu, C.H. Tung, S.P. Zhao and J.L.S. Wang, *Carbon*, **38**, 363 (2000).
9. M.L. Chen, F.J. Zhang and W.C. Oh, *J. Korean Ceram. Soc.*, **45**, 651 (2008).
10. M.L. Chen, F.J. Zhang, K. Zhang, Z.D. Meng and W.C. Oh, *J. Photocata. Sci.*, **1**, 19 (2010).
11. W.C. Oh, *J. Photocata. Sci.*, **1**, 29 (2010).
12. W.C. Oh, F.J. Zhang and M.L. Chen, *Asian J. Chem.*, **22**, 2231 (2010).
13. W.C. Oh, M.L. Chen, F.J. Zhang, Y.M. Lee and W.B. Ko, *J. Ind. Eng. Chem.*, **15**, 190 (2009).
14. W.C. Oh, F.J. Zhang and M.L. Chen, *J. Ind. Eng. Chem.*, **16**, 299 (2009).
15. M.L. Chen, F.J. Zhang, K. Zhang, Z.D. Meng and W.C. Oh, *J. Chem. Res.*, **34**, 283 (2010).
16. W.C. Oh, F.J. Zhang and M.L. Chen, *J. Ind. Eng. Chem.*, **16**, 321 (2010).

17. M.L. Chen, F.J. Zhang and W.C. Oh, *J. Korean Ceram. Soc.*, **47**, 283 (2010).
18. H.H. Tseng, M.C. Wie, S.F. Hsiung and C.W. Chiou, *Chem. Eng. J.*, **150**, 160 (2009).
19. L.L. Ren, Y.P. Zeng and D.L. Jiang, *Soild State Sci.*, **10**, 138 (2010).
20. L. Zhu, Z.D. Meng, M.L. Chen, F.J. Zhang, J.G. Choi1, J.Y. Park and W.C. Oh, *J. Photocatal. Sci.*, **1**, 69 (2010).
21. W.C. Oh, M.L. Chen and C.S. Lim, *J. Ceram. Proc. Res.*, **8**, 119 (2007).
22. J.P. Cheng, X.B. Zhang and Y. Ye, *J. Solid State Chem.*, **179**, 91 (2006).
23. W.C. Oh and M.L. Chen, *Bull. Korean Chem. Soc.*, **29**, 159 (2008).
24. M.L. Chen, F.J. Zhang and W.C. Oh, *New Carbon Mater.*, **24**, 159 (2009).
25. W.C. Oh, F.J. Zhang and M.L. Chen, *Bull. Korean Chem. Soc.*, **30** 2637 (2009).
26. H. Yu, X.J. Li, S.J. Zheng and W. Xu, *Mater. Chem. Phys.*, **97**, 59 (2006).