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Visible Light Photoelectrocatalytic Degradation of Methylene Blue by Platinum-Treated Carbon Nanotube/Titania Composites

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Photoelectrocatalytic degradations of methylene blue in the presence of two types of carbon nanotube/titania and platinum-treated carbon nanotube/titania electrodes in aqueous solutions were studied under visible light. The prepared composite electrodes were characterized by X-ray diffraction, transmission and scanning electron microscopy, energy dispersive X-ray analysis and photoelectrocatalytic activity. It was found that the photoelectrocatalytic degradation of a methylene blue solution could be attributed to the combined effects caused by the photo-degradation of titania, the electron assistance of carbon nanotube network, the enhancement of platinum and a function of the applied potential. The composites treated with platnium revealed enhanced photo degradation behaviours of the methylene blue.

Key Words: Platinum-carbon nanotuble/titania, Electrode, Photoelectrocatalytic, Methylene blue, Visible light.

INTRODUCTION

Although titanium dioxide (TiO_2) has been extensively employed as photocatalytic (PC) material for the successful removing of pollutants in both liquid and gas phases, especially for eliminating toxic chemicals from waste water. It can be excited only under illumination with UV light at wavelengths below 400 nm because of the large band gap (3.2 eV) for anatase TiO_2. Unfortunately, only *ca*. 4 % of the solar radiation that reaches the Earth's surface exists in the UV region; indeed, more than 45 % lies in the visible region[1]. Therefore, the development of photocatalysts that can be excited by visible light has received much attention. Various efforts have been attempted to extend the light absorption of the photocatalysts to the visible region[2-4].

Recently, porous carbon materials have been widely used in waste water treatment to remove various pollutants because of their large surface area and high adsorption capacity. Carbon/TiO_2 composites have attracted much attention and have become a very active field of research[5-10]. Carbon nanotubes (CNTs), as a new class of nanomaterials, have been drawn to considerable attention for their applications as

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catalyst supports[11-16] owing to their unique electrical properties, high chemical stability and high surface-to-volume ratio. Moreover, carbon nanotubes have a variety of electronic properties. They may also exhibit metallic conductivity as one of the many possible electronic structures. Carbon nanotubes have a large electron-storage capacity (one electron for every 32 carbon atoms)[17], the ability of carbon nanotube can promote the electron-transfer reactions at carbon nanotubes modified electrodes.

CNT/TiO_2 composite systems are currently being considered for many applications including their potential use to address environmental problems. An *et al.*[18] deposited anatase TiO_2 onto carbon nanotubes *via* hydrolysis of titanium isopropoxide in supercritical ethanol and studied the photocatalytic activity of these composites in terms of their ability to mediate the degradation of phenol under visible light. Wang *et al.*[4,19] used a modified sol-gel method to prepare carbon nanotube/TiO_2 composites that exhibited photocatalytic activity under both UV and visible light. Jitianu and his co-workers[20] coated carbon nonotubes with anatase by using a sol-gel method and titanium alkoxides as precursors. Although these reports reveal that carbon nonotubes have a positive impact on the photocatalytic activity of TiO_2 under both UV and visible light, two problems that need to be addressed with nanosize photocatalysts is the difficulty in distributing single particles and collecting them after use. Support structures are needed. Embedding them into a matrix is a possible approach. Moreover, the photocatalytic activity of these composites remains low and must be improved if they are to be used for commercial applications, particularly under visible light.

The platinum nanoparticles are very effective as a matrix of enzyme sensors by taking advantage of the biocompatibility and huge surface of platinum nanoparticles and good electrocatalytic activity to hydrogen peroxide. Highly dispersed nanoscale platinum particles have been an intensive research subject as the electrocatalyst for methanol oxidation[21]. The electrocatalytic activity of platinum nanoparticles for this reaction is dependent on various factors, which involves the size and dispersion of the particles, preparation methods, supporting materials and their surface conditions. Carbon nonotubes are good supporting materials, which can support a high dispersion of platinum nanoparticles due to their large surface area and particular morphology. As TiO_2, CNT and Pt nanoparticles are excellent materials for the construction of catalyst, through a suitable combination of these materials, novel modified surfaces could be generated with higher surface area and enhanced catalytical/electrocatalytical activities, which is also expected to be an excellent platform for photoelectrocatalytic (PEC) applications.

In this study, we focused on the fabrication and characterization of the Pt-CNT/TiO_2 composite electrodes in a preparation procedure. Structural variations, surface state and elemental compositions were investigated for preparation of Pt-CNT/TiO_2 composite. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and transmission electron microscopy (TEM) were employed for characterization of these new photocatalysts. The catalytic efficiency of the Pt-CNT/TiO_2 electrode was evaluated by the photoelectrocatalytic degradation of methylene blue (MB, $C_{16}H_{18}N_3SCl\cdot3H_2O$) under visible light.

EXPERIMENTAL

Carbon nanotubes (CNTs) were selected as the support material. The carbon nonotubes (multiwall nanotubes, diameter: *ca.* 20 nm, length: *ca.* 5 μm), were supplied by carbon Nano-material Technology Co., Ltd., Korea and used without further purification. Titanium *n*-butoxide (TNB, $Ti(OC_4H_7)_4$) as a TiO_2 source for the preparation of Pt-CNT/TiO_2 composites were purchased from Acros Organics, New Jersey, USA. For the oxidization the surface of CNT, *m*-chloroperbenzoic acid (MCPBA)was used as an oxidized reagent which was purchased from Acros Organics, New Jersey, USA. Hydrogen hexachloroplatinate(IV) hydrate ($H_2PtCl_6\cdot6H_2O$) was obtained from Kojima Chemical Co., Ltd. Reagents (benzene and ethylene glycol) were purchased as reagent-grade from Duksan Pure Chemical Co. and Daejung Chemical Co. and used without further purification. The novolac typed phenol resin was supplied by Kangnam Chemical Co., Ltd, Korea. The methylene blue was used as analytical grade which was purchased from Duksan Pure Chemical Co., Ltd, Korea. It was selected because under anaerobic conditions it has the potential to produce more hazardous aromatic amines.

Preparation of CNT/TiO_2 composite electrodes: To begin preparing this experiment, the oxidizing agent 2 g of *m*-chloroperbenzoic acid was mixed in 60 mL benzene. Then 0.6 g carbon nonotubes was put into the oxidizing agent, refluxed for 6 h, filtered and dried. The oxidized carbon nonotubes were put into the mixing solution of titanium *n*-butoxide and benzene with the volume ratio of 4:16. Then the solutions were homogenized under reflux at 343 K for 5 h using a magnetic stirrer in a vial. After being stirred, the solutions became CNT/TiO_2 gels and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. Then 0.4 g phenol resin was added to these CNT/TiO_2 composites and the composites were pressed at a pressure of 250 kg/cm^2 in a mould with dimensions of 9.95 mm × 39.5 mm × 5.95 mm. This mixture was then heat treated at 673 K for 1 h. This concluded the preparation of the CNT/TiO_2 electrodes. The preparation conditions and sample codes are listed in Table-1.

TABLE-1
NOMENCLATURES OF CNT/TiO_2, Pt-CNT AND Pt-CNT/TiO_2 COMPOSITES

Preparation method	Nomenclatures
MCPBA+ CNTs + (400 mg $H_2PtCl_6\cdot6H_2O$ + 50 mL ethylene glycol)	Pt-C
MCPBA + CNTs + (4 mL TNB + 16 mL benzene) + phenol resin	CT
MCPBA + CNTs + (200 mg $H_2PtCl_6\cdot6H_2O$ + 50 mL ethylene glycol) + (4 mL TNB + 16 mL benzene) + phenol resin	2Pt-CT
MCPBA + CNTs + (500 mg $H_2PtCl_6\cdot6H_2O$ + 50 mL ethylene glycol) + (4 mL TNB + 16 mL benzene) + phenol resin	5Pt-CT
MCPBA + CNTs + (800 mg $H_2PtCl_6\cdot6H_2O$ + 50 mL ethylene glycol) + (4 mL TNB + 16 mL benzene) + phenol resin	8Pt-CT

MCPBA = *m*-chloroperbenzoic acid; TNB = titanium *n*-butoxide

Preparation of Pt-CNT/TiO_2 composite electrodes: The oxidized carbon nonotubes were added to ethylene glycol solution containing $H_2PtCl_6 \cdot 6H_2O$, of various concentration and then the solutions were homogenized under reflux at 343 K for 2 h using a magnetic stirrer in a vial. After being heat treated at 773 K for 1 h with a heating rate of 279 K/min, the platinum treated CNT composites were obtained. The platinum treated CNT composites were put into the mixing solution of titanium *n*-butoxide and benzene with a volume ratio of 4:16. Then the solutions were homogenized under reflux at 343 K for 5 h after stirring in a vial. After being stirred, the solutions were transformed to Pt-CNT/TiO_2 gels and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. After cooling, the Pt-CNT/TiO_2 composites were obtained. Then 0.4 g phenol resin was added to the Pt-CNT/TiO_2 composites and the composites were pressed at a pressure of 250 kg/cm^2 in a mould with dimensions of 9.95 mm × 39.5 mm × 5.95 mm. The mixture was then heat treated at 673 K for 1 h. This concluded the preparation of the Pt-CNT/TiO_2 electrodes. The preparation conditions and the nomenclatures of the samples are listed in Table-1.

Characterization of the Pt-CNT/TiO_2 composite: The Brunauer-Emett-Teller (BET) surface area of the Pt-CNT/TiO_2 composites was evaluated from N_2 adsorption isotherm at 77 K using a BET analyzer (Monosorb, USA). XRD technique 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 Cu K_α radiation. SEM was used to observe the surface state and porous structure of the Pt-CNT/TiO_2 composites using a scanning electron microscope (JOEL, JSM-5200, Japan). EDX spectroscopy was used to measure the elemental analysis of the Pt-CNT/TiO_2 composites. TEM (JEOL, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to investigate the size and distribution of the platinum and titanium deposits on the CNT surface on various samples. TEM specimens were prepared by placing a few drops of sample solution on a carbon grid.

Photoelectrocatalytic degradation: The photoelectrocatalytic degradation was performed by using CNT/TiO_2 and Pt-CNT/TiO_2 electrodes in a 100 mL glass container and then irradiating the system with visible light (8W, KLD-08L/P/N, FAWOO Technology), which was used at the distance of 100 mm from the solution in darkness box. The counter electrode was artificial graphite (TCK, Korea), which dimension was 9.95 mm × 39.5 mm × 5.95 mm. The CNT/TiO_2 and Pt-CNT/TiO_2 electrode were placed in 50 mL of 1×10^{-5} mol/L methylene blue solution. The photoelectrocatalytic degradation of methylene blue was performed with voltage of 6 V and visible light. The photoelectrocatalytic activities of the CNT/TiO_2 and Pt-CNT/TiO_2 electrodes were investigated using the photoelectrocatalytic rate of methylene blue solution, which was measured as function of time. The blue colour of the solution faded gradually with time due to the adsorption and degradation of methylene blue solution. And then the concentration of methylene blue in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

RESULTS AND DISCUSSION

Structure and morphology of CNT/TiO_2 and Pt-CNT/TiO_2 composites: The values of BET surface areas of CNT/TiO_2 and Pt-CNT/TiO_2 composites are shown in Table-2. As shown in Table-2, the BET surface areas of CNT/TiO_2 and Pt-C were 198 and 288 m^2/g, respectively, while the BET surface areas of platinum treated CNT/TiO_2 composites decreased gradually from 183-116 m^2/g with an increase of H_2PtCl_6 concentration. Moreover, the BET surface area of the sample of Pt-C was 288 m^2/g and larger than that of the other platinum treated CNT/TiO_2 composites. At the same addition of titanium *n*-butoxide, it was thought that the intensity of the platinum particle aggregation increased with the increase of H_2PtCl_6 concentration. These particles were heavily agglomerated to gather into a rounded mass. These results can be seen clearly from SEM images obtained from powdered Pt-CNT/TiO_2 composites. The results showed that there is a decrease in the BET surface area of the Pt-CNT/TiO_2 composites after formation of platinum particles by H_2PtCl_6 treatment. This was suggested that some porosity was developed during the heat treatment. It was thought that the composites are nano materials that include a lot of micropores. It was thought that there are two possible reasons. First, it could be attributed to the micropores being partly blocked by the formation of platinum particles on the CNT/TiO_2 surface during heat treatment. Second, the BET surface area decreased due to the curing of polymer resin with heat treatment, which blocked the micropores and formed some new mesopores. It was possible that the phenol resin had coated some CNT/TiO_2 particles to form some larger composite particles during the curing process. As expected, the BET surface area is thought to decrease due to the blocking of the micropores by surface complexes introduced through the formation of Pt-CNT/TiO_2 composites.

TABLE-2
SURFACE AREAS OF CNT/TiO_2, Pt-CNT AND Pt-CNT/TiO_2 COMPOSITES

Sample	S_{BET} (m^2/g)
Pt-C	288
CT	198
2Pt-CT	183
5Pt-CT	134
8Pt-CT	116

The XRD results for the catalyst samples are shown in Fig. 1. Diffraction peaks corresponding to anatase and rutile phases are marked with 'A' and 'R', respectively. Diffraction peaks corresponding to platinum phases are marked with 'Pt'. The structures for CNT/TiO_2 showed a mix of anatase and rutile crystals. It is well known that the crystal structure of the TiO_2 is mainly determined by heat treated temperature. The peaks at 25.3, 37.8, 48.0 and 62.5° are the diffractions of (101), (004), (200) and (204) planes of anatase, indicating the prepared CNT/TiO_2 composite existed in anatase state. The peaks at 27.4, 36.1, 41.2 and 54.3° belong to the different peaks

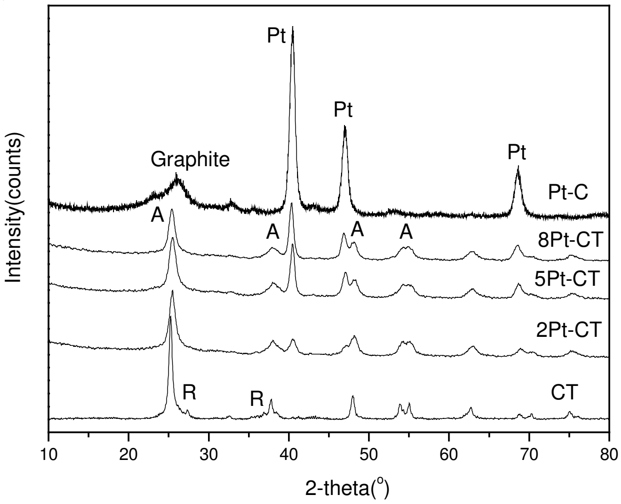
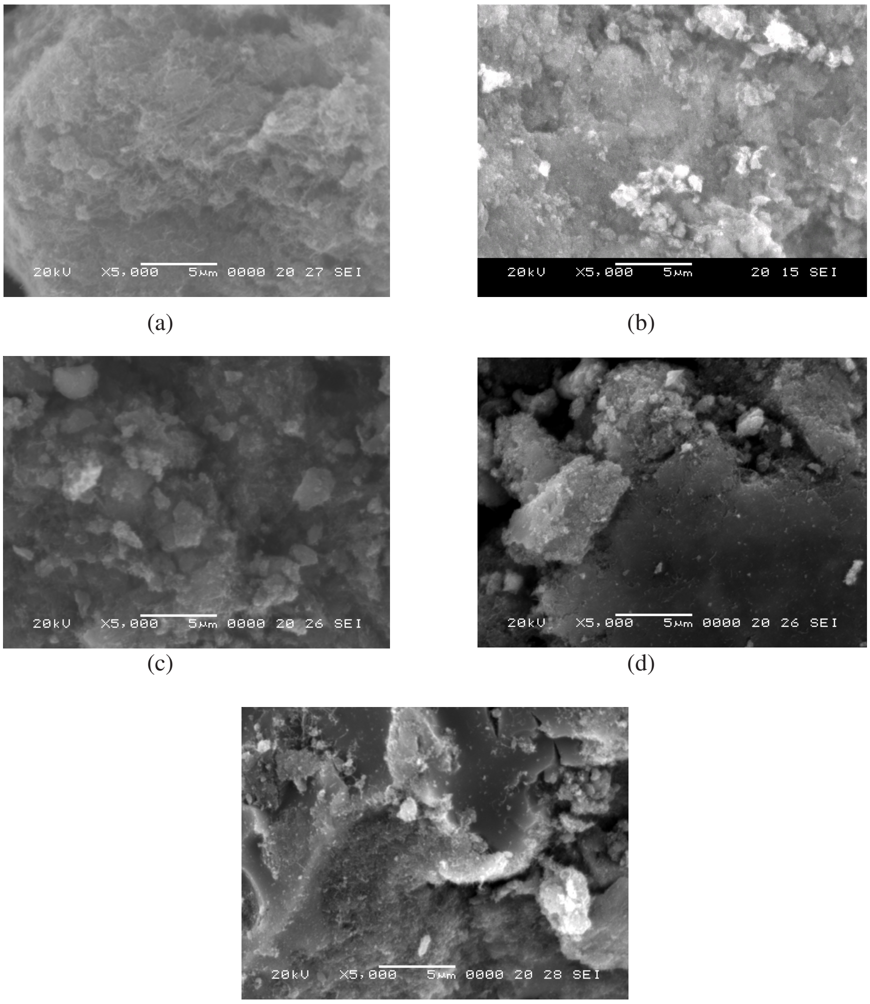


Fig. 1. XRD patterns of CNT/TiO_2, Pt-CNT and Pt-CNT/TiO_2 composites

of (110), (101), (111) and (211) of rutile. Therefore, it can be concluded that the developed CNT/TiO_2 composite had a mixing structure of anatase and rutile crystals when annealed at 973 K. According to Inagaki *et al.*[22], a sample phase formed below 773 K is transformed from an anatase to a rutile-type structure above 873 K and changes into a single phase of rutile at 973-1173 K. We have previously demonstrated that the crystallization phenomena in CNT/TiO_2 composites heat treated at 973 K results in a mixed anatase-rutile structure[23,24]. However, for the platinum treated CNT/TiO_2 composites, the structures for Pt-CT series showed an anatase crystal. It was considered that the introduction of platinum suppress the phase transform of TiO_2 from anatase to rutile-type structure during the heat treatment.

In addition, for the Pt-CNT/TiO_2 samples, the characteristic peaks of face centered cubic crystalline platinum at 39, 46 and 68° are assigned as the (111), (200) and (220) plane, respectively[25,26]. It considered that intensity of the peaks from platinum metal is derived from the Pt-CNT/TiO_2 composite and strengthened with an increase of H_2PtCl_6 concentration. Sharp diffraction peaks indicated the formation of pure platinum with high crystalline.

The micro-surface structures and morphology of Pt-CNT, CNT/TiO_2 and Pt-CNT/TiO_2 composites were characterized by SEM (Fig. 2) and TEM (Fig. 3). Fig. 2 shows the changes in the morphology of Pt-CNT, CNT/TiO_2 and Pt-CNT/TiO_2 composites. TiO_2 particles were fixed well on the surface of the CNT network of non Pt treated CNT/TiO_2 samples. As shown in Fig. 2(c-e), it was also observed that the amount of rounded mass increased with an increase in the amount of H_2PtCl_6 and that the size of platinum particles became large with an increase in the amount of platinum. According to Wang's reports[27], a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. At the same time, the conduction of a CNT network can facilitate the electron transfer

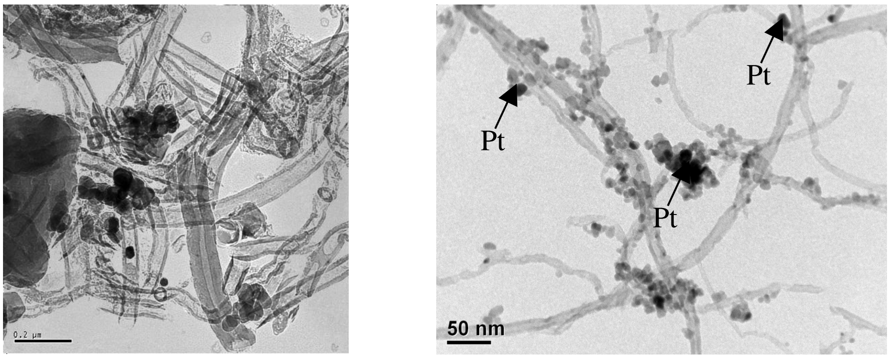


(a) (b) (c) (d) (e)

Fig. 2. SEM images obtained from powdered CNT/TiO_2, Pt-CNT and Pt-CNT/TiO_2 composites; (a) Pt-C, (b) CT, (c) 2Pt-CT, (d) 5Pt-CT and (e) 8Pt-CT

between the adsorbed dye molecules and the catalyst substrate[28]. It was beneficial for the enhancement of the photoelectrocatalytic activity of these composites.

As shown in Fig. 2(c-e), platinum particles were attached on the surface of the CNT network in the form of round mass and the distribution was not uniform. Moreover, the intensity of aggregation increased with an increase of H_2PtCl_6 concentration. These particles were heavily agglomerated to form lager clusters [Fig. 2(e)]. These results can be seen clearly in Fig. 2(c-e). These results are as well confirmed by TEM inspection of Pt-CNT/TiO_2 composites. As shown in Fig. 3, for the CNT/TiO_2 composites, the TiO_2 particles were distributed uniformly outside surface of CNT tube; for the Pt-CNT/TiO_2 composites, the TiO_2 particles were still distributed



(a) (b)

Fig. 3. TEM micrographs obtained from powdered CNT/TiO_2 and Pt-CNT/TiO_2 composites; (a) CT, (b) 5Pt-CT

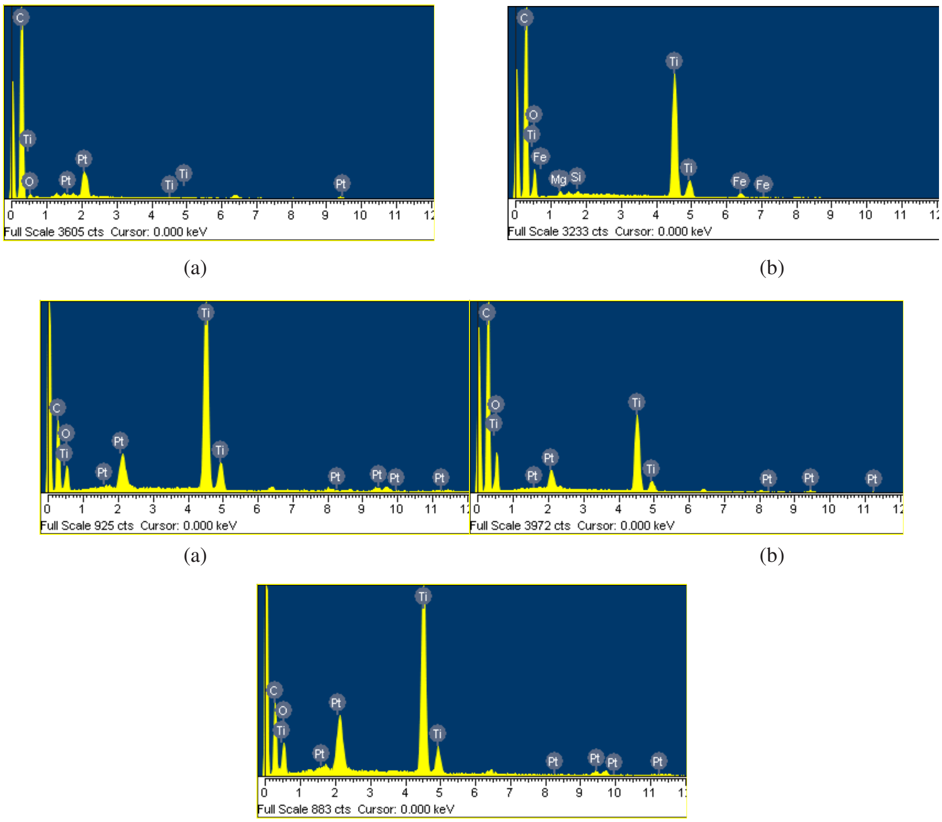
uniformly outside surface of CNT tube, platinum particles were completely attached on the surface of the tube although this caused partial agglomeration. However, in most cases, due to the capillary effect, platinum particles were formed outside the tubes[29,30], leading to poor synergic effect of the Pt-CNT/TiO_2 composites.

Fig. 4 shows the EDX spectra of prepared Pt-CNT, CNT/TiO_2 and Pt-CNT/TiO_2 composites. From the EDX data, the main elements such as C, O, Ti and Pt were created and other impure elements were also made. The results of EDX elemental microanalysis of CNT/TiO_2 and Pt-CNT/TiO_2 composites are listed in Table-3. The platinum contents of 2Pt-CT 5Pt-CT and 8Pt-CT are 1.9, 5.5 and 8.1 %, respectively. As expected the platinum contents in the composites increased with an increase of H_2PtCl_6 concentration. It was proposed that the increase of platinum content increased the amount of agglomerated platinum particles. The same phenomena can be observed in the micro-surface structures and the morphology of Pt-CNT/TiO_2 composites (Fig. 2).

TABLE-3
ELEMENTAL MICROANALYSIS OF CNT/TiO_2,
Pt-CNT AND Pt-CNT/TiO_2 COMPOSITES

Sample	Element (wt. %)				
	C	O	Ti	Pt	Total
Pt-C	83.3	4.8	0	11.9	100
CT	53.3	23.0	21.7	0	100
2Pt-CT	28.6	35.3	34.2	1.9	100
5Pt-CT	29.3	29.8	35.4	5.5	100
8Pt-CT	26.8	30.1	35.0	8.1	100

Photoelectrocatalytic activities analysis: Fig. 5 shows the changes in relative concentration (c/c_0) of methylene blue with the CNT/TiO_2 and Pt-CNT/TiO_2 composite electrodes under visible light irradiation with electron currents in methylene blue solution (1×10^{-5} mol/L). Here we discussed three kinds of degradation process:



(a) (b)

(a) (b)

(e)

Fig. 4. EDX elemental microanalysis of CNT/TiO_2, Pt-CNT and Pt-CNT/TiO_2 composites; (a) Pt-C, (b) CT, (c) 2Pt-CT, (d) 5Pt-CT and (e) 8Pt-CT

(1) Photoelectrocatalytic: Visible light irradiation using the electrodes with a potential of 6 V; (2) Photocatalytic: Visible light irradiation using the electrodes; (3) Photo: Only visible light irradiation. From the results present in Fig. 5, compared with CNT/TiO_2 and Pt-CNT/TiO_2 composite electrodes, the photoelectrocatalytic and photocatalytic effects of the platinum treated CNT/TiO_2 composite electrodes were all better than that of non-platinum treated CNT/TiO_2. It was implied that the introduction of platinum enhanced the photoelectrocatalytic and photocatalytic degradation of methylene blue solution. However, for the platinum treated CNT/TiO_2 series, the photoelectrocatalytic and photocatalytic degradation efficiency of the sample 2Pt-CT is higher than that of the sample 5Pt-CT and 8Pt-CT in the same irradiation time, although the platinum content of the sample 2Pt-CT was lowest among the three platinum treated CNT/TiO_2 composites. The electrocatalytic activity of platinum nanoparticles for this reaction is dependent on various factors, which involves the size and dispersion of the particles, supporting materials and their surface conditions[21]. In the case of 5Pt-CT and 8Pt-CT, the Pt nanoparticles were heavily agglomerated

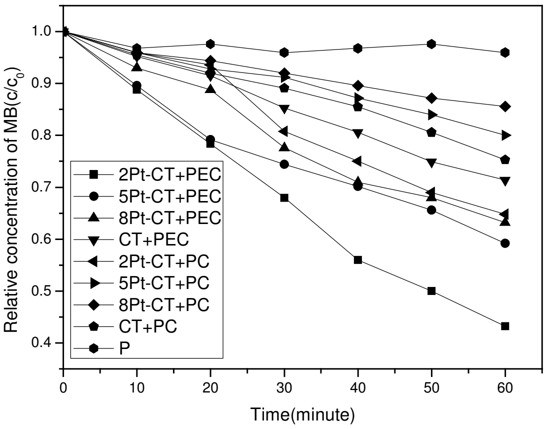


Fig. 5. Dependence of relative concentration (c/c_0) of methylene blue in the aqueous solution with different Pt-CNT/TiO_2 electrodes on time of PEC, PC and P reaction. (PEC: Visible light irradiation using the electrodes with a potential of 6 V; PC: Visible light irradiation using the electrodes; P: Only visible light irradiation)

to gather into a rounded mass [Fig. 2(d-e)], which leads to the significant reduction on its activity. It is well known that the PEC activity will increase with an increase of platinum content in a certain range. At the same time, the morphology of platinum in the Pt-CNT/TiO_2 composites is an important factor. Note that the optimization of PEC oxidation of methylene blue using Pt-CNT/TiO_2 composite electrodes will be studied in detail in another paper.

For CNT/TiO_2 composites, carbon nonotubes acting as electron sensitizer and donator in the composite photocatalysts may accept the electron (e^-) induced by light irradiation[7,31]. The electrons in carbon nonotubes may be transferred into the conduction band in the TiO_2 particles. It is thought that a photo-induced charge transfer occurs in the electronic interaction between the carbon layers or walls of the carbon nonotubes and TiO_2. The electrons formed by the light irradiation on the surface of the carbon nonotubes migrate to the surface of the TiO_2. 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 reported that the photo- or electro-induced charge transfer occurs in the electronic interaction between TiO_2 and carbon nonotubes[32]. Since they connect well with each other and there is a strong interaction between carbon nonotubes and TiO_2, we propose that electron transfer also happens in the CNT/TiO_2 composites, retarding the e^-/h^+ recombination and increase in photon efficiency. The light absorption capability of the photocatalyst and the separation of photogenerated e^-/h^+ pairs are crucial factors influencing the photoactivity.

For Pt-CNT/TiO_2 composites (with the exception of the photocatalysis of CNT/TiO_2 composites discussed above), the presence of platinum ion is believed to retard the e^-/h^+ pairs recombination by serving as an electron sink (schottky-barrier electron trapping) and to facilitate the interfacial electron transfer to dioxygen or other electron acceptors (*e.g.*, CNT networks)[33]. In this case, platinum nanoparticles adhered to the surface of carbon nonotubes in the forms of small clusters and the distribution was not uniform (Fig. 2). Moreover, when these platinum nanoparticles were heavily agglomerated to form round mass as shown in Fig. 3(b), some regional part on the CNT surface was completely enwrapped by the round mass. It is thought that the particles do not connect well with each other between carbon nonotubes and TiO_2. It is proposed that electron transfer also happens in the Pt-CNT/TiO_2 composites, but the round mass resulted in the increase of e^-/h^+ recombination and the decrease of photon efficiency.

Furthermore, the photoelectrocatalytic degradation of methylene blue was better than that of photocatalytic, it was thought that the recombination of photogenerated e^-/h^+ pairs was suppressed by the externally applied electric field in the photoelectrocatalytic reaction. Thus the life of the e^-/h^+ is prolonged, with electrons that are able to migrate to the solid-liquid interface and promote redox reactions. At the same time, the holes are removed *via* their reaction with the methylene blue in the solution, which occurs only at those TiO_2/solution interfaces. The photocatalytic reaction occurs when $HO^\bullet$ radically reacts with the methylene blue molecule.

In this study, it was considered that the photoelectrocatalytic degradation of the methylene blue solution could be attributed to the synergetic effects of photodegradation of TiO_2, the electro-assistant of carbon nonotubes, the enhancement of platinum and the function of applied potential. So this expatiation for the degradation mechanism is in accord with results of methylene blue degradation by photoelectrocatalytic using the Pt-CNT/TiO_2 composite electrodes.

Effect of re-use on Pt-CNT/TiO_2 electrode performance: The stability of 2Pt-CT electrode was examined by five times of repeated use on methylene blue degradation, as shown in Fig. 6. A loss of the activity (12.4 % in 60 min) of 2Pt-CT electrode was found after its first use, whereas, the activity differences were inconspicuous among the second to fifth re-use of the 2Pt-CT electrode. The possible reason should be responsible for the activity loss of 2Pt-CT electrode. It is related to Pt change, either the leaching of platinum or covering of platinum sites by organic substances[34].

Conclusion

In this study, we presented the fabrication and characterization of CNT/TiO_2 and Pt-CNT/TiO_2 composite electrodes. The BET surface area of Pt-CNT/TiO_2 composites decreased with an increase of platinum component. XRD data revealed that the structure for the Pt-CNT/TiO_2 composites showed a single anatase crystal phase. The TEM microphotographs of CNT/TiO_2 and Pt-CNT/TiO_2 composites showed that TiO_2 particles were distributed uniformly in the carbon nonotubes network and the platinum particles were fixed on the surface of the carbon nonotubes, although they were partly aggregated. From the EDX data, the main elements such as C, O, Ti and Pt existed. The Pt-CNT/TiO_2 samples have a higher photoelectro-

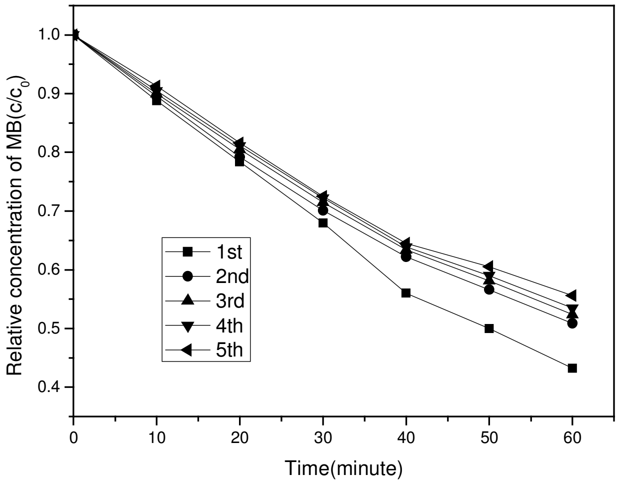


Fig. 6. Effect of reuse of 2Pt-CT electrode on the degradation of methylene blue in the aqueous solution with photoelectrocatalytic reaction. (PEC: Visible light irradiation using the electrodes with a potential of 6 V)

catalytic and photocatalytic degradation efficiency than that of the non-platinum treated CNT/TiO_2 sample. The results demonstrated that the photoelectrocatalytic degradation of methylene blue solution could be attributed to synergetic effects of the photo-degradation of TiO_2, the electron assistance of the carbon nanotubes network, the enhancement of platinum and a function of the applied potential. The morphology of platinum in the Pt-CNT/TiO_2 composites is an important factor. A loss of the catalytic activity (12.4 % in 60 min) of 2Pt-CT electrode was found after its first use.

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