

PHOTOELECTROCATALYTIC DEGRADATION OF METHYLENE BLUE USING PT-CNT/TiO₂ COMPOSITES UNDER VISIBLE LIGHT

Feng-Jun Zhang^{a,b}, Ming-Liang Chen^b and Won-Chun Oh^b

^a Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture, Anhui Hefei, P. R. China, 230022

^b Department of Advanced Materials & Science Engineering, Hanseo University, Seosan-si, Chungnam-do, Korea, 356-706

Introduction

Although titanium dioxide (TiO₂) has been extensively investigated as a photocatalyst for the environmental purification of contaminated water and air, it is active only under illumination with UV light at wavelengths below 400nm because of the large band gap (3.2 eV) for anatase TiO₂. 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. To develop a practical TiO₂-based photocatalytic process, majority of studies on TiO₂ focused on either enhancing its photocatalytic activity or extending its absorption spectrum from UV to the visible range by adding a second elements or support materials to the TiO₂ bulk structure.

Numerous investigations have reported that it is an effective method to add group VIII metals to TiO₂-based photocatalytic systems to enhance the photocatalytic reaction rate [13-15]. As all we know, platinum nanoparticles are very effective as a matrix of enzyme sensors by taking advantage of the biocompatibility and huge surface of Pt nanoparticles and good electrocatalytic activity to hydrogen peroxide.

Moreover, carbon nanotubes (CNTs), as a new class of nanomaterials, have been drawn to considerable attention for their applications as catalyst supports [1-3] owing to their unique electrical properties, high chemical stability and high surface-to-volume ratio. Moreover, CNTs have a variety of electronic properties. They may also exhibit metallic conductivity as one of the many possible electronic structures. CNTs have a large electron-storage capacity (one electron for every 32 carbon atoms), the ability of CNT can promote the electron-transfer reactions at carbon nanotubes modified electrodes. As TiO₂, 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.

The objective of this study is to investigate the PEC degradation for methylene blue (MB, C₁₆H₁₈N₃S·Cl·3H₂O) on Pt-CNT/TiO₂ composite electrodes under visible light. Structural variations, surface state, and elemental compositions were investigated for preparation of Pt-CNT/TiO₂ composite.

Experimental

Carbon nanotubes (CNTs) were selected as the support material. The CNTs (Multiwall Onanotubes, diameter: ~ 20nm, length: ~5µm), were supplied by Carbon Nano-material Technology Co., Ltd, Korea and used without further purification. Titanium *n*-butoxide (TNB, Ti(OC₄H₇)₄) as a TiO₂ source for the preparation of Pt-CNT/TiO₂ composites were purchased from Acros Organics, New Jersey, USA. Hydrogen hexachloroplatinate(IV) hydrate(H₂PtCl₆·6H₂O) 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 MB was used as analytical grade which was purchased from Duksan Pure Chemical Co., Ltd, Korea.

To begin preparing this experiment, the oxidizing agent 2.0 g MCPBA was melted in 60 mL benzene. Then 0.6 g CNTs was put into the oxidizing agent, refluxed for 6 h, filtered and dried. The oxidized CNTs were put into the mixing solution of TNB 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/TiO₂ gels, and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. Then 0.4g phenol resin was added to these CNT/TiO₂ composites, and the composites were pressed at a pressure of 250 kg/cm² in a mould with dimensions of 9.95mm×39.5mm×5.95mm. This mixture was then heat treated at 673 K for 1 h.

The oxidized CNTs were added to ethylene glycol solution containing H₂PtCl₆·6H₂O, 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 773K for 1 h with a heating rate of 279 K/min, the Pt treated CNT composites were obtained. The Pt treated CNT composites were put into the mixing solution of TNB 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/TiO₂ 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/TiO₂ composites were obtained. Then 0.4 g phenol resin was added to the Pt-CNT composites or Pt-CNT/TiO₂ composites, and the composites were pressed at a pressure of 250 kg/cm² in a mould with dimensions of 9.95mm×39.5mm×5.95mm. The mixture was then heat treated at 673 K for 1 h. This concluded the preparation of the Pt-CNT and Pt-CNT/TiO₂ electrodes.

The PEC degradation was performed by using CNT/TiO₂, Pt-CNT and Pt-CNT/TiO₂ 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 dark box. The counter electrode was artificial graphite (TCK, Korea), which dimension was 9.95mmX39.5mmX5.95mm. The CNT/TiO₂, Pt-CNT and Pt-CNT/TiO₂ electrodes were placed in 50 ml of 1.0×10⁻⁵ mol/l MB solution. The PEC degradation of MB was performed with voltage of 6.0V and visible light. The PEC activities of the CNT/TiO₂, Pt-CNT and Pt-CNT/TiO₂ electrodes were investigated using the PEC rate of MB solution, which was measured as function of time. The blue color of the solution faded gradually with time due to the adsorption and degradation of MB solution. And then the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

Results and Discussion

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/TiO₂ showed a mix of anatase and rutile crystals. It is well known that the crystal structure of the TiO₂ 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/TiO₂ composite existed in anatase state. The peaks at 27.4, 36.1, 41.2 and 54.3 ° belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. Therefore, it can be concluded that the developed

CNT/TiO₂ composite had a mixing structure of anatase and rutile crystals when annealed at 973K. We have previously demonstrated that the crystallization phenomena in C/TiO₂ composites heat treated at 973K results in a mixed anatase-rutile structure [24, 25]. However, the structure for the Pt treated CNT/TiO₂ composite showed an anatase crystal. It was considered that the introduction of Pt suppress the phase transform of TiO₂ from anatase to rutile-type structure during the heat treatment.

In addition, for the Pt-CNT sample, the characteristic peaks of face centered cubic crystalline platinum at 39, 46, and 68° are assigned as the (111), (200), and (220) plane, respectively [26, 27]. It is considered that intensity of the peaks from Pt metal is derived from the Pt-CNT composite and strengthened with an increase of H₂PtCl₆ concentration. Sharp diffraction peaks indicated the formation of pure Pt with high crystalline. Additional, for the Pt-CNT/TiO₂ sample, the ordered Pt₃Ti intermetallic structure formed as indicated by the presence of the [1 0 0], [1 1 0], and [1 1 1] superlattice diffraction peaks. It was indicated that partial Pt nanoparticles incorporated into the lattice of titanium dioxide phase, therefore the band gap of titanium dioxide would be decreased and visible light absorption would be increased.

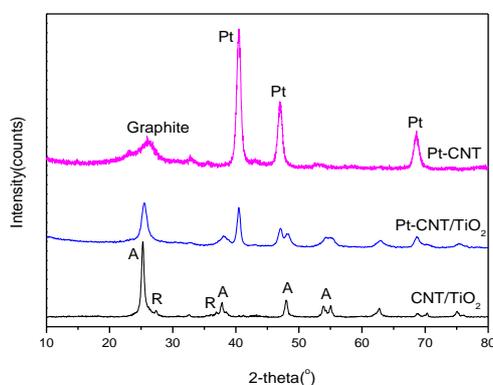


Fig. 1. XRD patterns of CNT/TiO₂, Pt-CNT and Pt-CNT/TiO₂ composites.

The micro-surface structures and morphology of CNT/TiO₂, Pt-CNT and Pt-CNT/TiO₂ composites were characterized by SEM (Fig. 2). Fig. 2 shows the changes in the morphology of Pt-CNT, CNT/TiO₂ and Pt-CNT/TiO₂ composites. As shown in Fig. 2, TiO₂ particles were fixed well on the surface of the CNT networks for CNT/TiO₂ and Pt-CNT/TiO₂ composites. The conduction of a CNT network can facilitate the electron transfer between the adsorbed dye molecules and the catalyst substrate. It was beneficial for the enhancement of the PEC activity of these composites. As shown in Fig. 2, Pt particles were attached on the surface of the CNT network in the form of round mass, and the distribution was not uniform. Several Pt particles between them.

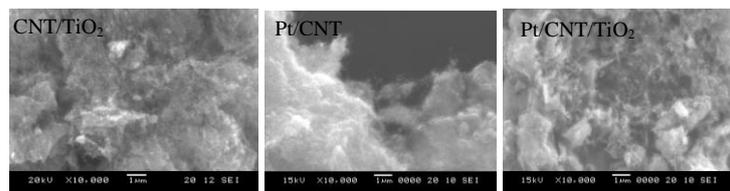


Fig. 2. SEM images of samples.

The pseudo-first-order kinetics of the PEC degradations is illustrated in Fig. 3. This suggests that the addition of Pt impurity was useful to the enhancement of photoelectroactivity. On the basis of the relevant band positions of Pt and TiO₂, Pt clusters at a lower

concentration act as a separation center. The photogenerated electrons are transferred from TiO₂ conduction band to the Pt conduction band and the holes accumulate in the TiO₂ valence band. Hence, photogenerated electrons and holes were efficiently separated. The observed kinetic constants of CNT/TiO₂, Pt-CNT and Pt-CNT/TiO₂ were 0.0055 min⁻¹ (R² = 0.9968), 0.0071 min⁻¹ (R² = 0.9952) and 0.0138 min⁻¹ (R² = 0.9979) respectively for the MB PEC degradation. However, the first-order kinetic constant of Pt-CNT/TiO₂ for the MB PEC degradation was about 2.5 times that of CNT/TiO₂. For the case of Pt-CNT/TiO₂, the PEC reactions are very versatile owing to their multicomponent nature and the kind of chemical substances that can be destructed or transformed photocatalytically is almost unlimited. It is well known that the PEC activity will increase with an increase of Pt content in a certain range. At the same time, the morphology of Pt in the Pt-CNT/TiO₂ composites is an important factor. Note that the optimization of PEC oxidation of MB using Pt-CNT/TiO₂ composite electrodes will be studied in detail in another paper.

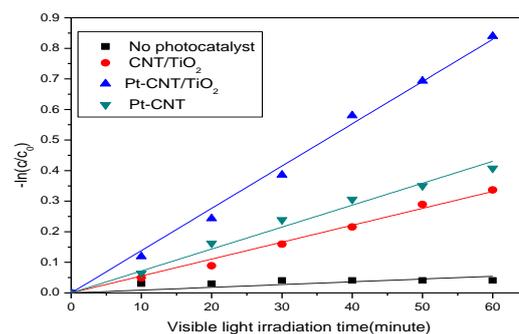


Fig. 3. The first-order kinetics of PEC degradation for MB solution using different electrodes.

Conclusions

In this study, we presented the fabrication and characterization of CNT/TiO₂ and Pt-CNT/TiO₂ composite electrodes. XRD data revealed that the structure for the Pt-CNT/TiO₂ composites showed a single anatase crystal phase. The TEM microphotographs of CNT/TiO₂ and Pt-CNT/TiO₂ composites showed that TiO₂ particles were distributed uniformly in the CNTs network, and the Pt particles were fixed on the surface of the CNTs. The Pt-CNT/TiO₂ samples have a higher PEC degradation efficiency than that of the non-Pt treated CNT/TiO₂ sample. The results demonstrated that the PEC degradation of MB solution could be attributed to synergistic effects of the photo-degradation of TiO₂, the electron assistance of the CNT network, the enhancement of Pt and a function of the applied potential.

References

- [1] Zhang FJ, Chen ML, Oh WC. Characterization of CNT/TiO₂ Electrode Prepared Through Impregnation with TNB and Their Photoelectrocatalytic Properties. *Environ. Eng. Res.* 2009; 14(1); 32-40.
- [2] Zhang FJ, Chen ML, Oh WC. Synthesis and characterization of CNT / TiO₂ photoelectrocatalytic electrodes for methylene blue degradation, *Mater. Res. Soc. Korea*, 2008;18, 583-591.
- [3] Garcia J, Gomes HT, Serp P, Kalck P, Figueiredo JL, Faria JL. Platinum catalysts supported on MWNT for catalytic wet air oxidation of nitrogen containing compounds. *Catal. Today* 2005;102:101-109.