Electrochemical Preparation of TiO_2/CNT Electrodes with a TNB Electrolyte and Their Photoelectrocatalytic Effects

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ABSTRACT

We investigate a method for the electrochemical preparation of titanium dioxide/carbon nanotube (TiO_2/CNT) composites involving the electroplating of Ti in a titanium n-butoxide (TNB) electrolyte into a CNT matrix. The BET surface areas of TiO_2/CNT composites decreased as electrochemical operating time increased. Changes in XRD patterns showed a typical anatase type on the TiO_2/CNT composite prepared with a CNT matrix by the electroplating method in the TNB solution. In SEM micrographs, the titanium complex particles were uniformly distributed on the CNT surface. The results of chemical elemental analysis for the TiO_2/CNT composites showed that most of the spectra for these samples produced stronger peaks for carbon and Ti metal than those of any other element. Finally, the prominent photoelectrocatalytic (PEC) activities of the TiO_2/CNT composites could be attributed to the combined effects of photodegradation of TiO_2 , electron assistance of CNT and the application of a sufficient voltage.

Key words : TiO_2 , CNT, Electrochemical, TNB, Photoelectrocatalytic activity

1. Introduction

Titanium dioxide (TiO_2) is an important semiconductor material which has always been one of the best candidate materials for various applications due to its photocatalytic properties, its relative nontoxicity, and long-term thermodynamic stability.^{1,2)} One of its most important applications is to act as photocatalyst for certain chemical reactions, especially for the decontamination of water containing organic pollutants.^{3,4)} However, low photocatalytic efficiency has limited application of this technology in practical treatment. At the same time, several groups have managed to enhance its photocatalytic properties and optimized the use of titania to degrade various organic and inorganic pollutants.⁵⁻⁷⁾

Recently, CNT-based composites have attracted much attention due to their unique properties and promising applications.⁸⁻¹⁰⁾ For example, metal oxides,^{11,12)} noble metal nanoparticles^{13,14)} and polymers and functional organic molecules,¹⁵⁻¹⁷⁾ etc., have been successfully decorated on CNTs. These composites not only exhibit their intrinsic properties, such as mechanical, adsorption and thermal properties, but also display cooperative or synergetic effects. Moreover, CNTs possess a variety of electronic properties. They may also exhibit metallic conductivity as one of many possible

electronic structures. CNTs have a large electron-storage capacity (one electron for every 32 carbon atoms),¹⁸⁾ and therefore may accept photon-excited electrons in mixtures or nanocomposites with titania, thus retarding or hindering recombination.

Carbon nanotube-anatase titanium dioxide (CNT- TiO_2) composite systems are currently being considered for many applications including environmental problems. The mixture of two types of semiconductor particles, semiconductor particles with metal particles, and, recently, carbon particles with anatase, has shown photocatalytic enhancements in many cases.¹⁹⁾ This concept can then be extended to defined carbon structures with tailored electronic properties. CNTs are excellent candidates to allow deeper insight into the semiconductor junction of titania with metallic or semiconducting carbons. Furthermore, CNTs have excellent mechanical properties and a large specific surface area. They also allow for surface chemical modifications to control the type of bonds that can be formed with titania, be they chemically bonded or van der Waals bonded. The mixture of titania and CNT also creates a large area that can absorb pollutants (organic or inorganic reactants). Thus, CNT- TiO_2 mixtures and composites are able to achieve photocatalytic activities well beyond the anatase/rutile composites.

Up to now, CNT has been turned into composites with titania in several ways.²⁰⁻³⁰⁾ The most common method is the sol-gel route,²⁰⁻²⁶⁾ although the chemical pathways and the composite configuration may vary. Jitianu and his colleagues coated MWCNT with anatase by a sol-gel method using classic alkoxides as precursors,²⁰⁾ whereas Wang et al.

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prepared TiO_2 /MWCNT composites with MWCNT embedded in TiO_2 nanoparticles by a modified sol-gel method and investigated their activity in the photodegradation of phenol under irradiation of visible light.²¹⁾

Recently, CNTs have also been coated via hydrothermal methods.²⁵⁾ To fully crystallize the coating, a heat treatment is required that usually occurs at 300~500°C in air to avoid CNT burnout and a phase transformation from anatase to rutile. A relatively new method of preparing such composites is the filter-mat or fiber-form via the electrospinning method.²⁶⁾ Typically, a fiber mat is formed, which is currently explored for a variety of catalytic applications. However, conventional preparation techniques usually suffer from inherent disadvantages. For example, the CNTs need to be treated with strong acids to introduce active function groups on their surface; some organic stabilizers must then be introduced in order to prevent nanoparticles from agglomerating. Therefore, simple and effective ways to synthesize TiO_2 /CNT composites must be explored.

Here we report on a simple and effective electrochemical route to deposit TiO_2 particles on CNT. In this method, TNB ($\text{Ti}(\text{OC}_4\text{H}_7)_4$) as a precursor was electrolyzed to form TiO_2 and deposited on CNT with the aid of the electrical driving force, resulting in TiO_2 /CNT composites. The resultant TiO_2 /CNT composites were characterized by different techniques including BET surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). The PEC activities of the as-prepared TiO_2 /CNT composite electrodes for methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}_3\text{H}_2\text{O}$) degradation under UV light irradiation were also investigated.

2. Experimental

2.1. Materials

The CNTs were selected as the support materials. The CNTs, supplied from Carbon Nanomaterial Technology Co., Ltd., Korea. (Multiwall nanotubes, diameter: ~20 nm, length: ~5 μm), were used without further purification. The TNB as a titanium source for the preparation of TiO_2 /CNT composites were purchased from Acros Organics, New Jersey, USA. The novolac-type polymer resin (PR) was supplied by Kangnam Chemical Co., Ltd., Korea. The MB used was analytical grade and purchased from Duksan Pure Chemical Co., Ltd., Korea. It was selected because under anaerobic conditions it can readily produce potentially more hazardous aromatic amines.

2.2. Preparation of TiO_2 /CNT Composites

First, 0.4 g phenol resin was mixed with 0.6 g CNT, then the CNT matrix electrodes were pressed in a mould at a pressure of 250 kg/cm^2 ; their dimensions were 9.95 mm $\times$ 39.5 mm $\times$ 5.95 mm. The curing temperature of the CNT matrix electrodes was 423 K, and the cured sample pyrolyzed at 673 K for 1 h in order to completely cure the binder. Then the mixing solution of TNB and benzene with a volume ratio of 1:1 was used as an electrolyte. The counter

Fig. 1. Conditions and procedure for preparing TiO_2 /CNT electrodes.

electrode of the same size was artificial graphite (TCK, Korea). The applied voltage of the preparation of TiO_2 /CNT composites was set to 9.0 V at different times. Before heat treatment, the solvent in the matrix was vaporized at 343 K for 1 h. Then, the CNT matrix electrodes treated with TNB were heated at 673 K for 1 h. Finally, several TiO_2 /CNT electrodes were obtained. The preparation procedure for the electrodes is given in Fig. 1.

2.3. Characterization of the TiO_2 /CNT Composite

The Brunauer-Emmett-Teller (BET) surface area of the TiO_2 /CNT composites was evaluated from an N_2 adsorption isotherm at 77 K using a BET analyzer (Monosorb, USA). Scanning electron microscopy (SEM, JSM-5200 JEOL, Japan) was used to observe the surface states and structures of TiO_2 /CNT composites. For the elemental analysis in TiO_2 /CNT composites, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimadzu XD-D1, Japan) with $\text{Cu K}\alpha$ radiation.

2.4. PEC Degradation

The PEC degradation was performed using TiO_2 /CNT electrodes in a 100 mL glass container and then the system was irradiated with 20 W UV light at 365 nm, which was used at a distance of 100 mm from the solution in a dark box. The counter electrode was artificial graphite (TCK, Korea), whose dimensions were 9.95 mm $\times$ 39.5 mm $\times$ 5.95 mm. The same TiO_2 /CNT electrode was placed in 50 mL of 1.0×10^{-5} mol/L MB solution. The PEC degradation of MB was performed with a voltage of 6.0 V and UV light. The PEC activities of the

Table 1. Nomenclatures of TiO₂/CNT Electrodes

Preparation method	Nomenclature
CNT:PR(8:2)+ TNB:Benzene (1:1) (electrolyte)+DC 9.0V+10 min	ECPT1
CNT:PR(8:2)+TNB:Benzene (1:1) (electrolyte)+DC 9.0V+30 min	ECPT2
CNT:PR(8:2) +TNB:Benzene (1:1) (electrolyte)+DC 9.0V+50 min	ECPT3

Table 2. Textural Properties of Pristine Materials and TiO₂/CNT Composites

Sample	S _{BET} (m ² /g)
ECPT1	408.6
ECPT2	208.2
ECPT3	147.4

TiO₂/CNT electrodes were investigated using the PEC rate of the MB solution, which was measured as a function of time. The blue color of the solution faded gradually with time due to the adsorption and degradation of the MB solution. And then the concentration of MB in the solution was determined as a function of irradiation time from the change in absorbance at a wavelength of 660 nm.

3. Results and Discussion

3.1. Structure and Morphology of TiO₂/CNT Composites

The values of the BET surface areas of TiO₂/CNT composites are shown in Table 2. From the results of Table 2, the BET surface areas of ECPT1, ECPT2 and ECPT3 were 408.6, 208.2 and 147.4 m²/g, respectively. This demonstrated that there is a marked decrease in the BET surface area of the TiO₂/CNT composites as electrolysis time increases, which suggests that some porosity developed during electrolysis. This could be attributed to the partial blocking of micropores by the formation of TiO₂ on the CNT surfaces with heat treatment. On the other hand, the BET surface area decreased due to the curing of the polymer resin with heat treatment, which blocked the existing micropores and formed some new macropores.

The XRD spectra of TiO₂/CNT are shown in Fig. 2. The structure for the TiO₂/CNT composites shows a typical single and clear anatase crystal structure. It is well known that the crystal structure of titanium dioxide is mainly determined by the heat-treated temperature. After heat treatment at 673 K for 1 h, the main crystalline phase is not transformed to the rutile structure. The major peaks at 25.3, 37.8, 48.0, 53.8 and 62.5 are the diffractions of (101), (004), (200), and (105) and (204) planes of anatase (JCPDS PD File No. 21-1272), indicating that the developed TiO₂/CNT composites existed in an anatase crystal phase. As we know, the anatase phase formed below 773 K started to transform into a rutile-type structure above 873 K and changed into a single phase of rutile at 973~1173 K.²⁷⁾ The result was consistent with the literature,²⁸⁾ so the results of XRD in this paper seem reliable.

Fig. 2. XRD patterns of TiO₂/CNT composites (ECPT1, ECPT2 and ECPT3).

Fig. 3 shows the SEM morphology of TiO₂/CNT composites. Fig. 3 shows that the TiO₂ particles were well distributed among the CNT network, and some TiO₂ particles aggregated into small clusters. According to Fig. 3 (f), the image presents a close-up scale view of TiO₂ introduced from composites with external diameters ranging from 0.5 to 1.0 μm. It was considered that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. But the dispersion of the TiO₂ particles for all TiO₂/CNT composites prepared at different electrolysis times did not clearly change among the CNT networks. Therefore, the higher photocatalytic activity of the TiO₂/CNT composites prepared might be attributed to chemical degradation. At the same time, the conductivity of CNT networks can facilitate electron transfer between the

Fig. 3. SEM and FE-SEM images obtained from powdered TiO_2/CNT composites: (a) ECPT1 (full view); (b) ECPT1 (close-up), (c) ECPT2 (full view); (d) ECPT2 (close-up); (e) ECPT3 (full view); and (f) ECPT3 (close-up).

adsorbed MB molecules and the catalyst substrate.²⁹⁻³¹⁾ This was beneficial for the PEC reaction because it was carried out on the surface of the TiO_2/CNT composites catalysts and the CNT network. So the TiO_2/CNT composite would show excellent PEC activity.

Fig. 4 shows the EDX spectra of the TiO_2/CNT composites that were prepared. The results of EDX elemental micro-analysis of the TiO_2/CNT composites are listed in Table 3.

From the EDX data, the main elements such as C, O and Ti existed and other impure elements also existed. It also shows that most of the spectra for these samples produced stronger peaks for carbon and Ti metal than that of any other element. The Ti content percentages of ECPT1, ECPT2 and ECPT3 were 14.09%, 16.82% and 18.08%, respectively. As expected, the Ti element content in the composites increased as electrolysis time increased. However,

Table 3. EDX Elemental Microanalysis of TiO₂/CNT Electrodes

Sample	C	O	Ti
ECPT1	64.59	17.81	14.09
ECPT2	62.59	17.20	16.82
ECPT3	61.82	16.51	18.08

(a)

(b)

(c)

Fig. 4. EDX elemental microanalysis of TiO₂/CNT composites: (a) ECPT1; (b) ECPT2; and (c) ECPT3.

the increase in Ti content was somewhat lower than expected; this could indicate that the Ti content introduced

into the composites has been affected by the pore structure of the prepared CNT matrix.

3.2. PEC Effect

In order to study the PEC effect of the prepared samples, the decomposition reaction of MB in water was followed. The UV/VIS absorbance spectra of an MB concentration of 1×10^{-5} mol/L with different TiO₂/CNT electrodes under various time conditions are shown in Fig. 5. As shown in Fig. 5, the absorbance maxima for all samples decreased as UV irradiation time increased. It is indicated that the MB solution increasingly lost its color, so its concentration also continued to decrease. From Figs. 5 (a), (b), (c), we can also observe that the absorbance maximum of the sample ECPT3 decreased much more than that of the sample ECPT1 and ECPT2 even at the same irradiation time. According to previous studies,^{32,33)} we can expect that the ECPT3 will have better PC degradation of an MB solution than the ECPT1 and ECPT2. Comparing with Figs. 5 (d), (e), (f), we can observe that the absorbance maxima for all samples decrease by the photocatalytic effect of TiO₂/CNT electrodes are much higher than that of the PEC effect. It is evident that two types of MB degradation are the electro-assistant activity of CNTs and the PC performance of TiO₂. This indicates that the efficiency of PEC oxidation for MB is higher than that of PC oxidation.

Fig. 6 shows the changes in relative concentration (c/c_0) of the TiO₂/CNT composites in an MB concentration of 1×10^{-5} mol/L under UV irradiation with or without an electron current in the aqueous solution. From the present results in Fig. 6 (a), it can be seen that fast MB degradation efficiency of ECPT3 was observed in the PC series. Thus it appeared that a decrease of MB concentration in the aqueous solution can occur in two physical phenomena such as adsorption by CNTs and PC decomposition by TiO₂, and that PC decomposition by TiO₂ was mainly in evidence here. As shown in Fig. 6 (b), the PEC oxidation for all TiO₂/CNT composites prepared at different electrolysis times did not change significantly. Since it is possible that the PEC oxidation increased with an increase of CNT composition, and the carbon content of ECPT3 was the lowest among the three samples, the CNTs' electro-assisted effect of ECPT3 was likely less than that of ECPT1 and ECPT2. Moreover, the relative concentration (c/c_0) of the MB solution was 35.9%~68.2% for PC decomposition after 60 min; however, for PEC decomposition at the same time, the relative concentration (c/c_0) of the MB solution was only 15.8%~25.7%. It is evident that the PEC decomposition rate was faster, with a slope higher than that observed in PC decomposition. So the applied voltage appears to have enhanced the decomposition rate of the MB solution.

In the TiO₂/CNT composite electrodes, electrons are transferred from the TiO₂ phase (low electron conductivity) into the carbon phase (high electron conductivity). This process must overcome interfacial resistance, which is largely fixed by the properties of the two solid phases. Therefore, to

Fig. 5. UV/Vis spectra of MB concentration against the TiO_2/CNT composites as a function of time: PC (UV irradiation using electrodes but without any electron current); PEC (UV irradiation using electrodes and with an electron current).

Fig. 6. Dependence of relative concentrations of MB in the aqueous solution c/c_0 on the time elapsed for UV irradiation for different TiO_2/CNT electrodes (ECPT1, ECPT2 and ECPT3): (a) PC (UV irradiation using electrodes but without any electron current); and (b) PEC (UV irradiation using electrodes and with an electron current).

enable electron transfer, a sufficient or higher anodic potential is needed. Furthermore, the presence of an electronic conductor (CNT) dispersed through the TiO_2 phase allows a local potential difference across the TiO_2 phase to be developed throughout the sample, resulting in more effective e/h^+ separation within the entire sample. In our case, a voltage of 6.0 V was employed in the PEC decomposition, the recombination of photogenerated e/h^+ pairs was suppressed by the externally applied electric field. So the life of the e/h^+ got longer, and these are able to migrate to the solid-liquid

interface and promote redox reactions.³⁴⁾

Based on these relationships, we can therefore conclude that the degree of removal of pollutants in the solution should be attributed to the combination effects of photodegradation of TiO_2 and the electron assistance of CNT, coupled with the application of a sufficient voltage.

4. Conclusion

In this study, we prepared TiO_2/CNT composite catalysts

through an electrochemical method in the TNB electrolyte. The prepared composite materials were characterized by surface properties, structural crystallinity between CNT and TiO₂, elemental identification, and photoelectrocatalytic activity. The BET surface area decreased as electrochemical operating time increased. The XRD patterns were shown as a typical anatase type on a TiO₂/CNT composite prepared with a CNT matrix by the electrochemical method in the TNB electrolyte. From the SEM results, the titanium complex particles were uniformly distributed on the CNT surface, although some large clusters were also found when electrochemical operating time increased. The EDX results of TiO₂/CNT composites showed that for most of the spectra from these samples, stronger peaks in carbon and Ti metal were present to a greater degree than for any other element. Finally, the prominent PEC activity of the TiO₂/CNT composites could be attributed to the combined effects of photodegradation of TiO₂ and electron assistance of CNT, and the application of a sufficient voltage.

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