Electro-chemical Preparation of TiO_2/CNT Electrodes with TNB Electrolyte and Their Photoelectrocatalytic Effect

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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 Brunauer-Emmett-Teller (BET) surface areas of TiO_2/CNT composites decrease as the electrochemical operating time increases. Changes in XRD patterns show a typical anatase type on the TiO_2/CNT composite prepared with a CNT matrix by the electroplating method in a TNB solution. In SEM micrographs, the titanium complex particles are uniformly distributed on the CNT surface. The results of chemical elemental analysis for the TiO_2/CNT composites show that most of the spectra for these samples produce stronger peaks for carbon and Ti metal than for any other element. Finally, the prominent photoelectrocatalytic activities of the TiO_2/CNT composites can 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. It has always been one of the best candidate materials for various applications due to its photocatalytic properties, its relative nontoxicity, and its long-term thermodynamic stability.^{1,2} One of its most important applications is to act as a photocatalyst for certain chemical reactions, especially for the decontamination of water that contains organic pollutants.^{3,4} However, low photocatalytic efficiency has limited the 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 molecules¹⁵⁻¹⁷ have been successfully decorated on CNTs. These composites exhibit intrinsic properties, such as mechanical, adsorption and thermal properties and 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 may therefore accept photon-excited electrons in mixtures or nanocomposites with titania, thereby retarding or hindering recombination.

CNT-anatase titanium dioxide (CNT- TiO_2) composite systems are currently being considered for many applications, including environmental problems. A mixture of two types of semiconductor particles, namely 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 for allowing 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 enable 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 can achieve photocatalytic activities well beyond the anatase/rutile composites.

CNTs have been turned into composites with titania in several ways.²⁰⁻³⁰ The most common method is the sol-gel route,²⁰⁻²⁶ though the chemical pathways and the composite configuration may vary. Jitianu et al. coated a multi wall CNT (MWCNT) with anatase by using a sol-gel method with classic alkoxides as precursors.²⁰ In contrast, Wang et

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al. prepared $\text{TiO}_2/\text{MWCNT}$ composites with an MWCNT embedded in TiO_2 nanoparticles by using a modified sol-gel method; and they investigated their activity in the photo-degradation of phenol under irradiation of visible light.²¹⁾

Recently, CNTs have also been coated via hydrothermal methods.²⁵⁾ For full crystallization of the coating, a heat treatment is required that usually occurs at 300°C to 500°C in air to avoid a 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, and that type of mat is currently being 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 to prevent nanoparticles from agglomerating. Thus, simple and effective ways of synthesizing TiO_2/CNT composites must be explored.

Here we report on a simple and effective electrochemical route for the deposition of TiO_2 particles on a CNT. In this method, the precursor $\text{Ti}(\text{OC}_4\text{H}_7)_4$ (TNB) was electrolyzed to form TiO_2 and deposited on a CNT with the aid of an electrical driving force to produce TiO_2/CNT composites. The resultant TiO_2/CNT composites were characterized by different techniques, including the BET surface area technique, X-ray diffraction (XRD), scanning electron microscopy (SEM), and an energy dispersive X-ray (EDX) technique. The PEC activities of the as-prepared TiO_2/CNT composite electrodes for methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S} \cdot \text{Cl} \cdot 3\text{H}_2\text{O}$) degradation under UV light irradiation were also investigated.

2. Experimental

2.1. Materials

The CNTs, which we selected as the support materials, were supplied by the Carbon Nanomaterial Technology Co., Ltd., Korea. They were multiwall nanotubes with a diameter of approximately 20 nm and a length of approximately 5 μm , and they were used without further purification. The TNB, which we used as a titanium source for the preparation of TiO_2/CNT composites, was purchased from Acros Organics, New Jersey, USA. The novolac-type polymer resin (PR) was supplied by Kangnam Chemical Co., Ltd., Korea. The MB, which was of analytical grade, was 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 we mixed 0.4 g of phenol resin with 0.6 g of CNTs and then pressed the CNT matrix electrodes into a mould at a pressure of 250 kg/cm^2 ; the dimensions of mold 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

Fig. 1. Preparation conditions and procedure of TiO_2/CNT electrode.

was pyrolyzed at 673 K for 1 h to completely cure the binder. The mixing solution of TNB and benzene with a volume ratio of 1:1 was then used as an electrolyte. The counter electrode of the same size was artificial graphite (TCK, Korea). The applied voltage of the preparation of the TiO_2/CNT composites was set to 9.0 V at different times. Before the heat treatment, the solvent in the matrix was vaporized at 343 K for 1 h. The CNT matrix electrodes treated with TNB were then heated at 673 K for 1 h. This procedure, which is shown in Fig. 1, eventually produced several TiO_2/CNT electrodes.

2.3. Characterization of the TiO_2/CNT Composite

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

2.4. PEC Degradation

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

Table 1. Nomenclatures of TiO₂/CNT Electrodes

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

was performed with a voltage of 6.0 V and UV light. The PEC activities of the TiO₂/CNT electrodes were investigated at the MB solution's PEC rate, 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. The concentration of the MB in the solution was then 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. The results of Table 2 show that the BET surface areas of ECPT1, ECPT2 and ECPT3 were 408.6 m²/g, 208.2 m²/g, and 147.4 m²/g, respectively. These results demonstrate that there is a marked decrease in the BET surface area of the TiO₂/CNT composites as the electrolysis time increases, suggesting that some porosity developed during the electrolysis. This porosity can 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 decreases due to the curing of the polymer resin with heat treatment; the cured polymer resin blocks exist micropores and forms 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 temperature of the heat-treatment. 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 diffractions of the (101), (004), (200), and (105) and (204) planes of the anatase (JCPDS PD File No. 21-1272), indicating that the developed TiO₂/CNT composites exist in an anatase crystal phase. Thus, the anatase phase that forms below 773 K begins to transform into a rutile-type structure above 873 K and changes into a single-phase rutile at a temperature range of

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

973 K to 1173 K.²⁷⁾ These results are consistent with the literature;²⁸⁾ hence, the XRD results in this paper seem reliable.

The SEM morphology of TiO₂/CNT composites, as shown in Fig. 3, confirms that the TiO₂ particles are well distributed among the CNT network and that some TiO₂ particles aggregate in small clusters. Fig. 3(f) shows a close-up image of a TiO₂ sample taken from composites with external diameters ranging from 0.5 μm to 1.0 μm. A good dispersion of small particles was presumed to provide more reactive sites for the reactants rather than the aggregated particles. However, the dispersion of the TiO₂ particles for all the TiO₂/CNT composites prepared at different electrolysis times did not clearly change among the CNT networks. Thus, the higher photocatalytic activity of the prepared TiO₂/CNT composites may be attributed to chemical degradation. 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).

Table 3. EDX Elemental Microanalysis of TiO_2/CNT Electrode

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

conductivity of the CNT networks can also facilitate the transfer of electrons between the adsorbed MB molecules and the catalyst substrate.²⁹⁻³¹⁾ This electron transfer is beneficial for the PEC reaction because the reaction occurs on the surface of the TiO_2/CNT composites catalysts and the CNT network. Hence, the TiO_2/CNT composite shows excellent PEC activity.

Fig. 4 shows the EDX spectra of the prepared TiO_2/CNT composites. Table 3 lists the results of the EDX elemental microanalysis of the TiO_2/CNT composites. The EDX data confirms the existence of the main elements, namely C, O and Ti, as well as other impure elements. The data also shows that most of the spectra for these samples produce stronger peaks for carbon and Ti metal than for any other element. The Ti content percentages are 14.09% for ECPT1, 16.82% for ECPT2 and 18.08% for ECPT3. The Ti element content in the composites increases as the electrolysis time increases. However, the increase in Ti content is somewhat lower than expected, possibly indicating that the Ti content

Fig. 4. EDX elemental microanalysis of TiO_2/CNT composites (a) ECPT1, (b) ECPT2, and (c) ECPT3.

introduced into the composites is affected by the pore structure of the prepared CNT matrix.

3.2. PEC Effect

To study the PEC effect of the prepared samples, we investigated the decomposition reaction of MB in water. Fig. 5 shows the UV/VIS absorbance spectra of an MB concentration of 1×10^{-5} mol/L with different TiO_2/CNT electrodes under various time conditions. As shown in Fig. 5, the

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

absorbance maxima for all samples decreases as the UV irradiation time increases. Moreover, the MB solution increasingly loses its color and its concentration continues to diminish. From Figs. 5(a), 5(b), and 5(c), we can also see that the absorbance maximum of the sample ECPT3 decreases much more than that of samples ECPT1 and ECPT2, even for the same irradiation time. On the basis of previous studies,^{32,33)} we can expect ECPT3 to outperform ECPT1 and ECPT2 in terms of PC degradation of the MB solution. A comparison of Figs. 5(d), 5(e), and 5(f) shows that the decrease in the absorbance maxima for all samples as a result of the photocatalytic effect of the TiO_2/CNT electrodes

is much greater than that of the PEC effect. Thus, the two types of MB degradation are the electro-assistant activity of CNTs and the PC performance of TiO_2 . This outcome indicates that the efficiency of the PEC oxidation for MB is higher than the efficiency of the PC oxidation.

Fig. 6 shows changes in the relative concentration (c/c_0) of the TiO_2/CNT composites in an MB concentration of 1×10^{-5} mol/L under UV irradiation, with and without an electron current in the aqueous solution. The results in Fig. 6(a) highlight the fast MB degradation efficiency of ECPT3 in the PC series. Thus, a decrease in the MB concentration in the aqueous solution can occur in two physical phenomena,

Fig. 6. Dependence of relative concentrations of MB in the aqueous solution (c/c_0) on the time elapsed for UV irradiation for different TiO₂/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).

namely adsorption by CNTs and PC decomposition by TiO₂. There is also clear evidence of PC decomposition by TiO₂. Fig. 6(b) shows no significant change in the PEC oxidation for any of the TiO₂/CNT composites prepared at different electrolysis times. Given the possibility that the PEC oxidation increases with an increase of CNT composition and that the carbon content of ECPT3 is the lowest of the three samples, the electro-assisted effect of the CNTs is likely to be less for ECPT3 than for ECPT1 and ECPT2. Moreover, the relative concentration (c/c_0) of the MB solution is in the range of 35.9% to 68.2% for the PC decomposition after 60 min; however, for the PEC decomposition over the same duration, the relative concentration (c/c_0) of the MB solution is in a much lower range of 15.8% to 25.7%. The PEC decomposition clearly occurs at a faster rate and steeper incline than the PC decomposition. Hence, 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 (of low electron conductivity) into the carbon phase (of high electron conductivity). This process must overcome interfacial resistance, which is largely fixed by the properties of the two solid phases. Therefore, to enable electron transfer, we need a sufficient or higher anodic potential. Furthermore, the presence of an electronic conductor (CNT) dispersed through the TiO₂ phase enables a local potential difference across the TiO₂ 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 used in the PEC decomposition and the recombination of photogenerated e/h^+ pairs was suppressed by the externally applied electric field. This process prolongs the life span of the e/h^+ pairs and enables them to migrate to the solid-liquid interface and promote redox reactions.³⁴⁾

On the basis of these relations, we conclude that the degree of removal of pollutants in the solution can be attributed to the combined effects of the photodegradation of TiO₂ and the electron assistance of CNTs, coupled with the application of a sufficient voltage.

4. Conclusion

In this study, we prepared TiO₂/CNT composite catalysts through an electrochemical method in the TNB electrolyte. The prepared composite materials are characterized by surface properties, structural crystallinity between the CNTs and TiO₂, elemental identification, and photoelectrocatalytic activity. The BET surface area decreases as the electrochemical operating time increases. The XRD patterns show a typical anatase type on a TiO₂/CNT composite prepared with a CNT matrix by the electrochemical method in the TNB electrolyte. The SEM results show that the titanium complex particles are uniformly distributed on the CNT surface, though some large clusters are also found when the electrochemical operating time is increased. The EDX results of the TiO₂/CNT composites show that for most of the spectra from these samples there is a greater number of strong peaks in the carbon and Ti metal than in any other element. Finally, the prominent PEC activity of the TiO₂/CNT composites can be attributed to the combined effects of the photodegradation of TiO₂ and the electron assistance of CNTs, as well as the application of a sufficient voltage.

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