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Fabrication of CNT/TiO₂ electrodes and their photoelectrocatalytic properties for methylene blue degradation

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In this study, three kinds of CNT/TiO₂ electrodes were prepared. The electrodes prepared were characterized by BET surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, and it illuminated that the electrodes developed consisted of well mixed anatase and rutile TiO2 particles with the CNTs and they exhibited a higher catalytic activity. The catalytic efficiency of the electrodes developed was evaluated by the photoelectrodegradation of methylene blue (MB). The photoelectrodegradation of MB using the proposed electrode under different experimental conditions was investigated. The positive potential applied in photoelectrocatalytic (PEC) oxidation was also studied. It was found that catalytic decomposition of the MB solution could be attributed to the combination effects between TiO₂ photocatalyst and the electro-assistance of the CNTs, with the conductive of CNT network facilitating the electron transfer between the adsorbed MB molecules and the catalyst substrate, and that PEC oxidation increased with an increase of the CNT composition.

Key words: CNT/TiO₂ electrode, Photoelectrocatalysis, Methylene blue (MB), XRD, SEM, EDX.

Introduction

The azo dyes are an important class of materials in the textile and paper industries, while textile dyes and other industrial dye stuffs constitute one of the largest groups of organic compounds representing an increasing environmental danger [1]. Dyes are widely used and therefore wastewater is discharged into natural and domestic water systems including rivers, lakes and public sewage. As a result, these dye compounds can also generate dangerous by-products through some chemical reactions in environmental water, which will even imperil the health of human beings [2]. Moreover; concerns have been expressed about the potential toxicity of dyes and of their precursors. Environmental pollution caused by organic dyes also set a severe ecological problem, which has increased by the fact that most of them are difficult to degrade using standard methods [3].

Generally, traditional physical techniques, such as flocculation, air sparging, adsorption on activated carbon, ultra-filtration and reverse osmosis, may be employed efficiently to remove such recalcitrant pollutants. However, they are non-destructive, because they just transferr the dye compounds from water to another phase which would cause a secondary environmental pollution [4-6]. This has led to the requirement of regeneration of the adsorbent materials and post-treatment of solid wastes and both of them are expensive [7]. In the last decade, advanced oxidation methods (AOMs) have been widely used in the treatment of wastewater since they are able to handle the problem of organic pollutant destruction in aqueous solutions [8-10]. Among AOMs, photocatalytic (PC) technology has been applied to decolorize the azo dye in wastewater with TiO_2 as a photocatalyst; however, the low photocatalytic efficiency has limited the application of this technology in practical water treatment [11-16].

According to our former studies [17-20], carbon-TiO₂ composites having a high surface area and porous texture distribution, showed an excellent photoactivity. Wang et al. [21-22] have studied the nanostructure MWCNT-TiO₂ composite materials for photocatalytic water treatment applications, where MWCNT acting as a photo sensitizer rather than an adsorbent and dispersing agent. Phang et al. [23] considered that the addition of TiO₂, SWNT and MWNT, and different SWNT contents are significant factors which will affect the magnetization, dielectric and conductivity properties. There were many reports on photoelectrocatalytic degradation of organic pollutants using TiO₂ electrodes, which were prepared by coating the surfaces of electrically-conducting substrates with TiO_2 films [24-27]. In this method, a positive potential was applied on the working electrode, which could inhibit the recombination of electrons and holes and enhance the rate of photoelectrocatalytic degradation of organic compounds [28-30]. In our study, carbon nanotubes (CNTs) were selected as the support materials for catalyst deposition in order to obtain a large surface area, better catalyst dispersion, and a resulting high electroactivity.

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In this study, we have prepared some different CNT/ TiO₂ electrodes. The electrodes developed were characterized by BET surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) spectroscopy. The catalytic efficiency of the electrodes developed was evaluated by the photoelectrodegradation of an azo compound, methylene blue (MB, $C_{16}H_{18}N_3S$ ·Cl·3H₂O).

Experimental

Materials

CNTs were selected as the support material. The CNTs, supplied from carbon nano-material technology Co., Ltd, Korea. (Multiwalled nanotubes, diameter: ~20 nm, length: ~5 μ m), were used without further purification. The pristine TiO₂ was commercially available and was supplied from Duksan Pure Chemical Co., Ltd, Korea. The MB was used as analytical grade which was purchased from Duksan Pure Chemical Co., Ltd, Korea. It was selected because it can be readily under anaerobic conditions to produce potentially more hazardous aromatic amines.

Preparation of CNT/TiO₂ electrodes

Several CNT/TiO_2 electrodes were prepared. The preparation procedure for the electrodes is given in Fig. 1. The preparation conditions and the sample codes used in this study are listed in Table 1.

Characteristics and investigations of the samples

The Brunauer-Emett-Teller (BET) surface area of the CNT/TiO_2 composites was evaluated from the N_2 adsorption isotherms at 77 K using a BEL Sorp Analyzer (BEL, Japan). XRD was used for crystal phase identification



Fig. 1. The preparation procedure of fabrication of carbon nanotubes electrodes.

Table. 1. Nomenclatures	s of CNT/TiO ₂ electrode
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Weight ratio (wt %)	Nomenclature
$CNTs + Polymer resin + TiO_2 (5:4:1)$	CPT
$CNTs + Polymer resin + TiO_2 (3:4:3)$	CPT1
$CNTs + Polymer resin + TiO_2 (1 : 4 : 5)$	CPT2

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 CNT/TiO₂ composites were carried out using a JSM-5200 JOEL electron microscope (Japan). EDX was used to measure the elemental analysis of the CNT/TiO₂ composites. UV-VIS spectra for the MB solution obtained from degradation by CNT/TiO₂ composites dispersion under different conditions were recorded using a Genspec III (Hitachi, Japan) spectrometer.

Photoelectrocatalytic decompositions

The photoelectrocatalytic decomposition was performed using CNT/TiO₂ electrodes and an aqueous solution of MB in a 100 ml glass container and then irradiating the system with 20 W UV light at 365 nm, which was used at a distance of 100 mm from the solution in darkness box. The same CNT/TiO₂ electrode was placed in 50 ml of 1.0×10^{-5} mol/l MB solution. The photoelectrocatalytic degradation of MB was performed with a potential voltage of 3.0 V and UV light. The photoelectrocatalytic activities of the CNT/TiO₂ electrodes were investigated using the photoelectrodegradation rate of MB, which was measured for 10, 20, 30, 40 and 50 minutes. The blue color of the solution faded gradually with time due to the adsorption and decomposition of MB. And then the concentration of MB in the solution was determined as a function of the irradiation time from the absorbance change at a wavelength of 660 nm from UV spectra.

Results and Discussion

Structure and morphology of CNT/TiO₂ composites

The N_2 adsorption isotherms for CNT/TiO₂ composites are shown in Fig. 2. All of the isotherms can be ascribed to type II, which suggests a mixed micro-and mesoporous texture. The values of the BET surface areas of CNT/



Fig. 2. Adsorption isotherms of N_2 at 77 K on the pristine materials and CNT/TiO₂ composites.

Table. 2. Textural properties of pristine materials and CNT/TiO_2 composites

Sample	SBET (m2/g)
CPT	135.1
CPT1	100.4
CPT2	28.9
Pristine CNTs	299.2
Pristine TiO ₂	8.3

TiO₂ composites are shown in Table 2. From the results of Table 2, the BET surface areas of pristine TiO₂ and CNT were 8.3 and 299.2 m^2/g , respectively, this demonstrated that there is a marked decrease in the BET surface area of the CNT/TiO₂ composites with an increase of TiO₂ concentration, which suggest that some porosity was developed during the heat treatment. On the one hand, this could be attributed to the partial blocking of micropores by the formation of TiO₂ on the CNT surfaces with the 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 micropores and formed some new macropores. However, the BET surface areas of all composites were small, and all surface areas showed considerably more decrease than that of pristine CNTs, and an increased amount of CNTs would increase the surface area. The same phenomena had also been observed in Wang et al.'s studies [21, 22].

The XRD results for the catalyst samples are shown in Fig. 3. The structure for the CNT/TiO₂ composites showed a mixture of anatase and rutile crystals. The samples were heated at 673 K for 1 h. The peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions maxima of (101), (004), (200) and (204) planes of anatase, indicating the CNT/TiO₂ composites developed existed in an anatase state. The peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks from (110), (101), (111) and (211) of rutile. Therefore, it can be concluded that the CNT/TiO₂ composites developed had a mixture of structures of anatase and rutile crystals. In contrast to previous studies [17], we have evidence that C/TiO₂ composites had a mixed structure



Fig. 3. XRD patterns of CNT/TiO₂ composites.

of anatase and rutile crystals by crystallization when the temperature reached 973 K. But in the present case, we prepared CNT/TiO₂ composites using different amounts of CNT and TiO₂; the crystals transformed from anatase to rutile at 673 K, Moreover, the ratio of rutile to anatase crystals increased with an increase of the amount of TiO₂.

Fig. 4 shows the SEM morphology of CNT/TiO₂ composites. Fig. 4 shows that TiO₂ particles were mixed well with the CNT network, in which the conductive network of CNTs would facilitate the electron transfer between the adsorbed MB molecules and the catalyst substrate. This would be beneficial for the photoelectrocatalytic reaction because the photoelectrocatalytic reaction is carried out on the surfaces of the CNT/TiO₂ composites catalysts and the CNTs network. So the CNT/TiO₂ composites should show excellent photoelectrocatalytic activity. It was also observed that some clusters of TiO₂ particles were found in Fig. 4(e) and (f); the amount of clusters increased with an increase in the amount of TiO_2 . It was considered that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. This is consistent with the Wang et al.'s reports [21, 22] that CNTs introduced into TiO_2 can prevent TiO_2 particles from agglomerating. The size of the TiO₂ particles became larger with an increase in the amount of TiO₂. Therefore, the higher photocatalytic activity of the CNT/TiO₂ composites prepared might be attributed to chemical degradation.

Fig. 5 shows the EDX spectra of the CNT/TiO₂ composites



Fig. 4. SEM images obtained from powdered CNT/TiO₂ composites. (a) and (b): CPT, (c) and (d): CPT1, (e) and (f): CPT2.



Fig. 5. EDX elemental microanalysis of CNT/TiO₂ composites: (a) CPT, (b) CPT1 and (c) CPT2.

Table. 3. EDX elemental microanalysis of CNT/TiO₂ composites

Sample	Elements (wt. %)			
Sample —	С	0	Ti	Other
CPT	81.3	10.4	2.7	5.6
CPT1	57.0	19.0	17.3	6.7
CPT2	26.6	33.5	36.8	3.1

prepared. From the EDX data, the main elements such as C, O and Ti existed and other impurity elements also existed. The results of EDX elemental microanalysis of CNT/TiO₂ composites are listed in Table 3. As expected, the Ti element content in the composites increased with an increase of the amount of TiO₂. However, the Ti content of CPT was somewhat lower than expected, indicating the relatively small TiO₂ particles in the composites, the same phenomena can be observed in the SEM morphology of CNT/TiO₂ composites.

Catalytic activities

When the CNT/TiO₂ electrode was illuminated with UV light, the photo-induced electrons are transferred from the TiO₂ valence band (VB) into the conduction band (CB) [31-32]. The whole reaction process viewed on both a macroscopic and microscopic scales is shown in Fig. 6. From the Fig. 6(B) (1), it can be observed that a large number of electrons would be transferred from VB into CB by absorbing UV light quanta, leaving highly oxidative holes in VB and forming negative sites in CB. Meanwhile, the photo-generated holes and electrons could recombine as observed in Fig. 6(B) (2), which restrains



Fig. 6. Schematic representation of photo-induced electron transfer processes in the electrode /solution system from macroscopic (A) and microscopic (B) views. CB: conduction band, VB: valence band.

the charge transfer and leads to an efficient operation of the photocatalytic oxidation. In the photo-electrochemical cell, the efficiency of this process was improved by applying a suitable anodic potential to the circuit owing to the conducting CNT network. The photo-generated holes react with adsorbed water (or OH⁻) to produce hydroxyl radicals which could oxidize the organic compounds at the anode surface (Fig. 6(B) (3)), while the photo-generated electrons in the CB may react with O₂, which can be trigger the formation of very reactive superoxide radical ions (O₂⁻.) (Fig. 6(B) (4)). As is well known these radical groups are responsible for the decomposition of organic compounds.

Fig. 7 shows the changes in relative concentration (c/c0)of the MB concentration starting from 1×10^{-5} mol/l on the CNT/TiO₂ composites under UV irradiation in an aqueous solution. From the present results in Fig. 7(a), it can be seen that a PC process of MB with fast degradation efficiency was observed with an increase of the TiO₂ component. It is considered that the decreases of MB concentration in the aqueous solution can occurr in two physical phenomena such as adsorption by CNTs and photocatalytic decomposition by TiO₂, and that here it was mainly photocatalytic decomposition. As the result of EDX, the CPT had the largest content of carbon and CPT2 had the largest content of Ti. From the Fig. 7(b), the PEC oxidation increased with an increase of CNT composition. According to former studies [30, 33], it is possible that catalytic decomposition of MB solution could be attributed to combined effects between TiO₂ photocatalytic activity, electro-assisted by CNTs. With an applied potential in the PEC, the recombination of photo-generated hole/ electron pairs is suppressed by the externally applied electric field, and thus the life of the holes and electrons become



Fig. 7. Dependence of the relative concentration of MB in the aqueous solution c/c0 on time of UV irradiation for different CNT/TiO2 electrodes: (a) PC (UV irradiation using the electrodes but without any electron current); (b) PEC (UV irradiation using the electrodes with an electron current).

longer [32], so the conductivity of the CNT network facilitated the electron transfer between the adsorbed MB molecules and the catalyst substrate. This indicates that the decrease of MB can be concluded to be from combined effects of the photocatalytic decomposition by TiO_2 and electro-assistance from CNT network.

Conclusions

In this study, the properties of CNT/TiO_2 electrodes were investigated. The BET surface areas for CNT/TiO_2 composites decreased with an increase of the TiO_2 component. XRD data revealed that all samples had a mixture of anatase and rutile TiO_2 . The SEM microphotographs of CNT/TiO_2 composites showed the TiO_2 particles were well mixed with the CNTs network. From the EDX data, the main elements of C, O and Ti were shown to exist. A series of experiments under different conditions were carried out to study the photoelectrocatalytic behavior of the electrodes prepared. The results demonstrated that a decrease of the MB concentration in an aqueous solution occurs due to a combination of the effects of photocatalytic decomposition by TiO_2 and electro-assistance of the CNTs network, and that PC oxidation of MB increased with an increase of the TiO_2 composition and PEC oxidation increased with an increase of CNT composition.

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