Fabrication and Characterization of Tailored TiO₂ and WO₃/MWCNT Composites for Methylene Blue Decomposition

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Abstract: A sol-gel method was used to prepare WO₃/MWCNT-TiO₂ composites. Their photocatalytic activities were evaluated by the degradation of methylene blue (MB) solution under UV light. The catalysts were characterized by X-ray diffraction, specific surface area measurement, energy-dispersive X-ray analysis, transmission and scanning electron microscopy. Aqueous MB solutions of 100 ml were photodegraded by a small amount of the WO₃/MWCNT-TiO₂ composite under UV light irradiation. The photocatalytic data showed that the WO₃/MWCNT-TiO₂ composite achieved a high rate of MB photodegradation. This was attributed to the use of MWCNT which can absorb UV light to create photo-induced electrons, strong adsorption of dye molecules on the photocatalyst, and reduced recombination rate of electron-holes in the WO₃/MWCNT-TiO₂ composite due to the introduction of the WO₃ semiconductor.

Key words: tungsten trioxide; titanium dioxide; multi-walled carbon nanotube; photocatalytic activity; methylene blue

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Titanium dioxide (TiO₂) is an important semiconducting material that is used as a white pigment, cosmetic, catalyst, and carrier for its excellent physical and chemical properties [1–5]. One of its most important applications is as a photocatalyst, particularly for the decontamination of water polluted with organic pollutants [6–10]. The TiO₂/UV catalytic system has been examined widely as a heterogeneous photocatalytic process. The photocatalytic mechanism of TiO₂ involves the formation of hole-electron couples upon irradiation of sufficient energy to overcome the band gap, which move to the surface and react with OH[−] groups and O₂ absorbed on the surface of the catalyst to yield hydroxyl radicals and superoxide radical ions, respectively. These species have high activity and can oxidize organic compounds [11–14]. However, the use of TiO₂ as a photocatalysts is limited by the fast recombination of the generated photo-holes and photo-electrons. Photocatalysis involves the oxidation of a chemical by photo-holes from the semiconductor. Hence, every recombination event results in the loss of holes that might otherwise have caused degradation. Therefore, the transfer of photogenerated electrons and holes between the valence and conduction bands of semiconductors is important in photocatalysis.

As a good support for nanomaterials, multi-walled carbon nanotubes (MWCNTs) have attracted considerable attention owing to their unique structure and mechanical, chemical and electronic properties [15]. MWCNTs modified with nanocrystalline semiconductor particles have unique

size-dependent non-linear optical and electronic properties that can have potential applications in many areas [16,17]. In this study [18], the photocatalytic efficiency of TiO₂ was increased by using MWCNTs to prepare MWCNT/TiO₂ photocatalytic composites. MWCNT is an ideal 1D carbon-based molecule with nano-cylinders that can conduct electricity at room temperature with essentially no resistance. This phenomenon is known as ballistic transport [19,20], where electrons move freely through the structure without any scattering from atoms or defects. When electrons formed by UV irradiation migrate to the surface of a MWCNT, they can be easily transported to the conduction band (CB) of TiO₂ bonded to the MWCNT. The increased amount of generated photo-electrons would decrease the high rate of electron-hole pair recombination, which would reduce the quantum yield of the TiO₂.

Tungsten oxide (WO_x, $x = 1-3$) has attracted research interest over the past few decades due to its wide uses as gas sensors for SO₂ and H₂S [21,22] and excellent field emitters (specifically W₁₈O₄₉) [23]. The growth of WO_x on a MWCNT template may give very interesting functional structures for use as gas sensor, catalyst, and electrochromic devices because MWCNT can be grown easily on patterned substrates to give a variety of forms, such as vertically aligned tubes and arrays of pillars and sheets [24].

To improve TiO₂ photocatalytic efficiency, WO₃ compounded with TiO₂ has been used to decompose wastewater and air contaminants [25–28]. Zhang et al. [29] reported that

WO₃ thin films sputtered on TiO₂ can improve the rate of photo-catalytic degradation of methylene blue (MB). Since WO₃ is a semiconductor photocatalyst with a band gap of 2.8 eV, this combination of semiconductor photocatalysts may increase the efficiency of the photocatalytic process by increasing the charge separation and extending the energy range of photoexcitation. At the same time, the physical and optical properties are much modified. However, the WO₃/TiO₂ photocatalyst has some shortcomings. For example, a combined WO₃ semiconductor can easily become a recombination center for photo-electron-hole pairs, and it has a low specific surface area in most cases, which can limit the rate of photodegradation.

To solve this problem, a novel photocatalyst with improved photocatalytic efficiency was fabricated using a sol-gel method. The properties of the photocatalyst (WO₃/MWCNT-TiO₂) were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX). MB decomposition was determined under UV light irradiation.

1 Experimental

1.1 Synthesis of the WO₃/MWCNT-TiO₂ photocatalyst

To evaluate the photocatalytic effect of WO₃/TiO₂, a composite was prepared using a sol-gel method with anatase TiO₂ nanopowder in a solution of ammonium metatungstate hydrate (H₂₆N₆O₄₀W₁₂·xH₂O, Sigma-Aldrich). Some

H₂₆N₆O₄₀W₁₂·xH₂O powder was added to 15 ml of water with continuous stirring, which was followed by the addition of 4 ml titanium (IV) *n*-butoxide (TNB, 99%, reagent grade, Kanto Chemical Company, Japan) with magnetic stirring for 6 h at 100 °C. The mixture was dried at 120 °C for 8 h and calcined at 500 °C for 1 h. The preparation scheme is shown in Fig. 1.

A new synthesis process was used for the WO₃/MWCNT-TiO₂ photocatalyst. MWCNT (95.5%, diameter 20 nm, length 5 μm, Carbon Nano-material Technology Co., Ltd, Korea) is so stable that strong acids are needed to introduce active functional groups onto the surface. Therefore, 2 g of *m*-chloroperbenzoic acid (MCPBA, Acros) was dissolved in 80 ml benzene (99.5%, reagent grade, Duksan Pure Chemical Co., Korea) and 0.8 g of MWCNT powder was added to the oxidizing agent solution. This was refluxed at 80 °C for 6 h to form the solid precipitates, which was dried at 100 °C.

To synthesize the WO₃/MWCNT compounds, the appropriate content of H₂₆N₆O₄₀W₁₂·xH₂O powder was added to 60 ml of water in a 100 ml beaker and stirred until they had dissolved completely. Subsequently, 0.2 g of oxidized MWCNT was added to this mixture and stirred magnetically at 80 °C. After a reaction for 10 h, the formed gels were heated under reflux at 100 °C for 8 h and heat treated at 350 °C for 3 h to obtain the WO₃/MWCNT composite.

The WO₃/MWCNT composites obtained were placed into a sol containing 4 ml TNB and 40 ml benzene, homogenized at 100 °C for 10 h using a shaking water bath (Lab

Fig. 1. Preparation procedure of the WO₃/TiO₂ and WO₃/MWCNT-TiO₂ composites.

house, Korea) at a shaking rate of 120 r/min, and dried at 120 °C. Then after a thermal treatment at 500 °C for 1 h the WO₃/MWCNT-TiO₂ photocatalyst was obtained. This was called WCT. The preparation is also shown in Fig. 1.

For comparison, two other photocatalysts, named TiO₂ and MWCNT/TiO₂ were prepared using similar procedures.

1.2 Characterization of catalyst

The crystallographic structure of the inorganic constituent of the composites was examined by XRD (Shimadzu XD-D1, Japan) with Cu K_α radiation. EDX spectra were used for elemental analysis of the samples. SEM (JSM-5200 JOEL, Japan) was used to observe the surface state and structure of the three photocatalyst composites. The BET surface areas of the photocatalyst composites were determined by N₂ adsorption at −196 °C using a BET analyzer (Monosorb, USA). UV-Vis spectra were recorded using a Genspec (Hitachi, Japan) spectrometer.

1.3 Determination of photocatalytic property

The photocatalytic activity for the degradation of MB (C₁₆H₁₈N₃S·Cl·3H₂O, analytical grade, Duksan Pure Chemical Co., Ltd., Korea) was evaluated in aqueous medium at ambient temperature under ultraviolet light irradiation with a wavelength of 365 nm and 20 W output. The UV lamp was placed 100 mm from the solution in a dark box. The initial MB concentration (*c*₀) was 1.0 × 10^{−5} mol/L. The amount of the photocatalyst composites was 0.01 g. Before turning on the illumination, the suspension solution containing 100 ml of MB and the photocatalyst composites was stirred in the dark for 30 min to establish adsorption-desorption equilibrium. The experiments were carried out under UV light. Samples of the solution were withdrawn regularly from the reactor at 30, 60, 90, and 120 min, and centrifuged immediately to separate any suspended solid. The clear transparent solution was analyzed using a UV-Vis spectrophotometer. The concentration of MB in the solution was determined as a function of the irradiation time from the change in absorbance at 665 nm.

2 Results and discussion

2.1 BET surface area analysis

Table 1 lists the BET surface areas of TiO₂, MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂. The BET surface areas were 18.9, 109.2, 38.4, and 100.4 m²/g, respectively. Agglomeration occurred easily in the process of WO₃/TiO₂ preparation because of its higher surface energy. The addition of MWCNT to the WO₃/TiO₂ composite

Table 1 BET surface areas of the MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ composites

Sample	<i>A</i> _{BET} /(m ² /g)
Pure TiO ₂	18.9
MWCNT/TiO ₂	109.2
WO ₃ /TiO ₂	38.4
WO ₃ /MWCNT-TiO ₂	100.4

prevented the TiO₂ particles and WO₃ particles from agglomerating, resulting in a large change in the micropore size distribution for the WO₃/MWCNT-TiO₂ composite compared to that of WO₃/TiO₂. This suggested that the support MWCNT contributed directly to the adsorption ability of the photocatalyst composites.

2.2 SEM and TEM analysis

The micro-surface structures and morphologies of the MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ composites were characterized by SEM and TEM (Fig. 2). From Fig. 2(a), the TiO₂ particles were distributed uniformly over the entire MWCNT surface. Better dispersion would enable a larger number of active catalytic centers to be available for the photocatalytic reaction [30]. Figure 2(b) shows that WO₃ coupled TiO₂ particles aggregated, to a large extent, in the form of bundles. When the crystal particle size was very small, it can easily agglomerate due to the weak forces of the surface. Figure 2(c) shows a micrograph of WO₃/MWCNT-TiO₂, which showed the TiO₂ and WO₃ particles were distributed uniformly over the entire MWCNT surface. Figure 2(d) shows a TEM image of the particle shape, size, and distribution of WO₃/MWCNT-TiO₂. A few black dots were observed, which corresponded to WO₃ particles. Most of the WO₃ particles were quasi-spherical shapes, 5–15 nm in size, and coated on the outside surface of the MWCNT. Very few isolated WO₃ particles were observed. The average size of the TiO₂ particles was smaller than that of the WO₃ particles. Overall, the WO₃-TiO₂ nanoparticles were attached to the walls of the MWCNT with no apparent agglomeration of WO₃-TiO₂. This indicated that the presence of the MWCNT can efficiently inhibit the agglomeration of WO₃-TiO₂ and improve the dispersion of the nanoparticles.

2.3 XRD analysis

Figure 3 shows the XRD patterns of the catalysts. In the XRD patterns for the WO₃/TiO₂ composite not treated with carbon nanotubes, the diffraction peaks of tungsten oxide were clearly observed because of the high tungsten content and high crystallinity. The sharp peaks at 2θ = 23.2°, 24.5°, 28.3°, 34.1°, and 36.8° were indicative of monoclinic WO₃

Fig. 2. SEM images of MWCNT/TiO₂ (a), WO₃/TiO₂ (b), WO₃/MWCNT-TiO₂ (c), and TEM image of WO₃/MWCNT-TiO₂ composite (d).

Fig. 3. XRD patterns of WO₃/TiO₂ (1), MWCNT/TiO₂ (2), and WO₃/MWCNT-TiO₂ (3) composites.

[31]. For the WO₃/MWCNT-TiO₂ composites, the major peaks at $2\theta = 25.3^\circ$, 37.8° , 48.0° , 53.8° , 54.9° , and 62.5° were assigned to diffraction planes of (101), (004), (200), (105), (211), and (204) of anatase, indicating the prepared WO₃/MWCNT-TiO₂ composite existed as anatase. According to previous studies [32–35], the crystal structure of TiO₂ is determined mainly by the heat treatment temperature.

2.4 EDX analysis

Quantitative microanalysis of the MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ composites was performed by EDX and shown in Fig. 4. Figure 4 revealed the presence of C, O, and Ti, which confirmed the existence of

TiO₂ and C particles in the MWCNT/TiO₂ composite. From the analysis of the WO₃/TiO₂ and WO₃/MWCNT-TiO₂ photocatalysts, the elemental contents were composed mainly of Ti and O with a small quantity of W. There was less WO₃ in WO₃/MWCNT-TiO₂ than in WO₃/TiO₂.

Fig. 4. EDX analysis of MWCNT/TiO₂ (1), WO₃/TiO₂ (2), and WO₃/MWCNT-TiO₂ (3) composites.

2.5 Photocatalytic degradation of MB

The adsorption ability of pure TiO₂, MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ composites were evaluated after stirring for 30 min in the dark. There was a clear relationship between the surface areas listed in Table 1 and the adsorption efficiency in Fig. 5. The degradation of MB on the MWCNT/TiO₂ composite was faster than that on any other photocatalysts. This was attributed to the high

porosity of the MWCNT/TiO₂ surface due to the introduction of MWCNT, which correlated with an increase in adsorption ability. On the other hand, the BET surface area of WO₃/MWCNT-TiO₂ was similar to that of MWCNT/TiO₂ and it showed higher adsorption efficiency, which improved the degradation rate to some extent.

Fig. 5. Adsorption abilities in MB solution of pure TiO₂ (1), MWCNT/TiO₂ (2), WO₃/TiO₂ (3), and WO₃/MWCNT-TiO₂ (4) under magnetic stirring for 30 min.

The photocatalytic activities of pure TiO₂, MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ were tested with the photocatalytic degradation of MB solution under UV light irradiation as a test reaction. Figure 6 shows that MWCNT/TiO₂ exhibited a much higher activity than pure TiO₂ and WO₃/TiO₂ after irradiation for 120 min under UV light. This was because the MWCNT can absorb UV light to create photo-induced electrons (e⁻) into the conduction band of the TiO₂ particles, which increased the amount of electrons there [36,37]. The photocatalytic activity of WO₃/TiO₂ was higher than that of pure TiO₂ while the WO₃/MWCNT-TiO₂ photocatalyst exhibited the highest photocatalytic activity of all the samples.

Fig. 6. Photocatalytic activity evaluated by the decomposition of MB solution under UV irradiation for 120 min. (1) Pure TiO₂; (2) MWCNT/TiO₂; (3) WO₃/TiO₂; (4) WO₃/MWCNT-TiO₂.

The photodegradation results by UV light irradiation of a MB solution followed pseudo-first-order kinetics [38–40] with respect to the concentration of dyestuff in the bulk solution (*c*):

$$-dc/dt = k_{app}c \quad (1)$$

Integration of this equation (with $c = c_0$ at $t = 0$, with c_0 being the initial concentration in the bulk solution after dark adsorption and t the reaction time) gives

$$-\ln(c/c_0) = k_{app}t \quad (2)$$

where c and c_0 are the reactant concentrations at time $t = t$ and $t = 0$, respectively. k_{app} and t are the apparent reaction rate constants and time, respectively. Figure 7 shows a plot of $-\ln(c/c_0)$ vs t for MB degradation with pure TiO₂, MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ photocatalysts. The values of k_{app} were obtained from the slopes of the linear curves in the plot, and shown in Table 2. A combination factor (R) was defined as $R = k_{app}(\text{sample})/k_{app}(\text{TiO}_2)$ to quantify the combination effect. This is also showed in Table 2. Pure TiO₂, MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ photocatalysts gave apparent rate constants of 8.6×10^{-4} , 3.19×10^{-3} , 1.48×10^{-3} , and 4.99×10^{-3} , respectively. This suggested that the WO₃/MWCNT-TiO₂ photocatalyst has the highest efficiency for the photodegradation of MB solution. The introduction of MWCNT and WO₃ into the matrix obviously created a kinetic synergy effect in MB degradation with an increase in the rate constant by a factor of 4.2, which suggested that the rate of MB photodegradation using WO₃/MWCNT-TiO₂

Fig. 7. First-order linear kinetic plots of $-\ln(c/c_0)$ as a function of MB degradation of the different samples under irradiation of UV light.

Table 2 Apparent kinetic rate constants (k_{app}) of pure TiO₂, MWCNT/TiO₂, WO₃/TiO₂, and WO₃/MWCNT-TiO₂ composites

Sample	k_{app}/min^{-1}	R
Pure TiO ₂	8.60×10^{-4}	1
MWCNT/TiO ₂	3.19×10^{-3}	3.7
WO ₃ /TiO ₂	1.48×10^{-3}	1.72
WO ₃ /MWCNT-TiO ₂	4.99×10^{-3}	5.8

was 4.8 times higher than that with pure TiO₂.

Figure 8 shows the mechanism of the photocatalysis by WO₃/MWCNT-TiO₂. When MWCNT was introduced, MWCNT can absorb UV light and excite a photo-induced electron (e⁻) into the conduction band of the WO₃ particle and TiO₂ particles. When the WO₃/MWCNT-TiO₂ photocatalyst was exposed to light, TiO₂ particles absorb light to generate electron-hole pairs (Eq. (3)). Photoexcited electrons in the CB of the TiO₂ particles were injected easily into the CB of WO₃ particles due to the action of MWCNT and because the CB edge of WO₃ particle lies below the CB level of TiO₂. The injection of energetic electrons (those that have not relaxed to the CB of the TiO₂ particle) from TiO₂ to the CB of WO₃ particles can be excluded by considering the band gap energy and energy levels of WO₃ (2.8 eV) and TiO₂ (3.2 eV). Electron deficient anion vacancies present on the WO₃ surface can trap these excited electrons [25]. The electrons trapped in the electron defect sites can become localized in trap sites to form [W⁶⁺-O²⁻]⁻, while photogenerated holes remain on the TiO₂ particles to generate Ti-OH• species (Eqs. (4) and (5)). As a result, the photogenerated negative and positive charges are widely separated, and recombination is suppressed. The holes that remain on the TiO₂ crystalline particles eventually participate in the oxidation of MB by a direct reaction with the substrate or by the formation of OH radicals and electrons trapped on WO₃ that can react with molecular O₂ to form O₂•⁻ radicals, which eventually oxidize MB. This is shown in Fig. 8.

Fig. 8. Schematic diagram of the photocatalysis mechanism of the WO₃/MWCNT-TiO₂ composite.

3 Conclusions

TiO₂ and WO₃/MWCNT composites were prepared using a modified sol-gel method. A porous structure and TiO₂

agglomerates coated on the WO₃/MWCNT composite were observed. Photodegradation of MB by the TiO₂ and WO₃/MWCNT composites showed that TiO₂ absorbed more energy in the UV light region due to the presence of MWCNT and WO₃, which promoted the photocatalytic activity of TiO₂. The WO₃/MWCNT-TiO₂ photocatalyst showed efficient charge separation during UV irradiation. The rate constant of methylene blue destruction was 0.72 times higher than that of WO₃/TiO₂ and 4.8 times higher than that of pure TiO₂.

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