Multiwalled carbon nanotube/TiO$_2$ nanocomposite as a highly active photocatalyst for photodegradation of Reactive Black 5 dye

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ABSTRACT

A nanocomposite UV-visible light-responsive multiwalled carbon nanotube (MWCNT)/titanium dioxide (TiO$_2$) nanophotocatalyst was successfully synthesized by a modified sol-gel method using titanium isopropoxide and functionalized MWCNTs as the starting precursors. The photocatalytic activity of the TiO$_2$ and the nanohybrid material was investigated through the photodegradation of Reactive Black 5 dye under ultraviolet light irradiation. X-ray diffraction analysis indicated that anatase phase was obtained for both the pure TiO$_2$ and the MWCNT/TiO$_2$ composite, while Raman spectroscopy confirmed the presence of MWCNTs in the composite. Field emission scanning electron microscopy revealed that TiO$_2$ nanoparticles with an individual diameter of about 10–20 nm were coated on the surface of the MWCNTs. The specific surface areas of the samples were found to be 80 and 181 m$^2$/g for the pure TiO$_2$ and MWCNT/TiO$_2$, respectively. As a result, MWCNT/TiO$_2$ showed better photocatalytic performance than pure TiO$_2$ because the high surface area of MWCNTs enabled them to function as good electron acceptors for the retardation of electron-hole pair recombination.

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1. Introduction

The quality of global water sources is affected by various kinds of pollutants produced by industrial, agricultural, and domestic activities. Examples of industrial effluents are synthetic dyes, which are normally toxic and carcinogenic in nature [1,2]. Among the new advanced semiconducting materials reported for use in electronic, magnetic, optical, and photocatalytic application, titanium dioxide (TiO$_2$) remains a promising photocatalyst for the degradation of organic pollutants owing to its remarkable characteristics such as high photocatalytic efficiency, non-toxicity, low cost, eco-friendliness, photostability, and chemical inertness [3–6].

However, the photocatalytic efficiency of TiO$_2$ is hindered by its low solar light absorption of about 4% [7]; it is only excited under UV irradiation of wavelengths shorter than 384 nm [4]. Subsequently, the wide band-gap energy of TiO$_2$ (3.2 eV for anatase phase and 3.0 eV for rutile phase) may induce the fast recombination of electron-hole pairs, which may extensively restrict the photoconversion efficiency achievable over TiO$_2$ nanoparticles [5,6].

Generally, a good photocatalyst must at least have a large specific surface area with a high photocatalytic efficiency in the visible light region for it to effectively adsorb organic pollutants and conduct photogenerated electrons [8,9]. Much effort has been made to overcome the limitations of TiO$_2$ photocatalysts through retardation of electron-hole pair recombination, modification of its band-gap energy, creation of active sites for photocatalytic reaction, and increasing of its surface area [7–10].

Nanocomposites of TiO$_2$ nanoparticles with carbonaceous materials have become of major interest to researchers because of their unique properties in terms of physical, structural,
chemical, thermal, mechanical, electrical, and optical application [11–13]. Among such carbonaceous materials, multiwalled carbon nanotubes (MWCNTs) show good intrinsic properties as an adsorbent and dispersing agent and may create more active sites for photon absorption [14,15]. In this manner, MWCNTs play an essential role as a good electron acceptor for photoexcited TiO\textsubscript{2} by facilitating the separation of electron-hole pairs and modifying its optical band gap, which may enhance the photocatalytic efficiency [5,15].

Previously, MWCNTs coupled with TiO\textsubscript{2} nanocomposites have been prepared via several synthesis methods including sol-gel, hydrothermal, impregnation, chemical and physical vapor deposition, and electrophoretic deposition [5,7,16]. However, some of these methods are costly, time-consuming, and require multiple steps or higher temperature and pressure during the synthesis process [8,9]. Therefore, in the present work, a simple, cost-effective, and high-homogeneity approach is employed to synthesize MWCNTs/TiO\textsubscript{2} nanocomposites by depositing TiO\textsubscript{2} nanoparticles on the large surface of MWCNTs using modified sol-gel method.

2. Experimental

2.1. Materials

MWCNTs (>95%, 10–20 nm in diameter) were supplied by Bayer Material Science AG (Germany). Titanium isopropoxide (TTIP, 97%), concentrated nitric acid (65%), sodium dodecylbenzenesulfonate (SDS, 98%), and Reactive Black 5 (55%, molecular formula C\textsubscript{26}H\textsubscript{21}N\textsubscript{5}Na\textsubscript{4}O\textsubscript{19}S\textsubscript{6}) were purchased from Sigma-Aldrich, USA. Absolute ethanol (>99.8%), glacial acetic acid, and dilute ammonia solution (30%) were obtained from Fisher Scientific, UK. All chemicals were used as received without further purification. Deionized water was used throughout the experiment.

2.2. Functionalization of MWCNTs

The pure MWCNTs were functionalized using concentrated HNO\textsubscript{3} under reflux with vigorous magnetic stirring at 100 °C for 2 h. Under these conditions, the remaining iron particles are removed and hydroxyl and carboxyl groups are introduced onto the surface of the MWCNTs [17]. About 500 mL of HNO\textsubscript{3} was sufficient for 10 g of carbon sample. Then, the solution was cooled to room temperature, washed with distilled water, and oven-dried at 100 °C.

2.3. Synthesis of MWCNTs-TiO\textsubscript{2} nanocomposites

In a typical synthesis, MWCNTs/TiO\textsubscript{2} nanocomposites were prepared via a simple modified sol-gel method. An appropriate amount of functionalized MWCNTs was added to an aqueous solution of SDS with continual stirring for 24 h. The prepared MWCNTs solution was then dispersed in ethanol and stirred for 30 min to achieve homogeneity (solution A). A mixture of TTIP, ethanol, and acetic acid was subjected to vigorous stirring for 30 min to form a clear solution (solution B). Then, solution B was added dropwise into solution A under vigorous stirring at 28 °C for 2 h. Dilute ammonia solution was then added drop-wise into the mixture to hydrolyze the TTIP and form a uniform TiO\textsubscript{2} coating on the surface of the MWCNTs. The sample was centrifuged and rinsed with ethanol, oven-dried at 80 °C, and then calcined at 450 °C for 2 h. A schematic representation of the preparation of the TiO\textsubscript{2}-coated MWCNTs is shown in Fig. 1.

2.4. Characterization

X-ray diffraction (XRD) was used to study the crystal structure and degree of crystallinity of MWCNTs/TiO\textsubscript{2}. The XRD was performed at 40 kV and 30 mA at a scanning rate of 0.01°/s from 10° to 80° with Cu K\textsubscript{a} radiation (λ = 0.15406 nm) on a Bruker AXS D8 Advance diffractometer. The morphology and particle size were determined by field emission scanning electron microscopy (FESEM) using a Quanta FEG 450 operated at 5.00 kV and high vacuum with a magnification of 100 000. Determination of the Brunauer-Emmett-Teller (BET) specific surface area, S\textsubscript{BET}, of the samples was performed on a Micromeritics ASAP 2010 sorptometer with N\textsubscript{2} adsorption-desorption isotherm measurements at –196 °C. The required 1.0 g of sample was degassed at 200 °C. Raman spectroscopy (Renishaw inVia) with a 514.5 nm Ar\textsuperscript{+} laser as an excitation source was used to confirm the graphic structure of the carbon bond and analyze defects.

2.5. Photocatalytic activity of MWCNTs/TiO\textsubscript{2} nanocomposites

The photocatalytic degradation of Reactive Black 5 over the obtained nanocomposites was evaluated under ultraviolet (UV) light irradiation using a UV lamp (96 W). Typically, 0.05 g of the MWCNTs/TiO\textsubscript{2} photocatalyst was added to 100 mL of Reactive Black 5 solution (15 mg/L). Initially, the mixture was ultrasonicated in a water bath for 10 min to ensure good dispersion of the photocatalyst. The suspension was then stirred in dark-
ness for 30 min to reach adsorption equilibrium before the UV lamp was switched on to initialize the photodegradation of the Reactive Black 5. Part of the reaction solution was collected at certain time intervals and centrifuged to separate the photocatalyst, and the concentration of Reactive Black 5 in the supernatant was then determined by UV-vis spectrophotometry.

3. Results and discussion

3.1. Morphology and elemental analysis results

The surface morphologies of the functionalized MWCNTs, pure TiO2 nanoparticles, and MWCNTs/TiO2 nanocomposites were examined using FESEM. From Fig. 2(a), it can be observed that the functionalized MWCNTs were intertwined with each other. The individual MWCNTs exhibited a tubular-like structure with an average diameter of 20 nm [18]. The sol-gel synthesized pure TiO2 nanoparticles had an almost spherical shape with an individual diameter of 10–20 nm (Fig. 2(b)). From Fig. 2(c), the TiO2 nanoparticles were found to be homogenously deposited on the MWCNTs but showed some agglomeration along the MWCNTs [19, 20].

HRTEM images of the pure TiO2 (Fig. 3(a)) revealed an almost spherical shape with an average particle size of 10–20 nm. The distance between the adjacent lattice fringes was measured and found to match the d-spacing of the TiO2 lattice plane in the XRD results. The TiO2 nanoparticles showed a lattice spacing of d = 0.35 nm, corresponding to the (101) plane of anatase TiO2, in both the pure TiO2 and MWCNTs/TiO2 composites [21,22].

Quantitative elemental analysis of the functionalized MWCNTs, TiO2, and MWCNTs/TiO2 nanocomposites was carried out by FESEM-EDX, and the percentage of each element detected is presented in Table 1. For functionalized MWCNTs, only the presence of C and O elements and no other trace impurities were found. The highest mass percent of Ti and O was observed for the pure TiO2 nanoparticles. For the MWCNTs/TiO2 nanocomposites, Ti and O were present as the major elements with a minor amount of C element [11,20].

3.2. Phase structure and BET surface area analysis results

The XRD patterns of MWCNTs, TiO2 nanoparticles, and MWCNTs/TiO2 nanocomposites are shown in Fig. 4. For the MWCNTs sample, the diffraction peaks observed at 2Θ = 25.9° and 43.2° correspond with the (002) and (100) diffractions of the hexagonal graphite structure [23]. The sharp crystalline peaks at 2Θ = 25.2°, 37.8°, 47.9°, 54.0°, and 62.6° observed for the nanoparticles were assigned to the (101), (004), (200), (105), (211), and (204) planes, respectively, of pure anatase phase tetragonal TiO2 (JCPDS 21-1272) [24,25]. In the TiO2/MWCNTs composites, the peaks of anatase TiO2 were still observable after incorporation with the MWCNTs. The graphite

![Fig. 2. FESEM images of (a) MWCNTs, (b) TiO2, and (c) MWCNTs/TiO2 nanocomposites.](image)

![Fig. 3. HRTEM images of (a) TiO2 and (b) MWCNTs/TiO2.](image)

![Fig. 4. XRD patterns of (1) MWCNTs, (2) TiO2, and (3) MWCNTs/TiO2.](image)
peak at $2\theta = 25.9^\circ$ could not be seen in the pattern of the MWCNTs/TiO$_2$ nanocomposites owing to overlapping by the strong anatase TiO$_2$ peak at $2\theta = 25.2^\circ$. The higher intensity of the TiO$_2$ peaks caused by the higher crystallinity of the TiO$_2$ nanoparticles compared with that of the MWCNTs shielded the peaks of the MWCNTs [11,14]. However, the presence of MWCNTs in the composites was further confirmed by Raman analysis as discussed later.

Table 2 presents the crystallite size, BET surface area, and pore volume of the MWCNTs, TiO$_2$ nanoparticles, and MWCNTs/TiO$_2$ nanocomposites. A correlation between crystallite size and surface area was observed; the smaller the crystallite size, the larger the surface area. The crystallite size of the samples was calculated by the well-known Scherrer’s equation: $D = \frac{0.9}{\beta \cos \theta}$, where $D$ is the crystallite particle size, $k$ is a constant of 0.9, $\lambda$ is the wavelength (nm) of the X-rays used, $\beta$ is the FWHM, and $\theta$ is the Bragg angle [26].

The nitrogen sorption measurements revealed the surface area and porosity of the MWCNTs, TiO$_2$ nanoparticles, and MWCNTs/TiO$_2$ nanocomposites. As shown in Table 2, the incorporation of TiO$_2$ nanoparticles on the surface of the MWCNTs caused an increase in the $S_{\text{BET}}$ and the pore volumes compared with those of the pure TiO$_2$ nanoparticles, which may lead to an increase in pollutant adsorption capability. Thus, MWCNTs may act as both a support and strong adsorbent for enhancing the photocatalytic performance of TiO$_2$ materials by enhancing their surface properties [11,13].

### 3.3. Raman spectroscopic analysis results

The Raman spectra of the functionalized MWCNTs, TiO$_2$, and MWCNTs/TiO$_2$ nanocomposites are shown in Fig. 5. For the functionalized MWCNTs, two typical peaks were observed at around 1314.95 and 1593.54 cm$^{-1}$. The band at 1314.95 cm$^{-1}$ is the D-band, which is attributed to $sp^3$ defects in carbon [27,28], while the band at 1593.54 cm$^{-1}$ is the G-band, which corresponds to $sp^2$ carbon defects. The Raman spectrum of the TiO$_2$ nanoparticles shows four main peaks (141.85, 396.53, 517.12, and 641.86 cm$^{-1}$) assignable to the $E_{g(1)}$, $B_{2g(1)}$, $A_{1g}$ and $E_{g(2)}$ modes, respectively, of anatase. Although the XRD analysis of the MWCNTs/TiO$_2$ nanocomposites only reflected the presence of pure anatase TiO$_2$, the Raman results confirmed the presence of MWCNTs in the composite. While both the main peaks of anatase and MWCNTs appeared in the Raman spectrum, the peaks were slightly broadened because of interfacial integration between the TiO$_2$ and MWCNTs [13,29].

### 3.4. Optical properties

The optical properties of the TiO$_2$ and MWCNTs/TiO$_2$ nanocomposites were determined using UV-vis spectroscopy. As shown in Fig. 6(a), the absorption edges of MWCNTs/TiO$_2$ were red shifted towards a higher wavelength, which suggested a narrowing of the band gap caused by the introduction of MWCNTs. In addition, a typical absorption with an intense transition in the UV region was observed in the spectra of both samples, assignable to the intrinsic band-gap absorption of TiO$_2$. 

![Fig. 5. Raman spectra of (a) MWCNTs, (b) TiO$_2$, and (c) MWCNTs/TiO$_2$ nanocomposites.](image)

![Fig. 6. (a) UV-Vis diffuse reflectance spectra and (b) variation of ($\alpha h\nu$)$^2$ versus photon energy ($h\nu$) of (1) MWCNTs/TiO$_2$ and (2) TiO$_2$.](image)
for electron transition from the valence band into the conduction band \((O_2 p \rightarrow Ti_3 d)\) [21,30].

The optical band gap of the TiO\(_2\) and MWCNTs/TiO\(_2\) nanocomposites was determined using the Kubelka-Munk expression via the transformation of their diffuse reflectance spectra (Fig. 6(b)) according to the equation \([F(R)hv]^{1/2} = A(hv - E_g)\), where \(F(R)\), \(h\), \(E_g\), \(v\), and \(A\) are the Kubelka-Munk function, Planck’s constant, the band gap, and a constant, respectively. The estimated band gaps of TiO\(_2\) and MWCNTs/TiO\(_2\) were 3.23 and 3.02 eV, respectively, which are in accordance with the qualitative observation of a blue shift in the absorption edge of the TiO\(_2\) nanoparticles compared with that of the MWCNTs/TiO\(_2\) nanocomposite [23,31].

3.5. Thermal behavior

The thermal stability and oxidative mass loss conditions of MWCNTs and MWCNTs/TiO\(_2\) were determined via thermogravimetric analysis (TGA) (Fig. 7). The combustion point of the functionalized MWCNTs was found to be located at approximately 654 °C owing to the highest rate of mass loss, 86.8% (Fig. 7(a)). For the MWCNTs/TiO\(_2\) composites, the initial mass loss was caused by the evaporation of water at around 100 °C and was followed by the thermal decomposition of the MWCNTs at 637 °C. The total mass loss was determined to be 25.8%, indicating that TiO\(_2\) became the major component remaining after the combustion of the MWCNTs [7,11].

3.6. Photocatalytic activity

The schematic mechanism of the photocatalytic degradation of Reactive Black 5 over the MWCNTs/TiO\(_2\) nanocomposite is shown in Fig. 8. When the TiO\(_2\) photocatalyst is illuminated with photons having energy greater than the band-gap energy, the photons will excite electrons from the valence band of the TiO\(_2\) into the conduction band. The holes in the valence band will meet with \(OH^-\) and produce hydroxyl radicals. Therefore, the targeted pollutants adsorbed on the surface of the catalyst will be oxidized by \(^{•}OH\). However, the excited electron-hole pairs may instead recombine [6]. The MWCNTs act as a good electron acceptor and thereby facilitate the separation of the electron-hole pairs to prevent their recombination [15]. The more electrons that are transferred from the TiO\(_2\) to the MWCNTs, the better the retardation of electron-hole pair recombination [32,33].

The photocatalytic activity of pure TiO\(_2\) and MWCNTs/TiO\(_2\) was studied using the degradation of Reactive Black 5. In Fig. 9, \(C\) is the concentration of Reactive Black 5 after different light irradiation time, and \(C_0\) is the initial concentration of Reactive Black 5 before light irradiation. Reactive Black 5, which has a major absorption peak at 595 nm, is one of the most common organic pollutants in industrial wastewater. The fastest rate of Reactive Black 5 degradation was obtained during the first 15 min of irradiation, and the rate gradually decreased as time increased. The hybrid MWCNTs/TiO\(_2\) exhibited better performance for the photodegradation of Reactive Black 5 than the pure TiO\(_2\). This may be caused by the high surface area of the MWCNTs, which consist of multiple layers of graphite that can...
facilitate the separation of electron-hole pairs at TiO$_2$-CNT interfaces [26,6].

4. Conclusions

A simple sol-gel technique was used to synthesize MWCNTs/TiO$_2$ nanocomposites. A variety of techniques (FESEM, HRTEM, XRD, BET, Raman, TG-MS) were used to characterize the obtained materials, and the TiO$_2$/MWCNTs nanocatalyst was found to exhibit good physical, chemical, and optical properties that enhanced their activity for the photodegradation of Reactive Black 5 dye under UV light.

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References