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Abstract

Titanium dioxide/single-walled carbon nanotube TiO₂/SWNT composites were prepared for photocatalytic applications. The composites were characterized using UV-visible and Raman spectroscopy, zeta-potential measurements, cyclic voltammetry coupled with a photoreactor, scanning electron microscopy, and transmission electron microscopy coupled with energy dispersive X-ray spectroscopy. The photocatalytic activity of TiO₂ and the TiO₂/SWNT composite was investigated using the photo-oxidation of methanol in sulfuric acid as supporting electrolyte. The results indicate that the TiO₂/SWNT composite enhances the photocatalytic activity compared to TiO₂ alone. Electrochemical studies of the TiO₂/SWNT composite were also carried out in various supporting electrolytes and the presence of SWNTs was shown to increase the current achieved in voltammetric measurements.

Keywords

Photocatalytic, oxidation, methanol, using, titanium, dioxide, single, walled, carbon, nanotube, composite

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Photocatalytic Oxidation of Methanol Using Titanium Dioxide/Single-Walled Carbon Nanotube Composite

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Titanium dioxide/single-walled carbon nanotube (TiO₂/SWNT) composites were prepared for photocatalytic applications. The composites were characterized using UV-visible and Raman spectroscopy, zeta-potential measurements, cyclic voltammetry coupled with a photoreactor, scanning electron microscopy, and transmission electron microscopy coupled with energy dispersive X-ray spectroscopy. The photocatalytic activity of TiO₂ and the TiO₂/SWNT composite was investigated using the photo-oxidation of methanol in sulfuric acid as supporting electrolyte. The results indicate that the TiO₂/SWNT composite enhances the photocatalytic activity compared to TiO₂ alone. Electrochemical studies of the TiO₂/SWNT composite were also carried out in various supporting electrolytes and the presence of SWNTs was shown to increase the current achieved in voltammetric measurements. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2709498] All rights reserved.

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TiO₂ photocatalytic particles have been widely studied due to their application in the field of photocatalytic oxidation under UV illumination.¹⁻⁵ The properties of TiO₂ which make it useful in this application include its strong oxidizing power⁵⁻⁷ and its physical and chemical stability.^{7,8} The photocatalytic properties of TiO₂ can be generated with UV illumination due to the bandgap energy (3.2 eV) of anatase TiO₂.^{7,9} TiO₂ nanoparticles prepared by different methods have shown different photocatalytic efficiencies, due to variations in particle size, phase composition, surface area, pore volume, pore distribution, bandgap energy, crystallinity, and thermal stability.⁹⁻¹³

Due to their unique properties, including high surface area, high electrical conductivity, and significant mechanical strength,^{11,14,15} integrating carbon nanotubes with TiO₂ nanoparticles should result in changes in morphology and enhanced properties (in particular electrical conductivity) of TiO₂.^{15,16} Therefore, this study aims to elucidate the properties of TiO₂/single-walled carbon nanotube (SWNT) composites for the application of the degradation of an organic molecule.

In this paper, we present the preparation and characterization of a TiO₂/SWNT composite, and its preliminary study on methanol degradation in aqueous solution.

Materials.—TiO₂ nanoparticles with an average size of 20 nm were synthesized using the sol-gel technique according to Natda et al.¹⁷ Single-wall carbon nanotubes (Carbon Nanotechnologies, Inc., Houston), methanol (MeOH, Univar, Ajax), ethanol (EtOH, Univar, Ajax), sulfuric acid (H₂SO₄, Univar, Ajax), dichloromethane (DCM, Univar, Ajax), sodium nitrate (NaNO₃, Univar, Ajax), potassium ferrocyanide [K₄Fe(CN)₆, Univar, Ajax], sodium dodecyl sulfate (SDS, BDH chemical), 2,4-pentanedione (Aldrich), and acetone (Univar, Ajax) were used as received.

Indium-tin-oxide (ITO) coated glass was purchased from Delta Technologies Ltd. (USA). The ITO glass was washed with acetone overnight and treated in an ultraviolet ozone cleaner (model no. 42-220, Jelight Co. Inc., USA) for 30 min before use.

Experimental

Electrochemical testing of the TiO₂/SWNT composite electrode was performed by using an electrochemical hardware system comprising of an EG&G PAR 363 potentiostat/galvanostat, a Bioanalytical System CV27 Voltammograph, and a MacLab 400 with Chart v. 3.5.7/EChem v. 1.3.2 software (AD Instruments). All electrochemical experiments were performed at room temperature in a three-electrode cell. The modified ITO glass was used as the working

electrode coated with TiO₂, SWNTs, or the TiO₂/SWNT composite via screen printing. An Ag/AgCl electrode and cleaned platinum mesh were used as the reference and the auxiliary electrode, respectively.

The photocatalytic activity was investigated in a commercial photochemical reactor (Rayonet, Southern New England Ultraviolet Company, USA). Irradiations were carried out with ultraviolet lamps, RPR-3000 Å lamps (Branford, USA) and RPR-3500 Å lamps (Branford, USA) with the light intensity set at about 10 W m⁻² monitored using a LI-250 light meter (Model Pyranometer, LI-COR, Biosciences, USA).

UV-visible spectra of the samples were examined over the range of 300–1100 nm (Shimadzu UV1601 spectrophotometer). The zeta-potential of all dispersions was measured using a Zetasizer Nano 3600 (Malvern Instruments). The surface morphology of the composite was studied with scanning electron microscopy (SEM) using a LeicaStereo SS440 microscope. Transmission electron microscopy (TEM) analysis was performed using a Philips CM200 microscope (200 kV), equipped with energy dispersive X-ray spectroscopy (EDX, EDaX DX-4 EDX system) with 30 mm² active area (Detector Crystal).

Photoanode fabrication.—A TiO₂ paste was prepared by adding 0.25 mL 2,4-pentanedione (10 wt % in H₂O) and 1 mL deionized water to 3 g TiO₂ and the mixture was ground in a mortar for 15 min. This was repeated three times while adding 0.25 mL 2,4-pentanedione (10 wt % in H₂O) and 1 mL deionized water each time. 5 μL Triton X-100 was added into the paste to enhance film formation and ground for a further 5 min. The TiO₂ paste was screen printed onto a clean ITO substrate, followed by annealing at 150° and 450°C for 1 h at each temperature. The thickness of the resulting material was approximately 1.5 μm.

The TiO₂/SWNT composite was prepared by mixing 50 mg TiO₂ powder with 0.4 mg SWNTs and 40 mg of an aqueous SDS solution (1% w/v), in 10 mL ethanol and sonicating (Branson Digital Sonifier) for 1 h (sonication pulse; on 2 s, off 1 s, with amplitude of 30%). The composite powder was obtained via centrifugation, and then dried in the oven at 200°C for 1 h. The preparation of the composite paste used the same protocol as described for the TiO₂ paste, and the paste was screen printed onto an ITO substrate and annealed in the same way as the TiO₂ paste. The thickness of the resulting material is approximately 12 μm.

Results and Discussion

Characterization of TiO₂/SWNT composite.—The UV-visible spectra of TiO₂, SWNTs, and TiO₂/SWNT films are shown in Fig. 1. The absorbance of TiO₂ occurred below 350 nm, whereas the broad absorption peaks for SWNTs were observed between 450–1000 nm.

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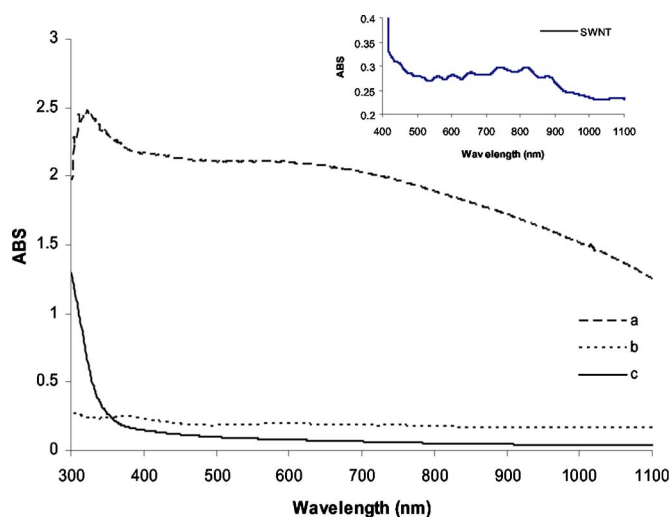


Figure 1. UV-visible spectra of (a) TiO₂/SWNT (12 μm) (b) SWNT (1.0 μm), and (c) TiO₂ (1.5 μm) films on ITO glass.

In the spectrum of the TiO₂/SWNT composite, the presence of the TiO₂ band below 400 nm was observed, as well as a broad spectrum between 450–1000 nm from the SWNTs.

Zeta-potential measurements were used to identify the stability and charge of the dispersions used (Table I). The TiO₂ was found to be positively charged with a value greater than +30 mV, which indicates a stable suspension. The SWNT/SDS dispersion was observed to be negatively charged due to the anionic surfactant SDS and the functional groups (COOH) on SWNTs obtained during the manufacturer's purification (CNI). An overall positive charge was measured for the TiO₂/SWNT composite, however with a value (<+30 mV) which indicates a less stable dispersion than that of the TiO₂ alone. The reduction of repulsive (positive) charges of TiO₂ by the negatively charged SWNTs/SDS may be responsible for this decrease in zeta-potential.

The Raman spectra of each film are shown in Fig. 2. Three characteristic peaks were observed at 411, 527, and 650 cm⁻¹ for TiO₂ (Fig. 2a). This indicates that the TiO₂ sample contained mainly the anatase phase of TiO₂.^{2,18,19} The Raman spectrum of the TiO₂/SWNT composite showed both the anatase phase peaks of TiO₂ and the D, G, and RBM bands of the SWNTs²⁰ (Fig. 2b). A shift of the D and G bands of SWNTs was observed for the TiO₂/SWNT composite. The D band of the SWNTs and TiO₂/SWNTs was observed at 1320 and 1324 cm⁻¹, respectively, while the G band of SWNTs and TiO₂/SWNTs shifted from 1598 to 1602 cm⁻¹, respectively. This is attributed to the interaction between TiO₂ and the SWNTs, which is desirable for its photocatalytic applications.

The surface morphology of TiO₂ and TiO₂/SWNTs was studied using SEM. Figure 3a shows the morphology of a single layer TiO₂ film after annealing at 150° and 450°C. The film obtained is uniform and porous. Figure 3b shows the morphology of the TiO₂/SWNT composite film, while Fig. 3c displays a bundle of SWNTs connects

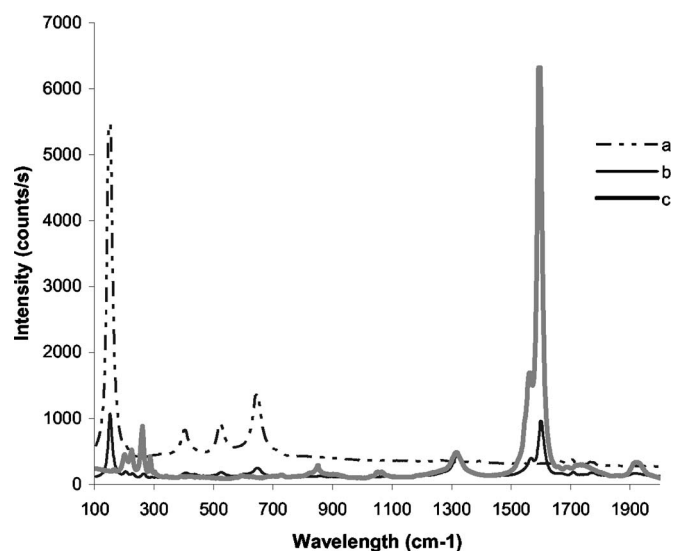


Figure 2. Raman spectra of films of (a) TiO₂, (b) TiO₂/SWNTs, and (c) SWNTs.

two different parts of the composite film. It can be seen that the aggregation of TiO₂ increases with the addition of SWNTs. The increased aggregation of TiO₂ in the presence of SWNTs may be due to the reduction of repulsive (positive) charges of TiO₂ by the negatively charged SWNTs/SDS as evidenced by zeta-potential measurements (Table I). It can also be seen that the surface of the composite film is porous and uniform.

The TiO₂/SWNT composite was also studied using TEM and EDX (Fig. 4a and b). The average size of the TiO₂ nanoparticles was approximately 20 nm. TEM imaging of the composite showed that it contains some large aggregated TiO₂ particles, which is consistent with the aggregation observed in SEM images (Fig. 3). TEM images also showed aligned carbon nanotube bundles with TiO₂ particles along the tubes. The EDX analysis shows that, at the analysis point, it contains the elements of Ti (from TiO₂) and Cu (due to the copper grid). This confirms that the (20 nm) particles attached to the SWNT bundles are TiO₂.

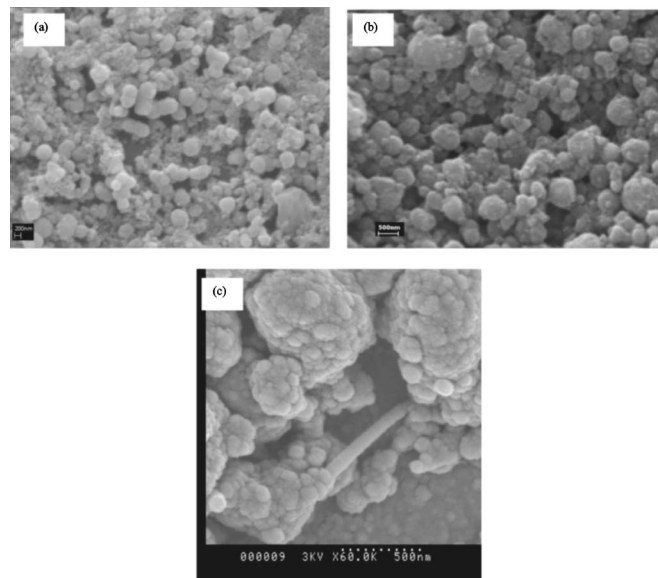


Figure 3. SEM images of (a) TiO₂ and (b) TiO₂/SWNT films after annealing at 150° and 450°C.

Table I. Zeta-potential analysis of TiO₂/SWNTs, SWNTs, and TiO₂ particles.

Samples	Temperature (°C)	Zeta potential (mV)	Mobility (μmcm/Vs)	Conductivity (mS/cm)
TiO ₂	25	34.28	2.703	37.4
SWNTs	25	-15.49	-1.221	0.116
TiO ₂ /SWNTs	25	8.71	0.6867	34.91

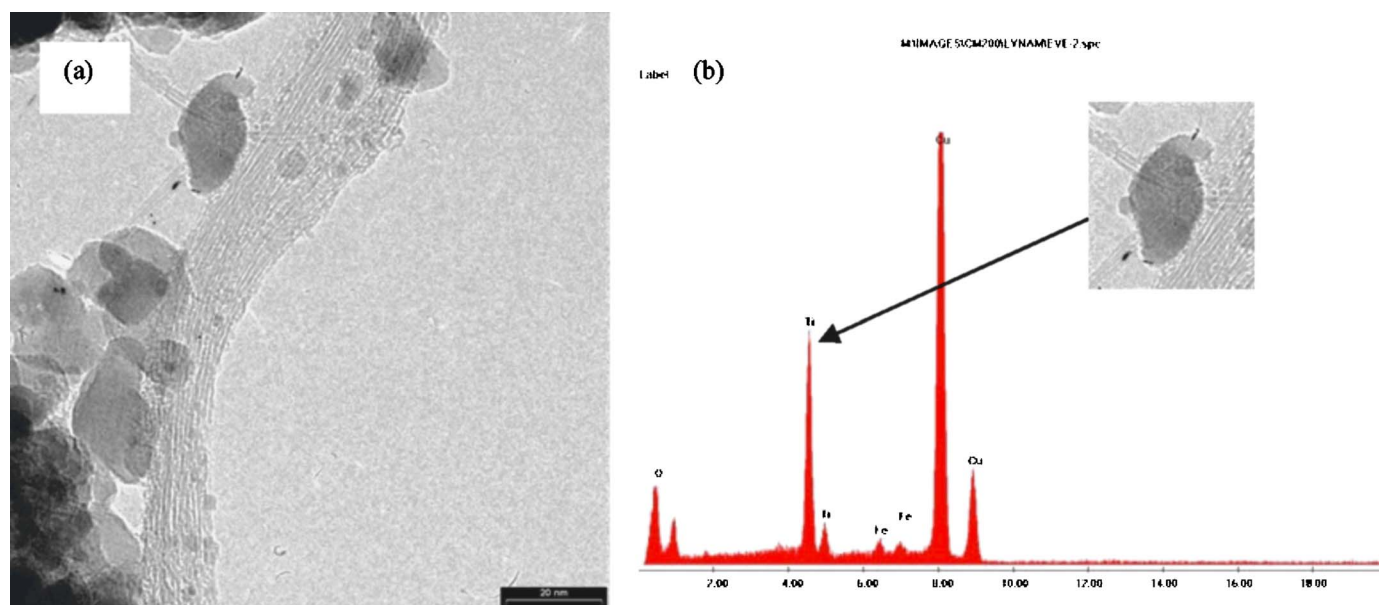


Figure 4. (Color online) (a) TEM image and (b) EDS spectrum of TiO₂/SWNTs.

Photoelectrochemical study.—Cyclic voltammetry.— In the following experiments, TiO₂ and TiO₂/SWNT film electrodes were annealed at 150° and 450°C for 1 h at each temperature before transfer into the appropriate electrolyte. To eliminate bubble formation due to dissolved oxygen in the aqueous electrolyte in all experiments, the solutions were purged with N₂ for 30 min before use in the photoreactor. Electrochemical analysis of TiO₂, SWNTs, and the TiO₂/SWNT composite film (containing equivalent masses of TiO₂ and SWNTs) on ITO glass substrates was performed in 0.1 M NaNO₃/0.01 M K₄Fe(CN)₆ (Fig. 5). The TiO₂/SWNT composites showed the highest current when compared with TiO₂ and SWNTs alone under identical conditions (equivalent testing area and material mass). This suggests that the addition of SWNTs to TiO₂ enhances the interaction not only among TiO₂ particles, but also between the TiO₂ and the ITO substrate.

Figures 6a and b show cyclic voltammograms (CVs) obtained from TiO₂ and the TiO₂/SWNT composite in 1.0 M NaNO₃ with and without UV illumination, respectively. A lower current was observed from both TiO₂ [Fig. 6a (2)] and TiO₂/SWNTs [Fig. 6b (2')] without UV illumination, whereas a much higher photocurrent was

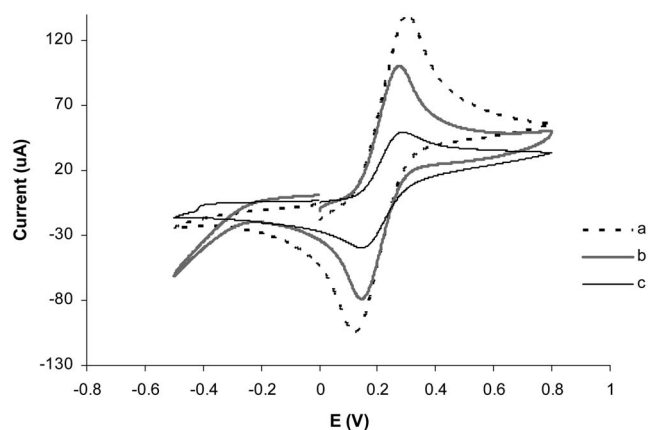


Figure 5. CVs of (a) TiO₂/SWNT, (b) SWNT, and (c) TiO₂ coated ITO electrode after annealing at 150° and 450°C. Supporting electrolyte: (0.1 M) NaNO₃/(0.01 M)K₄Fe(CN)₆. Scan rate: 50 mV s⁻¹.

observed under illumination. This shows that the TiO₂ is photoactive, and the addition of SWNTs improves its photoactivity possibly due to the enhancement of the electrical interaction between TiO₂ particles. Figure 6c compares the CVs obtained from all electrodes under UV-illumination. The TiO₂/SWNT composite displayed a photocurrent response of 268 μA/mg (at 0 V) and 350 μA/mg (at 0.2 V), which are five and six times higher than that of TiO₂ electrode, respectively. The photocurrent data obtained from SWNTs showed no difference in signal with and without UV illumination (data not shown).

Amperometry.— Further investigations were carried out using amperometry (at +0.8 V) to monitor the current in the dark and under UV illumination. The cell compartment contained an aqueous solution of 1.0 M NaNO₃. After a constant base line was obtained (in the dark) the working electrode was illuminated with UV light and the photocurrent was recorded. Typical results are shown in Fig. 7. The presence of SWNTs in the TiO₂ film shows an increase in photocurrent response of 48 μA/mg under UV illumination, which is approximately six times of that of the pure TiO₂ film. The increased photocurrent clearly indicates the beneficial effect of SWNTs on the electrochemical properties of the TiO₂. This experiment was done with the same testing area for TiO₂ and TiO₂/SWNTs.

Photocatalytic methanol oxidation.— The response of cyclic voltammetric and amperometric techniques was investigated and the mass of the electrodes was recorded. In the following experiments, a 1.0 M H₂SO₄ solution was used as electrolyte. For methanol degradation experiments, the electrolyte (1.0 M H₂SO₄ in water) contained 1.0 M methanol. Amperometry (at 0.8 V) was used to monitor the current response of TiO₂ and the TiO₂/SWNT composite film with UV illumination in the presence and absence of 1.0 M methanol (Fig. 8). When the potential was applied in the dark, a constant base line was observed for each electrode around zero μA. A stable photocurrent density of about 15 μA/mg Fig. 8a and 35 μA/mg Fig. 8b was obtained from TiO₂ in the electrolyte without and with methanol, respectively. This was done to elucidate what influence TiO₂ has on the photocatalytic degradation. The photocatalytic degradation of methanol by the TiO₂/SWNT film led to a higher photocurrent output under UV illumination than the TiO₂ only electrode. As in Fig. 8, constant photocurrents were observed at 336 μA/mg for TiO₂/SWNTs in methanol/H₂SO₄ electrolyte Fig. 8d and the TiO₂/SWNT composite displayed a photocurrent response

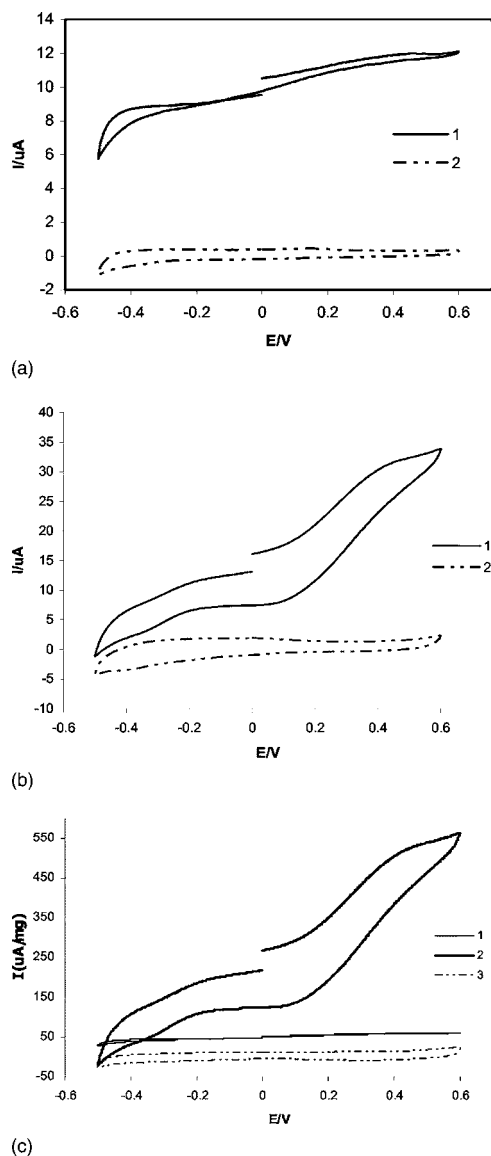


Figure 6. CVs of (1) illuminated and (2) nonilluminated TiO_2 coated ITO electrode after annealing at 150° and 450°C . Supporting electrolyte: 1 M NaNO_3 . Scan rate: 50 mV s^{-1} . (b) CVs of (1') illuminated and (2') nonilluminated TiO_2/SWNT coated ITO electrode after annealing at 150° and 450°C . Supporting electrolyte: 1 M NaNO_3 . Scan rate: 50 mV s^{-1} . (c) CVs of UV-illuminated (1) TiO_2 , (2) TiO_2/SWNT , and (3) SWNT coated ITO electrode after annealing at 150° and 450°C . Supporting electrolyte: 1 M NaNO_3 . Scan rate 50 mV s^{-1} .

which is about 10 times higher than TiO_2 only electrode, indicating that the presence of SWNTs with TiO_2 electrode significantly improves its photocatalytic activity for methanol degradation. This again suggests that the addition of SWNTs into TiO_2 has built up and enhanced the interaction not only among TiO_2 particles but also between TiO_2 particles and substrates.

Conclusion

In this report, we successfully prepared and characterized a TiO_2/SWNT nanocomposite with improved photocatalytic properties under UV illumination. The presence of SWNTs in the TiO_2 film was found to be able to photocatalyze the oxidation of methanol, 10 times higher than a pure TiO_2 electrode. This is an attractive way for further application in the field of photocatalytic decompo-

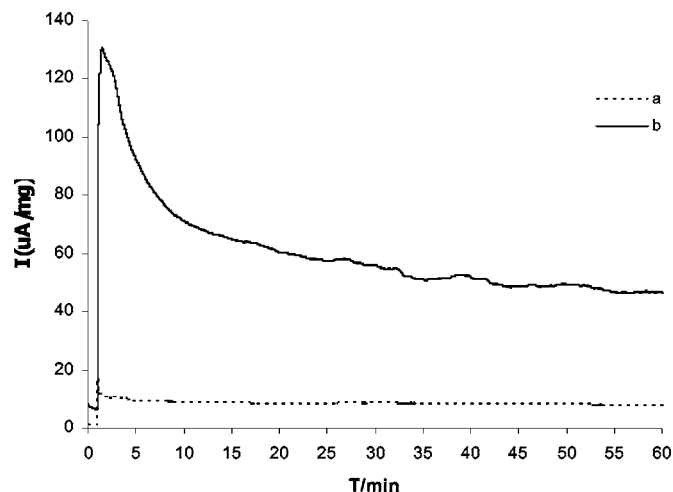


Figure 7. Amperogram of (a) TiO_2 and (b) TiO_2/SWNT films on ITO electrodes under UV illumination (300 and 350 nm lamps) after annealing at 150° and 450°C . Supporting electrolyte: 1 M NaNO_3 . Potential: 0.8 V.

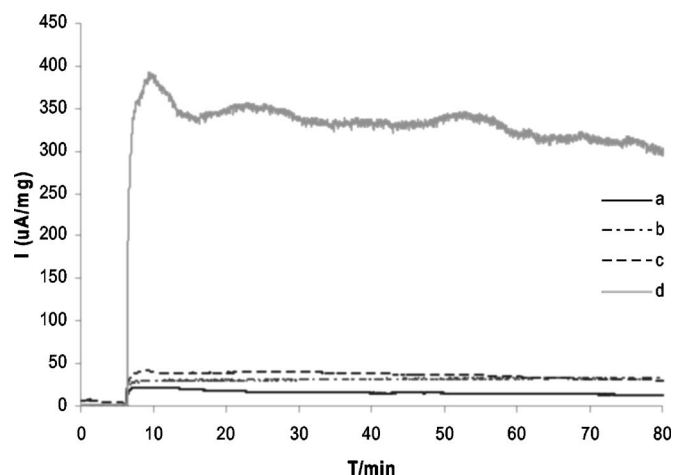


Figure 8. Amperogram of (a) TiO_2 in H_2SO_4 , (b) TiO_2 in $\text{H}_2\text{SO}_4\text{-MeOH}$, (c) TiO_2/SWNT in H_2SO_4 , and (d) TiO_2/SWNT in $\text{H}_2\text{SO}_4\text{-MeOH}$ coated ITO electrode after annealing at 150° and 450°C . Applied constant potential: $+0.8 \text{ V}$.

sition of organic compound in aqueous media under UV irradiation, and a potential material for applications involving photocatalyzed fuel cells.

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