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Photocatalytic activity of TiO_2 supported on multi-walled carbon nanotubes under simulated solar irradiation

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Abstract

TiO_2 particles supported on multi-walled carbon nanotubes (MWCNTs) were prepared using a sol–gel method to investigate their photocatalytic activity under simulated solar irradiation for the degradation of methyl orange (MO) in aqueous solution. The prepared composites were analyzed using XRD, SEM, EDS and UV–vis absorption spectroscopy. The results of this study indicated that there was little difference in the shape and structure of MWCNTs/TiO_2 composite and pure TiO_2 particles. The composite exhibited enhanced absorption properties in the visible light range compared to pure TiO_2. The degradation of MO by MWCNTs/TiO_2 composite photocatalysts was investigated under irradiation with simulated solar light. The results of this study indicated that MWCNTs played a significant role in improving photocatalytic performance. Different amounts of MWCNTs had different effects on photodegradation efficiency, and the most efficient MO photodegradation was observed for a 2% MWCNT/TiO_2 mass ratio. Photocatalytic reaction kinetics were described using the Langmuir–Hinshelwood (L–H) model. The photocatalyst was reused for eight cycles, and it retained over 95.2% photocatalytic degradation efficiency. Possible decomposition mechanisms were also discussed. The results of this study indicated that photocatalytic reactions with TiO_2 particles supported on MWCNTs under simulated solar light irradiation are feasible and effective for degrading organic dye pollutants.

Keywords: A. Sol-gel processes; B. Nanocomposites; D.TiO_2; MWCNTs; E. Photocatalysis

1. Introduction

Direct photocatalytic reactions using semiconductor particles as photocatalysts have recently attracted considerable attention as a promising method to degrade organic pollutants [1]. Among the various semiconductors, titanium dioxide (TiO_2) is one of the most widely used photocatalysts because of its exceptional optical and electronic properties, strong oxidizing power, non-toxicity, chemical stability and low-cost. However, the primary drawback of TiO_2 is its relatively large band gap (anatase: 3.2 eV, rutile: 3.0 eV). Consequently, TiO_2 only exhibits photocatalytic activity in the near ultraviolet region [2], which substantially limits the use of TiO_2 as a catalyst for photoreactions in the presence of sunlight. The band gap of TiO_2 hinders the commercialization of TiO_2 photocatalysts because only approximately 3–4% of solar light is in the UV range [3,4]. Therefore, considerable effort has been made to modify TiO_2 to enhance its photocatalytic activity in the visible region of the spectrum [5].

Multi-walled carbon nanotubes (MWCNTs) have attracted attention because they exhibit good adsorption characteristics, high chemical stability, and unique thermal, optical, and electronic properties [6–9]. The addition of MWCNTs is expected to improve TiO_2 photocatalytic activity. Some authors have reported that MWCNTs increased adsorption and photocatalytic activity of TiO_2 in the UV range [1,6,8]. Although several studies have focused on preparation of carbon nanotube/TiO_2 composites [10–12], relatively few studies have examined photocatalytic properties of MWCNT/TiO_2 composite photocatalysts in solar light, particularly the influence of amount of MWCNTs on composite photocatalysts.

Methyl orange (MO) is a representative dye compound. The molecular structure of MO contains benzene rings, which strongly inhibit biodegradation. It is very difficult to degrade MO molecules into smaller organic molecules using common

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methods [3,13]. Recent studies have focused on using semiconductor particles to photocatalyze MO degradation [14].

In this paper, the preparation of MWCNT–TiO_2 composites by a sol–gel method is reported. The objective of this study was to evaluate photocatalytic activity of these new photocatalysts under simulated solar light irradiation using MO as a model pollutant. The results from this study can provide fundamental information about treatment and purification of practical industrial effluents.

2. Methods and materials

2.1. Materials

Methyl orange (MO, $C_{14}H_{14}O_3N_3SNa$, molecular weight = 327.35 g mol^{-1}, analytical grade) was purchased from the XiLong Fine Chemical Reagent Co. Ltd., Shantou, China. Tetrabutyl titanate ($Ti(OC_4H_9)_4$, analytical grade) was obtained from the YongDa Chemical Regent Co. Ltd., Tianjin, China. Raw MWCNTs were purchased from the Shenzhen Nanotech Port Co., Shenzhen, China. Chloroform and the other analytical grade reagents, including nitric acid, hydrochloric acid, sodium hydroxide, anhydrous ethanol, and acetic acid, were obtained from the Tianjin DaMao Chemical Reagent Co. Ltd., Tianjin, China. Deionized water was used to prepare photocatalysts. Reagents were used as received without further purification. Solution pH values were adjusted with 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl.

2.2. Preparation and characterization of MWCNT/TiO_2 composites

A modified sol–gel method from Wang et al. [1] was used to prepare TiO_2 and MWCNT/TiO_2 composite photocatalysts. A typical synthesis procedure was as follows: MWCNTs were pretreated with 69% nitric acid and introduced into a flask that contained 10 mL of $Ti(OC_4H_9)_4$, 30 mL of ethanol, and 3 mL of anhydrous acetic acid. This mixture was stirred magnetically for 2 h. Then, another solution of 20 mL of anhydrous ethanol, 4 mL of deionized water, and 2 mL of nitric acid was added dropwise. After 6 h of stirring, this colloidal solution formed a sol. The sol was stored at ambient temperature for 24 h, and the solvent was then evaporated at 80 °C for at least 24 h. The resulting solids were crystallized at 500 °C under N_2 for 2 h to obtain a MWCNT/TiO_2 composite. For comparison, TiO_2 materials were prepared using similar procedures.

2.3. Characterization of photocatalysts

The UV–visible absorption was measured using a spectrophotometer (Helios Alpha, UK). An X'Pert PRO advance diffractometer (Panalytical Netherlands) was used to obtain XRD patterns. A Nova Nano SEM-430 (FEI Inc.) electron microscope, which was equipped with an energy dispersive analysis system (EDS), was used for SEM-EDS studies.

2.4. Photocatalytic activity

To simulate sunlight, a 300 W Xe arc lamp (BL-GHX-V, Xi'an Depai Biotech. Co. Ltd., Xi'an, China) was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket to cool the lamp. Various amounts of TiO_2 or MWCNT/TiO_2 particles were added to 150 mL of aqueous solutions of MO at various concentrations. Each suspension was stirred for 30 min without illumination to reach the adsorption–desorption equilibrium of MO on the catalyst surface and then irradiated with the Xe lamp [15]. Samples were removed at 10 min intervals, and aliquots (3 mL) were centrifuged and separated. The concentration of MO in the supernatant was determined using a UV–vis spectrophotometer at 464 nm.

Photocatalytic reactions on TiO_2 surfaces were described using the Langmuir–Hinshelwood model. Degradation experiments performed with simulated solar irradiation of aqueous MO solutions followed pseudo-first-order kinetics [16,17]:

$$lnC_0/C_t = kt \qquad (1)$$

where C_0 is the initial concentration of MO after adsorption without illumination, C_t is the concentration of MO at time t, and k denotes the apparent pseudo-first-order rate constant. According to Eq. (1), a plot of $\ln(C_0/C_t)$ versus time (t) has a slope equal to k.

3. Results and discussion

3.1. XRD analysis

The XRD patterns for TiO_2 and MWCNT/TiO_2 composites are presented in Fig. 1. As shown in curve a, diffraction peaks at (2θ) values of 25.4°, 37.9°, 48.1° and 56.2° can be indexed to the anatase phase of TiO_2, and diffraction peaks at (2θ) values of 27.4°, 36.1°, 41.4° and 54.4° can be indexed to the rutile phase of TiO_2 [1,13], which confirms that this TiO_2 was a mixture of anatase and rutile forms. As reported in many other studies, the anatase phase begins to transform into a rutile structure at temperatures greater than 500 °C [2,13].

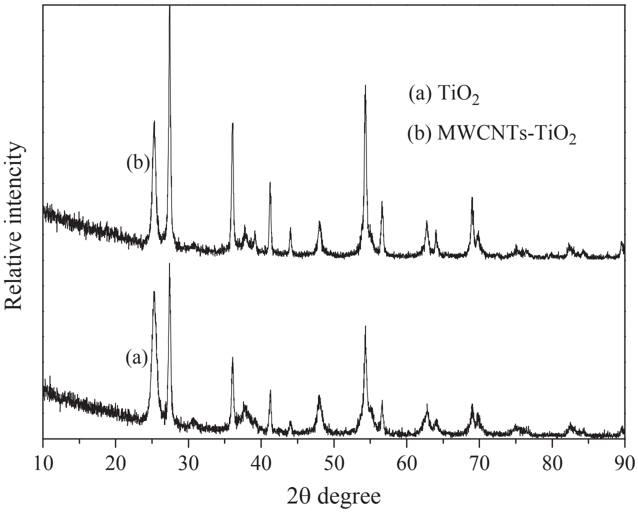

Fig. 1. XRD patterns for (a) TiO_2 and (b) MWCNT/TiO_2.

There is a little difference between curves (a) and (b) in terms of shapes and positions of diffraction peaks. For MWCNT/TiO_2 samples, the carbon peak was not detected due to its trivial amount of addition. Similar results were observed in XRD patterns for TiO_2 and MWCNT/TiO_2 composites, which indicated that introduction of MWCNTs did not influence TiO_2 phase transitions.

3.2. SEM

Surface morphologies of pure TiO_2, MWCNTs and MWCNT/TiO_2 composite nanoparticles are shown in Fig. 2. Irregular spherical nanoparticles of TiO_2 appear to be agglomerated. For MWCNT/TiO_2 composites, MWCNT surfaces were coated with TiO_2 particles.

3.3. UV–vis analysis

The UV–vis absorption spectra of pure TiO_2 and MWCNT/TiO_2 composites are shown in Fig. 3. Pure TiO_2 exhibited a clear absorption peak in its UV spectrum. As reported in many other studies [18–21], TiO_2 cannot absorb visible light because it has a wide band gap (3.0–3.2 eV). For MWCNT/TiO_2 composites, the optical absorption spectrum extended to wavelengths greater than 400 nm in the visible part of the spectrum. Enhanced absorption by MWCNT/TiO_2 composite particles between 400 and 800 nm was attributed to MWCNTs. Improvements in absorption efficiency of visible light by MWCNT-modified TiO_2 particles meant that these composite particles could excite more photogenerated electrons than pure TiO_2 under visible light irradiation. Therefore, observations of absorption properties in this study implied that composite materials had greater photocatalytic activity than unmodified TiO_2 [22–24].

3.4. Photocatalytic activity

Photocatalytic activity of TiO_2 and MWCNT/TiO_2 composites was investigated through MO photodegradation. These results for MO photodegradation are presented in Fig. 4. In every experiment, concentrations of MO and catalyst were 15 mg/l and 1.0 g/l, respectively. As shown in curve d, no MO degradation was observed without irradiation and catalyst. Under direct photolysis conditions (curve c), approximately 32.0% of MO degraded after 90 min of simulated solar irradiation in the absence of catalyst. For pure TiO_2 conditions (curve b), the MO degradation rate catalyzed by pure TiO_2 particles under 90 min of simulated solar irradiation was 73.4%. However, MWCNT/TiO_2 composite catalysts achieved almost 97.4% MO removal efficiency (curve a). In the presence of composite photocatalysts, the MO removal rate

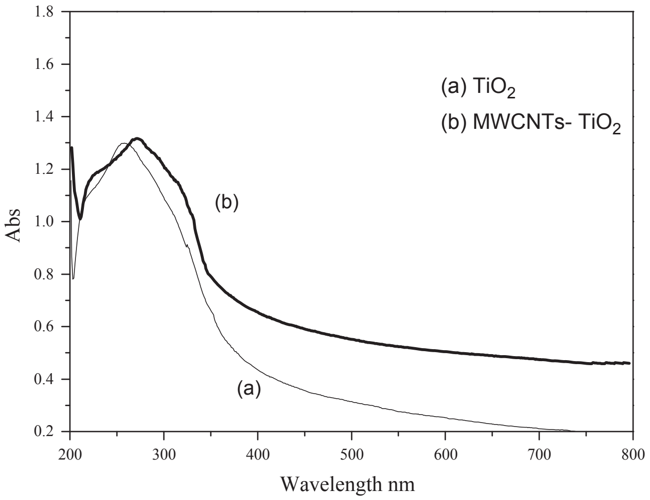

Fig. 3. UV–vis spectra for (a) TiO_2 and (b) MWCNT/TiO_2.

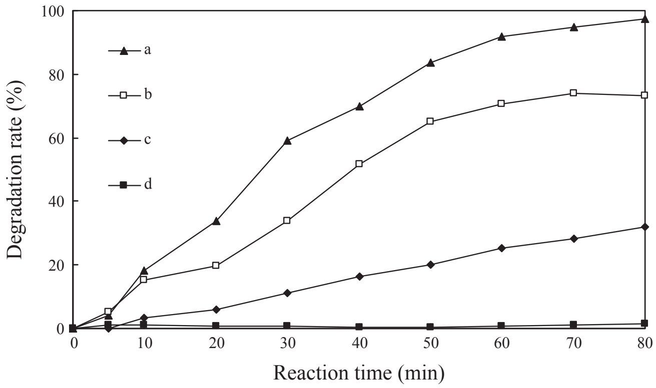

Fig. 4. Degradation efficiency of MO under different reaction conditions: (a) MWCNT/TiO_2, (b) TiO_2, (c) direct photolysis, and (d) reaction without irradiation and catalyst.

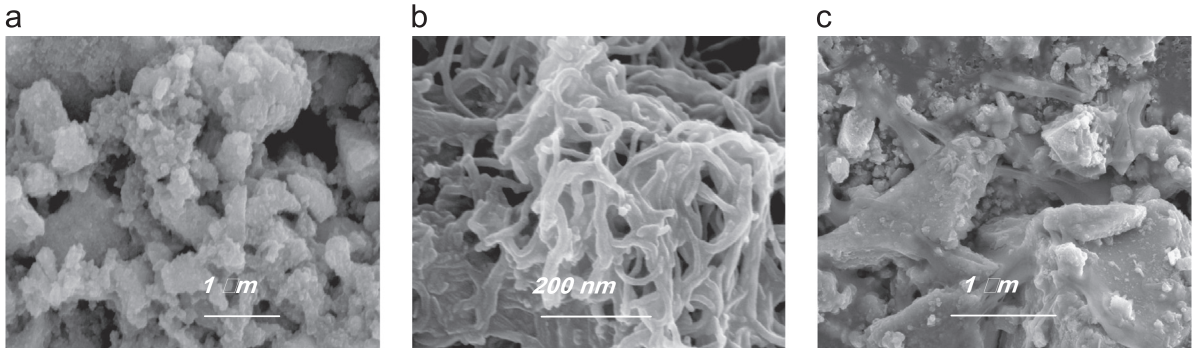

Fig. 2. SEM images of samples: (a) TiO_2, (b) MWCNTs and (c) MWCNTs/TiO_2.

was considerably greater than rates without catalyst or with pure TiO_2 particles alone. These results indicated that addition of MWCNTs significantly enhanced photoactivity of TiO_2 catalyst in the visible light region of the spectrum.

Because photo-oxidation reactions occur at catalyst surfaces, solid MWCNT/TiO_2 composites were separated from solutions before and after photocatalytic reactions and analyzed by EDS to further investigate elemental changes in catalyst surfaces. The primary elements on catalyst surfaces after (a) adsorption and (b) irradiation are listed in Table 1. In this study, adsorption experiments were conducted without illumination for 30 min to ensure saturated adsorption. The Ti content decreased from 27.8 on as-prepared surfaces to 11.9% after adsorption, and C content increased from 17.4% to 31.4%, which was attributed to adsorption of a large quantity of MO on catalyst surfaces. However, after 90 min of irradiation with simulated solar light, Ti and C recovered almost to levels observed for as-prepared catalysts. These results for Ti and C indicated that adsorbed MO completely degraded after 90 min, which was consistent with results where MO degradation efficiency exceeded 97%. The signal for Au can be ascribed to the Au grid.

3.5. *Effects of MWCNT/TiO_2 mass ratios*

Effects of amount of MWCNTs on photocatalytic degradation efficiency were investigated using MWCNTs/TiO_2 mass ratios from 0% to 4% under 80 min of simulated solar irradiation with catalyst and MO concentrations of 1.0 g/l and 20 mg/l, respectively. Results for different mass ratios are presented in Fig. 5. Fig. 6 shows plots for MO reaction kinetics with different amounts of MWCNTs in MWCNT/TiO_2 composites, and Table 2 lists corresponding apparent rate constants and linear regression coefficients for MO photodegradation reactions.

As shown in Table 2, linear regression coefficients (R^2) for fitted lines were between 0.9837 and 0.9965, which indicated that MO photodegradation followed first-order kinetics. The introduction of MWCNTs improved TiO_2 photoactivity, as shown in Fig. 5. The fastest degradation was observed for the MWCNT(2%)/TiO_2 composite. Degradation rates increased with MWCNT/TiO_2 mass ratio up to 2%, and then decreased with further increases in mass ratio. The apparent rate constant for the MWCNTs(2%)/TiO_2 composite was 0.0421 min^{-1}, which was approximately 1.7-times greater than the rate constant for the MWCNT(4%)/TiO_2 composite (0.0250 min^{-1}). This result can be attributed to faster electron–hole recombination with increasing MWCNT content (over 2%) in MWCNT/TiO_2 composites [1]. Another possible reason for this result is blocking of photocatalytically active sites on TiO_2 surfaces by MWCNTs, which consequently reduces photon interactions with these sites. However, when the amount of MWCNTs increases, photon absorption would also increase, but increased adsorption capacity could not counteract the influence of fewer active sites [25,26].

Table 1
Surface composition of MWCNT/TiO_2 composites.

Element	MWCNTs/TiO_2 (at%)		
	As-prepared	After adsorption	After irradiation
C	17.4	31.4	19.8
O	54.3	56.5	55.7
Ti	27.8	11.9	24.2
Au	0.5	0.2	0.3

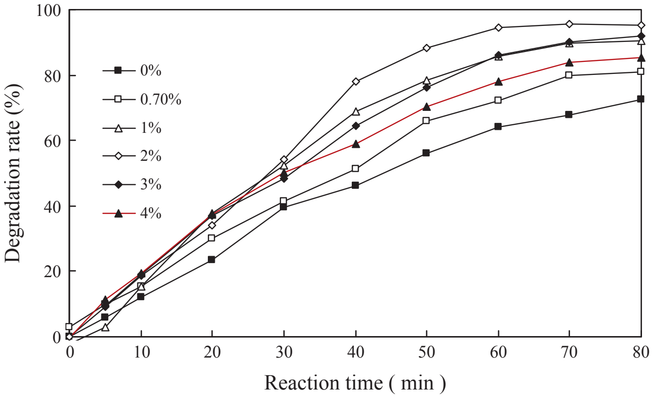

Fig. 5. The degradation efficiency of MO with different amounts of MWCNTs in MWCNT/TiO_2 composites.

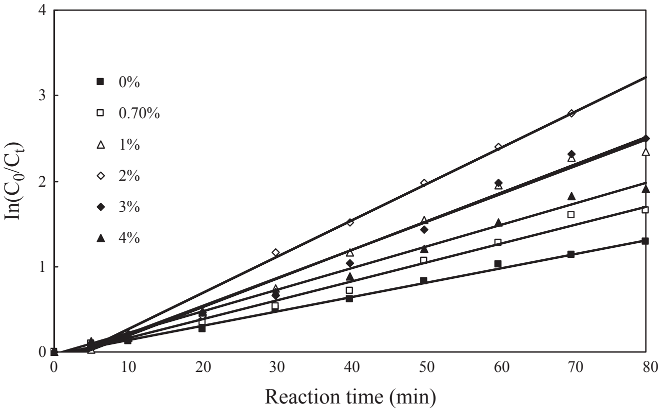

Fig. 6. Plots of MO reaction kinetics with different amounts of MWCNTs in MWCNT/TiO_2 composites.

Table 2
Pseudo-first-order apparent constant values for MO degradation using MWCNs/TiO_2 composites with different MWCNT contents.

MWCNT/TiO_2 mass rate (%)	Rate constant (1/min)	R^2
0	0.0166	0.9965
0.7	0.0219	0.9889
1	0.0325	0.9917
2	0.0421	0.9880
3	0.0331	0.9837
4	0.0250	0.9945

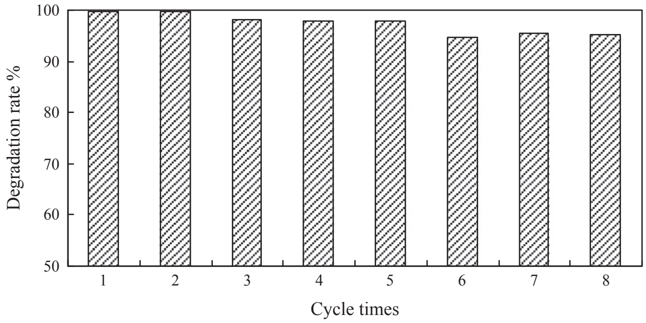

Fig. 7. The MO degradation efficiency of a MWCNT(2%)/TiO_2 composite in eight consecutive cycles.

3.7. Photocatalytic stability of MWCNT/TiO_2 composites

The photocatalytic stability of MWCNT/TiO_2 composites was investigated using MO (10 mg/l) mixed with 0.8 g/l of catalyst under simulated solar irradiation for 90 min. After completing the photocatalytic degradation of MO, photocatalyst was collected, dried at 60 °C for 1 h, and reused in the next cycle under the same initial conditions.

As shown in Fig. 7, the photocatalyst achieved a 95.2% degradation efficiency after 8 cycles under 90 min of irradiation with visible light. This result indicated that the MWCNT/TiO_2 composites had excellent reproducibility for photocatalytic degradation, and these composites have potential for practical applications.

3.8. Photocatalytic mechanism

Ordinary anatase TiO_2 requires UV irradiation to initiate photoactivity due to the large band gap (3.2 eV) of this material. However, MWCNTs can absorb visible light. When MWCNTs are combined with TiO_2 and composite are activated by visible light, electrons can be excited by photons from MWCNTs. Photogenerated electrons can immediately transfer to TiO_2 surfaces, while holes are left in MWCNTs [14,22]. Subsequently, photogenerated electrons can be scavenged by electron acceptors, commonly oxygen molecules absorbed on composite surfaces, and yield $\cdot O_2^-$. This $\cdot O_2^-$ can further react with H^+ and yield H_2O_2. $\cdot O_2^-$ can react with H_2O_2 to form •OH. Simultaneously, positively charged holes (h^+) can react with H_2O to generate •OH [1,2,27,28].

The •OH radical, a strong oxidant and a dominant species in photocatalytic processes, is responsible for degradation of organic compounds on catalyst surfaces [1,3]. This series of reactions can be expressed as follows [27–29]:

$$\text{MWCNTs–TiO}_2 + h\nu \rightarrow \text{MWCNTs}(h^+, e^-)\text{–TiO}_2 \tag{2}$$

$$\text{MWCNTs}(h^+, e^-)\text{–TiO}_2 \rightarrow \text{MWCNTs}(h^+)\text{–TiO}_2(e^-) \tag{3}$$

$$O_2 + e^- \rightarrow \cdot O_2^- \tag{4}$$

$$\cdot O_2^- + 2H^+ \rightarrow H_2O_2 \tag{5}$$

$$H_2O_2 + O_2^- \rightarrow \cdot OH + OH^- + O_2 \tag{6}$$

$$H_2O_2 \rightarrow 2 \cdot OH \tag{7}$$

$$H_2O + h^+ \rightarrow \bullet OH + H^+ \tag{8}$$

$$\bullet OH + MO \rightarrow CO_2 + H_2O \tag{9}$$

4. Conclusions

Results of our study indicated that combinations of MWCNTs with TiO_2 extended the photo-response range of TiO_2, and MWCNT/TiO_2 composites effectively degraded MO under simulated solar light illumination. The UV–vis absorption spectra confirmed that these modified catalysts possessed stronger absorption bands in the visible range of 400–800 nm compared to pure TiO_2. The fastest MO degradation was obtained with a composite with MWCNT(2%)/TiO_2 mass ratio. Photodegradation kinetics obeyed first-order kinetics according to the Langmuir–Hinshelwood model. Photocatalytic stability tests indicated that MWCNT/TiO_2 composites possessed excellent photocatalytic stability. The MO degradation efficiency remained greater than 95% after eight consecutive cycles, which showed that it is practical to apply MWCNT/TiO_2 composite catalysts for degrading organic pollutants from aqueous solutions under solar irradiation.

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