

## Research Article

# Preparation and Photocatalytic Performance of MWCNTs/TiO<sub>2</sub> Nanocomposites for Degradation of Aqueous Substrate

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In this study, multiwalled carbon nanotubes (MWCNTs)/TiO<sub>2</sub> nanocomposites were obtained by constant volumetric wet impregnation processes. The prepared catalysts were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The effect of reaction conditions on photocatalytic performance of the catalysts was investigated by the degradation of methyl orange (MO) under UV irradiation, in a new type of reactor with unique structure. The results showed that the prepared nanocomposite exhibited higher MO degradation efficiency than that of pure nano-TiO<sub>2</sub>. Besides, in batch experiments of influencing factors, including ionic strength, oxidant amount, and response times, the presence of H<sub>2</sub>O<sub>2</sub> would contribute to increasing the MO degradation rate of MWCNTs/TiO<sub>2</sub> samples. Ionic concentration and long reaction times are adverse to the MO degradation in the processes.

## 1. Introduction

The color and high COD of dye wastewater cause serious environmental contamination problems. Particularly, modern dyes are diverse and they are often resistant to long-term exposure in sunlight, water, and other atrocious conditions, thus making the treatment of dye wastewater more difficult [1]. An effective decolorization method is therefore needed to remove the toxic or carcinogenic dye residues and their by-products, which is an important issue in the field of wastewater treatment. Methyl orange (MO), with one azo bond (-N=N-) in association with one aromatic system, is a sort of typical azo dyestuff and is a model compound of a series of common water soluble azo dyes widely used in chemistry, textiles, and paper industries [2].

Methods of MO wastewater treatment have received widespread attention of many scholars in recent years. Of varied methods, photocatalytic removal of pollutants is an important means for dye wastewater treatment, especially for degradation of organic pollutants [3–6]. Nanometer titanium dioxide (nano-TiO<sub>2</sub>) was one of the most popular photocatalysts with the characters of stability, low cost, and nontoxicity and applied widely for treating organic pollutants in the fields of environmental purification [7–10]. However,

due to the wide band gap (3.0–3.2 eV), nano-TiO<sub>2</sub> is only capable of absorbing UV light, accounting for a small fraction (5%) of the sun energy, and the TiO<sub>2</sub>/UV system has been widely investigated in heterogeneous photocatalysis [1, 11]. Besides, as the photocatalytic activity of TiO<sub>2</sub> is also limited by the photogenerated electron-hole pairs recombination, a suppression of this undesired reaction is an important factor for achieving a high catalytic activity [12, 13].

To increase the photodegradation efficiency of TiO<sub>2</sub>, several attempts have been made by noble metal deposition, ion doping, or adding a coadsorbent [2, 13–16]. In particular, some porous materials have been reported to improve the catalytic performance of TiO<sub>2</sub> as a coadsorbent with a very porous and high adsorption capacity when used to support TiO<sub>2</sub> [13, 17–19]. Among them, carbon nanotubes received extensive attention because of their unique structure and properties, since found in 1993 [20]. They can be combined with TiO<sub>2</sub> to form composite structures and used as photocatalysts. Carbon nanotubes not only provide a large surface area support for TiO<sub>2</sub> particles but also greatly delay the recombination of electrons and holes [19]. And, according to different carbon atoms layer, the carbon nanotubes would be divided into single-walled carbon nanotubes and multiwalled carbon nanotubes [2]. Although these porous materials

would improve the degradation ratio, they usually were used in the form of dispersed solid particles, which were hard to be recycled [21], especially, in photocatalytic experimental operation.

In this study, multiwalled carbon nanotubes/TiO<sub>2</sub> nanocomposites (denoted as CN<sup>G</sup>/TiO<sub>2</sub>) will be synthesized. At the same time, a new type of reactor with unique structure will be designed for evaluating the photocatalytic performance of CN<sup>G</sup>/TiO<sub>2</sub> by the reaction of decomposition of aqueous methyl orange (MO). In addition, the effect of reaction conditions, including ionic strength, oxidant amount, and response times, on photocatalytic performance of the catalysts was investigated by calculating the degradation ratio of methyl orange (MO).

## 2. Materials and Methods

A high-purity MWCNT (HGCF-350, Huijiang Chemical Products Co., Shanghai, China; the diameter is 8–13 nm, and the length is 3–5 μm.) was adopted. The titanium dioxide precursors, tetrabutyl orthotitanate (TBOT) and absolute ethyl alcohol (EtOH), were obtained from Fuxing chemical reagent factory in Tianjin, China, without further purification. All chemicals used in the experiments were of analytically pure grade. Besides, glass slides (75 × 25 mm<sup>2</sup>) were fully washed by sodium hydroxide (NaOH) aqueous solution (0.1 mol/L) and ethanol (99.9%) and then dried adequately at room temperature (RT).

**2.1. Preparation of CN<sup>G</sup>.** A nitric acid washing procedure was achieved for the acid treatment of MWCNTs. 2.0 g of raw MWCNTs was immersed into 50 mL of concentrated nitric acid, and the mixture was sonicated in an ultrasonic washer for 1 h to form oxygenated functionalities on the MWCNTs' surface. Subsequently, the MWCNTs were filtered from the acid pickle, washed with distilled water several times to nearly neutral pH, and baked at 423 K. Then, some clean MWCNTs were obtained. 1.0 g of them was sonicated in the distilled water for 1 h. Finally, the MWCNTs suspension was obtained.

Then the as-obtained colloid (1 mL) was coated evenly on the surface of a glass substrate and was baked for 30 min at 453 K. Subsequently, the obtained sample was rinsed with distilled water for 2–3 times and dried for 1 h at 353 K. Finally, several pieces of glass slides attached MWCNTs were obtained (denoted as CN<sup>G</sup>).

**2.2. Preparation of TiO<sub>2</sub>.** Some TBOT (10 mL) and absolute EtOH were mixed under vigorous stirring (15 min) for obtaining solution A. 10 mL of distilled water mixed with EtOH and 2 mL nitric acid were dropwise added to this mixed solution to obtain solution B. Subsequently, solution A was dripped slowly into B to mix together under vigorous stirring for 3 h. A kind of stable yellowish colorless titania colloid was prepared after aging for 12 h.

**2.3. Preparation of the CN<sup>G</sup>/TiO<sub>2</sub>.** Some prepared titania colloids (1 mL) were dripped slowly onto CN<sup>G</sup> and were rinsed slowly by EtOH after reaching adsorption balance. Then, these nanocomposites were dried in vacuum drier for

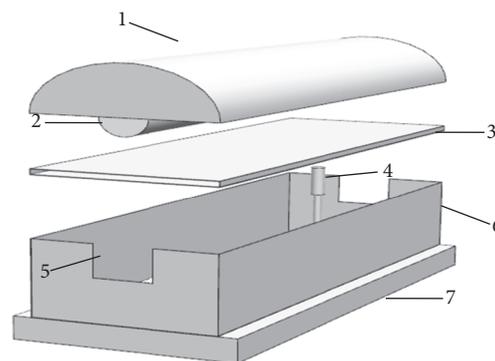


FIGURE 1: Reactors: 1: ultraviolet collector, 2: UV light source, 3: glass slide, which was loaded with catalyst, 4: sampling mouth, 5: the overflow mouth, 6: the reaction zone, and 7: pedestal.

12 h at 353 K and were in a muffle at 823 K for 2 h. After that, they were rinsed with distilled water softly for 2–3 times and were dried for 1 h at 353 K. Finally, attached carbon nanotubes (MWCNTs)/TiO<sub>2</sub> nanocomposites (namely CN<sup>G</sup>/TiO<sub>2</sub>) were obtained using a sol-gel method.

## 3. Characterization and Measurement

The sample's surface composition was analyzed using X-ray photoelectron spectroscopy (XPS, AXIS, ULTRA, Kratos Analytical, Japan) equipped with an Ag K<sub>α</sub> source. The morphology was examined using scanning electron microscopy (SEM, FEI Quanta200, USA).

The photocatalytic activities of prepared photocatalysts were evaluated by degradation of aqueous MO with an initial concentration of 0.1 g/L under UV irradiation. In order to meet the requirements of this experiment, we designed a new type of reactor with unique structure (Figure 1).

Prior to photoreaction, a prepared catalyst (CN<sup>G</sup>/TiO<sub>2</sub> nanocomposites) was placed in a reactor (6, Figure 1), and then 10 mL of MO solution (0.1 g/L) was injected, and it stood for 2 h in dark to ensure the establishment of adsorption-desorption equilibrium before UV irradiation. After that, the photocatalytic reactions were carried out under UV irradiation. The UV light source was provided using a black lamp (2, Figure 1) with an intensity of 1 mW cm<sup>-2</sup> and the main UV peak was located at 254 nm. 1.5 mL of reactant solution was sampled at the interval of 15 min (the cumulative reaction time was 2 hours) from the sampling mouth (4, Figure 1) using a syringe sampler, and cumulative reaction time was 2 hours. After the measurement of absorption spectra of sample, the sample solution was injected back into the reactor immediately. The blank control groups were also carried out for all photocatalytic experiments of MO degradation under 254 nm UV.

## 4. Photocatalytic Evaluation

The UV-VIS absorption spectrophotometer was used for testing the absorption spectra of the sampling solutions. From

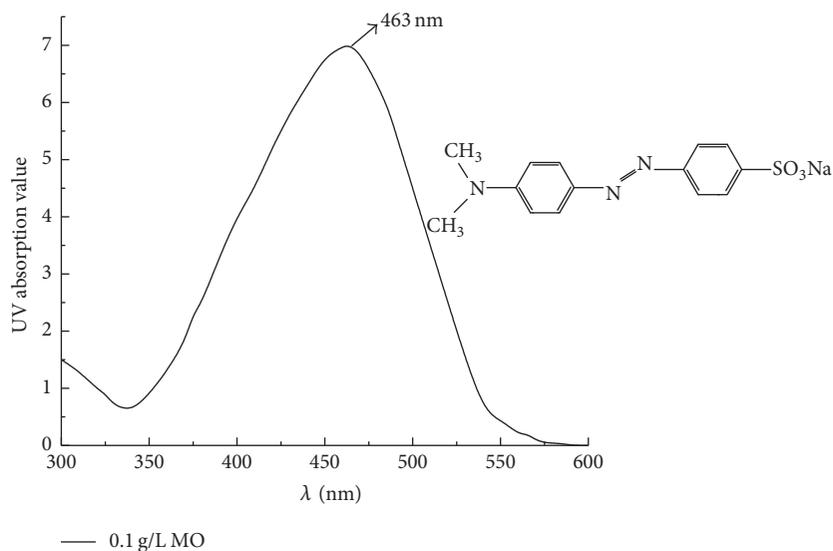


FIGURE 2: The UV-VIS absorption spectra of 0.1 g/L MO.

the UV absorption spectra (Figure 2), we can see the characteristic absorption peaks located at 463 nm, corresponding to the “-N=N-” azo bonding of MO. So  $\lambda = 463$  nm was as the wavelength of determination in absorption spectra for as-prepared and completely degraded MO solution. Photocatalytic degradation over each nanocomposites was evaluated by the MO degradation ratio ( $D_t$ ) and relative degradation ratio ( $RD_t$ ) at  $t_{\min}$  during the degradation reaction, which were calculated as follows:

$$D_t = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (1)$$

$$RD_t = \frac{D_t - D_0}{D_0} \times 100\%,$$

where  $C_0$  and  $C_t$  are the MO concentrations at  $t = 0$  and  $t_{\min}$  during the degradation reaction, respectively.  $C_0 = 0.1$  g/L, and  $C_t$  was determined in terms of the absorbance of MO (463 nm).  $D_0$  was  $RD_t$  of  $CN^G/TiO_2$  at  $t_{\min}$ .

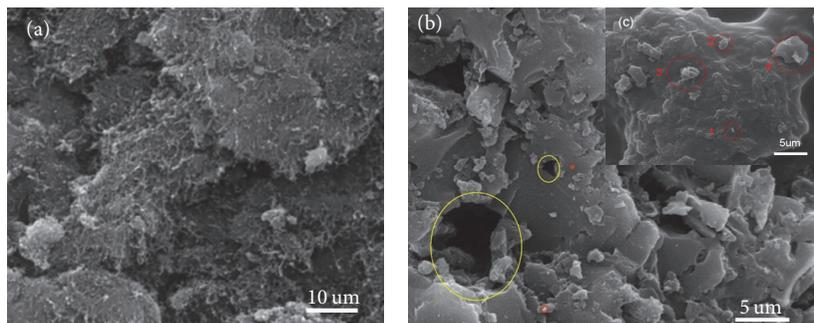
## 5. Results and Discussion

**5.1. Characterization Analysis.** Figures 3(a), 3(b), and 3(c) showed the SEM images of  $CN^G/TiO_2$ . MWCNT presented obvious burrs in Figure 3(a). Due to the effect of strong acid, the wall started thinning, and even the rupture appeared on some week places. In this case, the adhesion of MWCNT became strong, which was help for them to adhere to the glass slide. The adopted  $TiO_2$  nanoparticles exhibited regular granules (particle size: 5–70 nm), confirmed by the photos of SEM (the red frames marked in Figure 3(c)). Meanwhile, the aggregation (4, Figure 3(c)) was also attributed to  $TiO_2$  nanoparticles which were annealed under the calcining temperature of 823 K for 2 h during the preparation progress of  $TiO_2$  thin films. These various diameter particles improved the performance of  $CN^G/TiO_2$  photocatalyst. Additionally, there were some micropores that occurred on the surface of

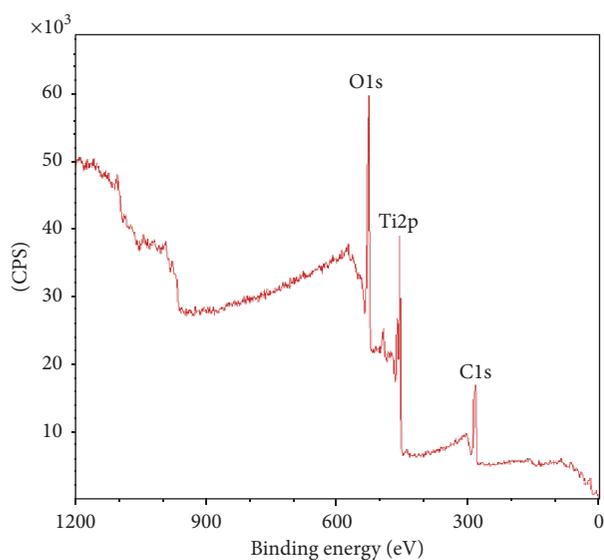
$CN^G/TiO_2$  (the yellow frame, Figure 3(b)). This micropore structure not only was beneficial to the doping metals but also increased the specific surface area of  $CN^G/TiO_2$  so as to promote the generation of photogenerated electron-hole pairs. So the micropores were able to improve the adsorption of dyes, which was an efficient way to promote the photo-degradation of dyes.

Figure 4 shows the overall XPS spectrum of  $CN^G/TiO_2$ . The characteristic peaks of the O and Ti elements were detected. Combining Table 1 and Figure 4, we could see that the O 1s peak at 530 eV was attributed to  $O^{2-}$  anion; the peak located at 459 eV was associated with Ti 2p<sub>3/2</sub>, which confirmed that the titanium species in the  $CN^G/TiO_2$  photocatalyst was  $Ti^{4+}$ . Another observed peak of C 1s was at 282–283 eV, and the main existing form was simple substance phase. The main elements of the  $CN^G/TiO_2$  consisted of the O, Ti, and C elements. As shown in Table 1, from the calculated surface element compositions of the  $CN^G/TiO_2$ , the O/Ti/C (54.46% : 32.41% : 13.13%) molar ratios of the above two samples were close to the theoretical value, in good agreement with the recording of XPS peaks of  $CN^G/TiO_2$ , implying the formation of homogeneous nano- $TiO_2$  thin film phase.

**5.2. Photocatalytic Activity.** The photocatalytic activities of all catalysts were evaluated by the degradation reactions of aqueous MO under UV irradiation. Figure 5 shows MO degradation ratio ( $D_t$ (MO)) after 2 h reaction, 12.29% and 21.03% of MO were degraded in the presence of  $TiO_2^G$ , and 28.54% and 46.91% of MO were degraded in the presence of  $CN^G/TiO_2$ , while approximately 0% and 5.78% of MO are decomposed without any photocatalyst under UV irradiation of  $\lambda = 365$  and 254 nm respectively. This indicates that  $i2$  photocatalyst is slightly more active. Obviously,  $D_t$ (MO)'s of  $CN^G/TiO_2$  were higher than that of  $TiO_2^G$  from 15 to 120 min both 365 nm and 254 nm UV. There was little MO degradation for the blank under 254 nm UV, and its  $D_{120}$ (MO) merely

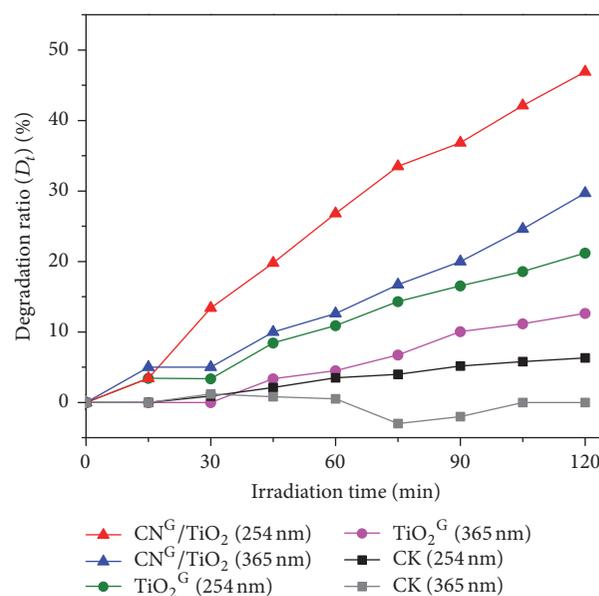
FIGURE 3: SEM images of (a), (b), and (c)  $\text{CN}^{\text{G}}/\text{TiO}_2$ .TABLE 1: Binding energies and surface element compositions of the  $\text{CN}^{\text{G}}/\text{TiO}_2$ .

Sample	Binding energy (eV)	M atom percent (at%) <sup>a</sup>	M loading (wt%) <sup>b</sup>
$\text{CN}^{\text{G}}/\text{TiO}_2$			
O 1s	530	54.46	39.84
Ti 2p <sub>3/2</sub>	459	32.41	58.03
C 1s	282	13.13	2.13

<sup>a</sup>Determined by the XPS.<sup>b</sup>Data calculated based on the XPS results according to conversion formula between at% and wt% of dopant.FIGURE 4: X-ray spectra of  $\text{CN}^{\text{G}}/\text{TiO}_2$ .

reached 5.78%. This was mainly due to the higher energy of 254 nm UV that can broke the chemical bond ( $-\text{N}=\text{N}-$ ) of MO molecule easily [22, 23].  $D_t(\text{MO})$ 's of the two catalysts were always higher than the blank samples under the same UV irradiation. This demonstrated that nano- $\text{TiO}_2$  attached to the surface of the glass slide exhibited photocatalytic performance to some extent. From these results, we found that the combination of MWNTs and  $\text{TiO}_2$  was effective in obtaining high reaction rate.

**5.3. Effect of Reaction Conditions on Photocatalytic Performance.** The composition of the real dye wastewater is always

FIGURE 5: Photodegradation of MO catalyzed by  $\text{TiO}_2^{\text{G}}$ ,  $\text{CN}^{\text{G}}/\text{TiO}_2$ , and 2 blank samples (without catalysts) under UV irradiation ( $\lambda = 254, 365 \text{ nm}$ ).

complex. The dyeing wastewater includes lots of inorganic salts such as KCl, which is a commonly used promoter and buffering agent in dyeing industry. Influence of aqueous ionic concentration was evaluated. Different ion concentrations had different effects on the adsorption performance of  $\text{CN}^{\text{G}}/\text{TiO}_2$ . Considering the common tendency of all  $D_t(\text{MO})$ 's curves (Figure 6), it can be seen that KCl had a negative effect on the decolorization of MO. As shown

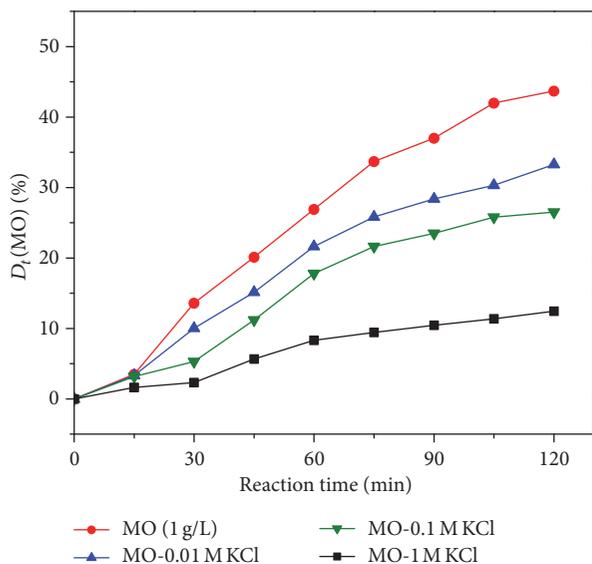


FIGURE 6: Variation of  $D_t(\text{MO})$ s with MO (0.1 g/L) in different concentration KCl solution under 254 nm UV at RT.

In Figure 6, the relative degradation ratio within 120 min reaction decreased from 44% to 12% as the concentration of KCl increased from 0 to 1.0 mol/L.  $D_t(\text{MO})$  in 1.0 mol/L KCl is the lowest, compared to other photocatalytic degradations, and its  $D_{120}(\text{MO})$  merely reached 12.45%. This phenomenon was mainly because the addition of salt solution of high concentration played an inhibitory role for the adsorption of MWNTs, and the MO was desorbed, and the effective contact rate between MO and  $\text{TiO}_2$  reduced [24, 25]. In addition, the possible reason for the decrease of  $D_t(\text{MO})$  caused by KCl is that  $\text{TiO}_2$  particles have an outside oxide surface, which is positively charged under the isoelectric point, and anions that have atoms with a lone pair of electrons can be adsorbed onto the surface of the particles through a coordinate bond, and thus  $\text{Cl}^-$  anions would compete with MO in occupying the reactive sites of  $\text{TiO}_2$  particle because of their similar anion structure. Ultimately, the decolorization efficiency of composite material decreased, when salts are present.

As shown in Figure 7, in presence of  $\text{H}_2\text{O}_2$ ,  $D_t(\text{MO})$ 's of  $\text{CN}^{\text{G}}/\text{TiO}_2$  significantly improved compared with the reaction without oxidant. From the tendency of all  $D_t(\text{MO})$ 's of  $\text{H}_2\text{O}_2$  reaction liquid curves, we found that most of the aqueous MO was degraded in the initial 60 min and the reaction speed is very high at this period. The difference in  $D_{60}(\text{MO})$  reflected the influence of oxidant amount. When the  $\text{H}_2\text{O}_2$  concentration was 3%,  $D_t(\text{MO})$  reached nearly 99% (at 45 min). With decline of the  $\text{H}_2\text{O}_2$  concentration,  $D_t$ s lowered gradually, while all the reactions were completed in 90 min. The results showed that the presence of  $\text{H}_2\text{O}_2$  contributed to improving the photocatalytic activities of  $\text{CN}^{\text{G}}/\text{TiO}_2$ . Since the  $\text{H}_2\text{O}_2$  could be the electron capturer, it would generate much of hydroxyl radical ( $\text{OH}^{\bullet}$ ) under the irradiation of ultraviolet light. As a strong oxidant,  $\text{OH}^{\bullet}$  was the initiator of photocatalytic chain reaction and was helpful for improving the photocatalytic activities of  $\text{CN}^{\text{G}}/\text{TiO}_2$  [26, 27].

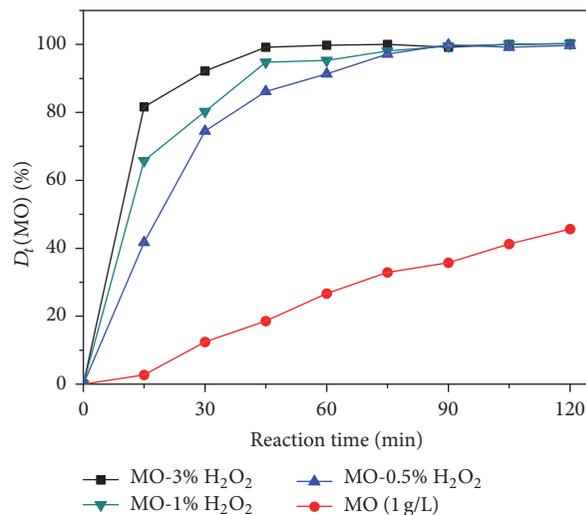


FIGURE 7: Variation of  $D_t(\text{MO})$ s with MO solution (0.1 g/L) in different concentration of  $\text{H}_2\text{O}_2$  solution under 254 nm at RT.

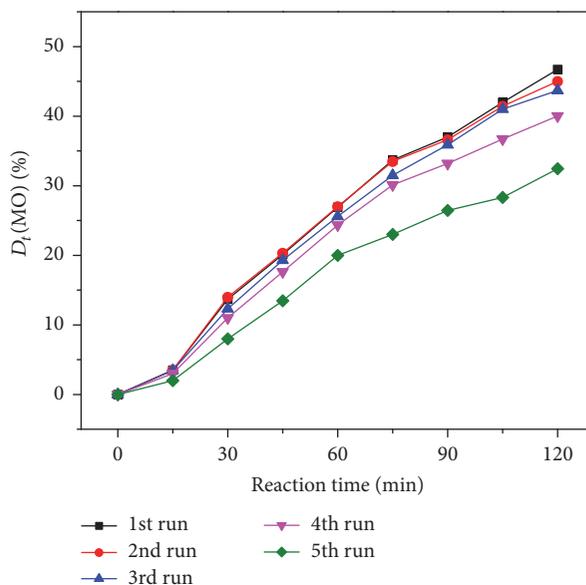


FIGURE 8:  $D_t(\text{MO})$  of reaction time referring to  $\text{CN}^{\text{G}}/\text{TiO}_2$  under different reaction times under 254 nm at RT.

Influence of reaction times on the photocatalytic performance of  $\text{CN}^{\text{G}}/\text{TiO}_2$  was evaluated by the degradation of MO aqueous solution. As shown in Figure 8, the common tendency lines of  $D_t(\text{MO})$ 's mostly overlap in previous four reaction times. It demonstrated the high recuperability of  $\text{CN}^{\text{G}}/\text{TiO}_2$  to some extent. While, for the fifth response, at 120 min, the degradation decreased to 32.45%. The tendency of variation of  $D_t(\text{MO})$ 's show that the photocatalytic performance of  $\text{CN}^{\text{G}}/\text{TiO}_2$  was declined in the fifth response, compared with the previous reactions. Some studies [2, 15] suggested that the adsorption principle of carbon nanotubes relied on its high surface activity and surface functional groups. Meanwhile, the high-energy ultraviolet light also

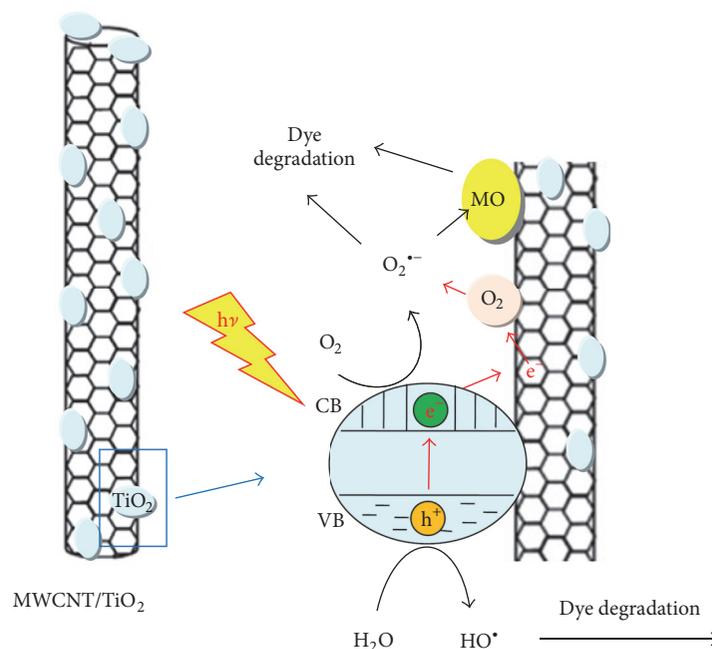


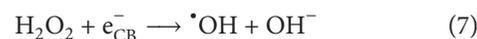
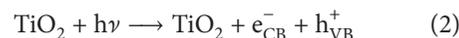
FIGURE 9: Schematic diagram of the proposed mechanism of photocatalytic degradation in MWCNTs/TiO<sub>2</sub> under UV irradiation.

could break the functional groups of catalyst and serious TiO<sub>2</sub> loss emerged. Thus, repeated use of carbon nanotubes supported titanium dioxide for a long time would be adverse to the degradation of MO.

**5.4. Photocatalytic Mechanism Discussion.** A complete photocatalytic process is generally divided into three stages, including light harvesting, separation of photogenerated charges, and interfacial reactions [1, 11]. So it is important for high-efficiency photocatalysts to have a fine implementation at each stage. Based on the above results, we proposed a photocatalytic mechanism for the degradation of MO catalyzed by MWCNTs/TiO<sub>2</sub> catalysts.

Normally, under UV light irradiation, electron e<sup>-</sup> was excited from the valence band (VB) to the conduction band (CB) of TiO<sub>2</sub>, leaving behind h<sup>+</sup> at original sites. These charge carriers quickly recombine, and only a fraction of the electrons and holes participate in the photocatalytic reaction, resulting in low reactivity [21]. However, as illustrated in Figure 9, when TiO<sub>2</sub> was modified by the MWCNT, the catalytic activity of TiO<sub>2</sub> was enhanced. It has been theorized that dominant contribution of nanotubes in MWCNT/TiO<sub>2</sub> composites is mainly due to an increase in recombination time for photogenerated electron-hole pair. It has been supported by the delocalized  $\pi$ -structure nature of MWCNT, which promotes the transfer of electrons and can be as an excellent electron acceptor causing hole-electron separation [19]. Thus, benefitted by the excellent optical property of MWCNTs/TiO<sub>2</sub> surface, some high-energy charge carriers pairs (e<sup>-</sup>/h<sup>+</sup>) are photogenerated after UV irradiation [26, 27].

Besides, O<sub>2</sub> adsorbed on surface was reduced to O<sub>2</sub><sup>-</sup> by e<sup>-</sup> and then converted into active hydroxyl radicals [19], which attacked persistently the MO molecules and are degraded completely [1]. Meanwhile, the surface h<sup>+</sup> is apt to undergo charge transfer with adsorbed water molecules or surface-bound hydroxide species to generate activity [1]. The mechanism was formulized:



## 6. Conclusions

Multiwalled carbon nanotubes/TiO<sub>2</sub> nanocomposite was obtained and a series of influencing factors were studied in a new type of reactor with unique structure. We found that the recombination of MWCNTs and nano-TiO<sub>2</sub> was effective in obtaining high degradation rate of methyl orange dye in aqueous solutions, and they showed a good recyclability in our study. In addition, the presence of H<sub>2</sub>O<sub>2</sub> would contribute to increasing the MO degradation rate of MWCNTs/TiO<sub>2</sub>

catalyst, while the ionic concentration performed the opposing effects.

## Competing Interests

The authors declare that they have no competing interests.

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