Comparison of visible-light-driven routes of anion-doped TiO₂ and composite photocatalyst

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This study investigates and compares the efficiency of visible-light-driven routes of anion-doped TiO₂ and composite photocatalyst by using preparation conditions as controls for crystal phase, crystallite size, and optical properties. Anion-doped TiO₂ was formed by doping nitrogen, and the composite photocatalyst was made from TiO₂ combined with Multi-Walled Carbon Nanotubes (MWCNTs) via the sol-gel process. The results of the evaluated performances of the photocatalysts with the photodegradation of methanol under visible-light radiation demonstrated that the anion-doped TiO₂ exhibited higher photocatalytic activity than that of the composite photocatalyst. It is concluded that the composite photocatalyst was induced into the visible-light region by the photosensitizer, which may decrease the efficiency of electron transfers between photosensitizer and TiO₂ phases, or that photosensitizer could not effectively induce the valance band electron of TiO₂ into photosensitizer to form positive holes. On the other hand, the anion-doped TiO₂ directly formed a new energy band gap, which indicates a superior route to visible-light response.

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1. Introduction

TiO₂ ($E_g = 3.0\text{--}3.2\text{ eV}$) has excellent photocatalysis, is environmental friendly, has chemistry stability, is abundant, and non-corrosive. However, raw TiO₂ only shows photocatalytic activity under UV light irradiation ($\lambda < 384\text{ nm}$) that accounts for only a small portion of solar energy ($\sim 5\%$). Therefore, how to effectively utilize sunlight is an essential issue. In recent decades, many approaches have been designed to shift its optical absorption region from the ultraviolet area to visible light. They were mainly carried out through two methods: the inorganic and the organic material modification.^{1)–4)} The inorganic material doping method is by far more popular because of its good activity and application, and has mainly three design types: (1) cation doping (Fe, Co, Ni, Cu et al.), (2) anion doping (mostly N, C, F, and S) and (3) composite photocatalyst (CdS–TiO₂, MWCNTs–TiO₂ et al.).

Although suitable metal ion dopants could increase the absorption region, they acted either as recombination center for the photogenerated charge carriers or were simply ineffective in aiding the surface redox reaction.^{5)–9)} However, even though the modified TiO₂, by doping with metal ion, has been prepared successfully, most of them either reduced the photoactivity because of their role as recombination centers, which increased the carrier-recombination rate¹⁰⁾ or resulted in thermal instability.^{9),11)} Furthermore, many transition metals are toxic and will diffuse from photocatalysts to the environment during the operation, which may lead to a second pollution, limiting their further application.¹²⁾ For these reasons, anion-doped photocatalysts are better than cation-doped types as a result of their good activity and non-toxic feature.

The visible-light-driven routes of anion-doped TiO₂ is

described as follows: Anion-doped TiO₂, forming new energy band that narrows the band gap of TiO₂, which was introduced by the mixture of substitutional anion dopants (C, F, N, etc.) 2p band and O 2p band. A theoretical calculation shows that the band gap shift induced by N doping resulted in the substitutional N 2p π state electrons taking the place of O 2p π state electrons in TiO₂.¹³⁾ Unfortunately, it was found that it was difficult to dope N in the TiO₂ lattice. Although it is hard to substitute the O from the TiO₂, it can occupy the oxygen defect sites. As a result, oxygen defects are necessary for preparing nitrogen-doped TiO₂. Liu et al.¹²⁾ reported that according to the PL (photoluminescence) spectra and UV-vis analyses, the substituted nitrogen atoms acted as acceptors and affected the valence band (VB) edge, and the oxygen defects were donors that disturbed the conduction band (CB) edge, as shown in Fig. 1(a).

In composite photocatalyst type, MWCNTs-based composite photocatalysts have attracted much attention owing to their electronic, adsorption, mechanical, thermal properties, and their non-toxicity.¹⁴⁾ The unique electronic properties of MWCNTs could either be metallic or semiconducting, depending on their geometry. MWCNTs mainly act as photosensitizers, which enhance their optical absorption from the ultraviolet to the visible light

Fig. 1. Visible-light driven routes of (a) nitrogen doped TiO₂ and (b) MWCNTs–TiO₂ composite photocatalyst.

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region.^{15)–18)} The probable schemes are shown in Fig. 1(b). MWCNTs were excited to form electron/hole pairs by visible light irradiation, and the electrons transferred to the CB of TiO₂. Furthermore, the electrons of the VB of TiO₂ were induced into MWCNTs, and the positive holes were left in the VB of TiO₂. As a result, MWCNTs acted as photosensitizers that get excited under visible light irradiation, triggering the formation of superoxide radical ions and hydroxyl radical, which are reactive enough to result in the degradation of the organic compound.^{15),17),18)}

Photocatalysis through visible-light-driven routes of different kinds of photocatalysts has been the subject of some investigation in this field. The rare studies focused on the comparison of visible-light-driven routes between anion-doped and composite photocatalyst. The research of this comparison provides the right aspect for further modification. For the same compared standard, N-doped TiO₂ and MWCNTs–TiO₂ composite photocatalyst are formed in almost the same crystal phase, crystallite size, and optical property by controlling preparation parameters.

2. Experimental section

2.1. Materials

Titanium (IV) propoxide (Ti(OC₃H₇)₄, Aldrich) was used as the precursor of Titanium. Commercial MWCNTs (Desunano Co., Ltd.) acted as the photosensitizer in composite photocatalyst, whose main physical data are as follows: Brunauer–Emmett–Teller surface area (*S*_{BET}) 40–300 m²/g, purity above 95%, average diameter around 10–30 nm, and length was 5–15 μm (L-Type). The main physical data for Degussa P25 (Desunano Co., Ltd.) are as follows: Brunauer–Emmett–Teller surface area (*S*_{BET}) 55 ± 5 m²/g, purity above 97%, average primary particle size around 30 nm, and anatase-to-rutile ratio of 75:25. All chemicals used in this study were of reagent-grade.

2.2. Photocatalysts preparation

(1) N-doped TiO₂

To form a colloidal solution, 25 mL of TIP was added into 120 mL of distilled water. After continuous stirring to obtain homogeneous sol, 16 and *X* mL concentrated nitric acid and ammonium hydroxide solution were added, respectively, where *X* was 34, 54, 74, and 94. After this, the hydroxyl group reacted with the metal center for nucleophilic substitution, resulting in the exchange of the alkyl group (OR) by hydrolysis reaction (Eq. (1)). After continuous stirring, the condensation reaction occurred to form Ti–O(N)–Ti bonds (Eq. (2)).⁹⁾

A floccule could be observed, which varied in color from white to yellow by increasing the amount of ammonia solution. The floccule was filtered and washed with deionized water, and then aged in air to form xerogel for a week. After being crushed into fine powder and calcined at 350°C for 3 h, the N-doped TiO₂ particles were coated in glass bead by impregnation method.

(2) MWCNTs–TiO₂ composite photocatalyst

TIP was dissolved in 200 mL of ethanol under continuous stirring. In order to obtain the same particle size with N-doped type, through the use of controlling pH value of sol during the sol–gel process, the pH values of sol were adjusted from 2 to 10 using

HNO₃ or NH₃·H₂O solution. An *X* weight ratio of MWCNTs–TiO₂ was added into the solution, where *X* was 2.5, 5, 10, 20, and 30%. The mixture was under ultrasonic-vibration treatment for 30 min, and continuously stirred until a homogenous gel formed. The gel was aged in air to form xerogel, and then it was crushed into a fine powder. The powder was calcined at 350°C for 3 h. The photocatalyst was coated in glass bead by impregnation method. The possible formation mechanisms of MWCNTs–TiO₂ photocatalysts had been described elsewhere.¹⁴⁾

2.3 Analysis

Particle sizes and shapes of N-doped TiO₂ and MWCNTs–TiO₂ photocatalysts were observed with a transmission electron microscope (TEM, JEOL Ltd., JEM–1200CXII) and a field emission scanning electron microscope (FE–SEM, Hitachi Ltd., S–2460N). The crystallite phase and size of the samples were measured with an X-ray powder diffractometer (XRD, Mac Science Co., M18XHF). Crystallite sizes of the samples were calculated through the widths of half-height in terms of the Scherrer equation:

$$d = \frac{0.89 \times \lambda}{\beta \times \cos \theta} \quad (3)$$

where λ is the X-ray wavelength corresponding to Cu K α radiation, β is the broadened profile width in radians, and θ is the diffraction angle with characteristic peak.¹⁹⁾

The chemical compositions of photocatalysts were evaluated by X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250). The optical absorptions of photocatalysts were determined by using a UV-vis diffuse reflectance spectrometer (UV-Vis/DRS, Hitachi Ltd., U3310). The Brunauer–Emmett–Teller (BET) surface area of the photocatalysts were determined by N₂ sorption at 77 K with a vacuum volumetric apparatus (Microrifice ASAP 2010 nitrogen adsorption apparatus).

2.4 Photoactivity measurements

The photocatalytic activities of the samples were evaluated by measuring the degradation of methanol under visible light irradiation. Photocatalytic reactions were carried out in a plug flow annular reactor (50 mm i.d.) interfaced with a gas chromatograph (Agilent HP 6890) for reactant and product analysis (Fig. 2). For packing media, 2 mm glass beads, which were coated photocatalysts were used. FL–10D (China Electric Manufacturing Corp.) was used as visible light source. Methanol vapors were diluted with zero air streams (21% oxygen, 79% nitrogen). The resulting gaseous mixture was allowed to flow through the dark photocatalytic reactor at a constant temperature of 30°C and relative humidity of 20%. Until adsorption equilibrium was reached, the

Fig. 2. Photocatalytic reaction system for degradation of methanol vapor.

visible light was turned on. No degradation of methanol was found when the gas was passed through the reactor without either visible light radiation or photocatalysts. Both blank tests showed that the removal of methanol vapors through photo-degradation or adsorption were negligible. All the experiments were carried out with a flow rate of 300 mL/min; vapor concentration was 200 mg/L, and the residence time was around 33 s.

3. Results and discussion

3.1 Effect of gelation pH during the sol–gel process

Figure 3 shows the influence of pH values on average crystallite size of TiO_2 photocatalysts. The results indicated that the average crystallite size of the photocatalysts was strongly dependent on the pH values of sol during the sol–gel process. By increasing the pH value, the amount of hydroxyl groups in the sol was increased and the hydrolysis of alkoxides was strengthened.²⁰ As the hydrolysis reacted completely, this resulted in greater crystallization and better crystallite size. The current work indicated that a low pH value revealed the fine crystallite size to around 8 nm. As a result, composite photocatalyst was selectively grown in acidic sol and obtain the same particle size with anion doped TiO_2 .

3.2 Characterization of the photocatalysts

Typically, the SEM images presented in **Fig. 4** show the surface morphology of the N-doped TiO_2 and MWCNTs– TiO_2 composite photocatalyst. **Figure 4(a)** indicates that the nitrogen-doped TiO_2 nanoparticles are homogenous. In **Fig. 4(b)**, it appears that MWCNTs can prevent TiO_2 particles from agglomerating, thus increasing the surface area. Some researchers^{15),17),21)} indicated that MWCNTs could act as dispers-

ing agents and prevent TiO_2 from agglomerating. **Figures 5(a)** and **(b)** show the TEM morphology of the N-doped TiO_2 and MWCNTs– TiO_2 , respectively. The N-doped TiO_2 and MWCNTs– TiO_2 are present in the form of spherical particles with the average size of around 8 nm, while both of them are present in cubic particles.

XRD patterns (**Fig. 6**) reveal that photocatalysts, which are mainly in the anatase phase, can be identified for N-doped TiO_2 and MWCNTs– TiO_2 . The rutile and brookite phases of TiO_2 are not observed. All the photocatalysts present symmetric peak of anatase (101) reflection. Additionally, the other intense peaks of **Figs. 6(a)–(c)** are anatase (004) and (200). The disappearance of MWCNTs' characteristic peaks in the XRD patterns (**Fig. 6(c)**) of composite materials was ascribed to the homogeneous coverage of TiO_2 on MWCNTs.¹⁵⁾ Crystallite sizes are estimated by using Scherrer's formula.¹⁹⁾ The crystallite sizes are 8.4 nm and 7.6 nm for N-doped TiO_2 and MWCNTs– TiO_2 , respectively. The results of the primary particles estimate from the TEM agree with the calculation from the XRD pattern using the Scherrer equation.

The XPS spectra were used to analyze the chemical state and concentration of each element possibly existing in the samples. **Figures 7(a)–(c)** show the XPS survey spectra of N-doped TiO_2 , which reveals the effect of nitrogen doping on the structure of the titanium dioxide. All of the N-doped TiO_2 samples exhibit a broad peak, which is fitted by three peaks at 396.0, 399.6, and 401.6 eV. The N 1s core level of N-doped TiO_2 shows a main peak at 399.6 eV, which is attributed to the O–Ti–N bonding, as likewise supported by the low $\text{Ti } 2p_{3/2}$ binding energy of N-doped TiO_2 compared with pure TiO_2 .^{5),22)–24)} The other peaks around

Fig. 3. Influence of gelation pH on average crystallite size of raw TiO_2 .

Fig. 4. SEM image of (a) N-doped TiO_2 photocatalyst and (b) MWCNTs– TiO_2 composite photocatalyst.

Fig. 5. TEM photographs of (a) N-doped TiO_2 photocatalyst and (b) MWCNTs– TiO_2 composite photocatalyst.

Fig. 6. XRD patterns of (a) Raw TiO_2 , (b) N-doped TiO_2 and (c) MWCNTs– TiO_2 composite photocatalyst.

Fig. 7. XPS spectra of (a) N 1s; (b) O 1s, (c) Ti 2p for nitrogen doped TiO₂ and (d) C 1s; (e) O 1s and (f) Ti 2p for MWCNTs–TiO₂ composite photocatalyst.

399–401 eV are associated with N-related bonds such as N–N and N–O bonds.²⁵⁾ The O 1s core level spectrum shows that the O in the N-doped TiO₂ films is composed of the lattice oxygen—Ti–O–Ti (529.6 eV).¹²⁾ The Ti 2p peaks divide into two parts which was ascribed to the spin-orbit coupling effect. The peaks are centered at 458.6 and 464.4 eV, which arose from Ti 2p_{3/2} and Ti 2p_{1/2}. They are ascribed to Ti³⁺ and Ti⁴⁺ in the film, respectively. It also shows that the doped N can induce the formation of Ti³⁺ in TiO₂ films.¹²⁾ Furthermore, the presence of Ti³⁺ enhances the separation of electron/hole pairs, thus resulting in the improvement of the photocatalytic activity in the visible-light region.²⁶⁾

The XPS patterns of C 1s, O 1s, and Ti 2p for the MWCNTs–TiO₂ composite material are shown in Figs. 7(d)–(f). It is observed that the binding energies of 284.8, 285.4, 286.7, and 290.0 eV, were attributed to C–C, C–O, C = O, and COO bonds, respectively. The existence of these polar groups confirms that the surface of MWCNTs was favorable to the adsorption of the precursor molecules and/or to the nucleation of TiO₂ on the surface of the MWCNTs.¹⁴⁾ The O 1s spectra of MWCNTs–TiO₂ mainly exhibit at 530.8 eV, which is due to the lattice Ti–O bond

Fig. 8. UV-vis diffuse reflectance spectra of various types of visible-driven photocatalyst.

of the TiO₂ phase. The curve fitting of O 1s spectra basically indicates three peaks centered at 530.8, 531.6, and 532.8 eV. The peak at 531.6 eV is assigned to C–O, C = O, and COO bonds,

and the peaks at 530.8 and 532.8 are ascribed to O 1s of H₂O and TiO₂, respectively.¹⁷⁾ The binding energies of Ti 2p_{3/2} and 2p_{1/2} are centered at 459.2 and 464.9 eV, respectively, which slightly shift toward higher binding energy. This implies that the Ti in TiO₂ particles decorate on MWCNTs, and also suggests that a strong interaction exists between TiO₂ and MWCNTs.¹⁴⁾

The absorption spectra of the MWCNTs–TiO₂, N-doped TiO₂, and raw TiO₂ are shown in Fig. 8 where Kubelka–Munk equivalent absorption units are used. A significant increase in the absorption at wavelength shorter than 400 nm can be assigned to the intrinsic band gap of pure anatase phase.²⁷⁾ In comparison with raw TiO₂, the UV-vis spectra of the N-doped TiO₂ and MWCNTs–TiO₂ show a stronger absorption in the visible range. It attributed the new absorption band to doped N atoms and MWCNTs.^{14),15),28)}

3.3. Visible-light driven photocatalysis

Figure 9(a) shows the photocatalytic activities of Degussa P25, raw TiO₂, and N-doped TiO₂ with different nitrogen concentrations. Raw TiO₂ is considered as pure TiO₂ without doping additional dopants. In the visible light region, Degussa P25 (anatase-to-rutile ratio 75:25) showed higher conversion rate than raw TiO₂ (anatase phase) because the rutile phase acted as an antenna to extend the photoactivity into visible wavelengths.²⁹⁾ Although rutile TiO₂ could enhance the absorption region, it also increased the carrier-recombination rate, which resulted in low activity.³⁰⁾ As a result, the modified photocatalysts are all prepared in the anatase phase. Based on the XRD analysis, only the samples of this experiment in anatase are found in the modified photocatalysts. The results indicate that photocatalytic activities of TiO₂ are greatly improved by doping

nitrogen. In order to specify the effect of the dopant concentration of N-doped TiO₂ on the photocatalytic activities, the different values of nitrogen ratio were carried out and compared with that of raw TiO₂. In this experiment, no correlation between N-concentration and photocatalytic activity was observed.

Figure 9(b) shows the photocatalytic conversion of methanol over different weight ratios of MWCNTs–TiO₂ from 2.5% to 30% under the visible light irradiation. It is obvious that raw TiO₂ and MWCNTs show little photocatalytic activity, about 7.0% and 0%, respectively. However, the conversion of MWCNTs–TiO₂ composite photocatalyst is around 57.5%, which exhibits good activity compared to raw TiO₂ and MWCNTs owing to synergetic effects between the metal oxides and carbon phases. The synergetic effect of MWCNTs on the activity of the composite photocatalyst can be ascribed to photosensitizer.^{15),16),18)} The introduction of MWCNTs into the composite photocatalyst provides an apparent effect on optical properties as the amount of additive. The increase of weight ratio from 2.5% to 20% favors the photocatalysis ascribed that MWCNTs act as photosensitizer enhancing absorption in the visible range. The decrease in activity with higher weight ratio is considered to be related to the shielding of photos by MWCNTs,^{31)–33)} and the unsuitable band gap also reduces the yield of hydroxyl radicals.

3.4. Comparison of composite photocatalyst with anion-doped TiO₂

Table 1 lists the properties of MWCNTs–TiO₂ and N-doped TiO₂, both with anatase phases and with all crystallite sizes around 8 nm. The presence of MWCNTs can efficiently inhibit the agglomeration of the TiO₂ nanoparticles, so that the composite possesses more active sites than that of N-doped TiO₂. Although MWCNTs–TiO₂ shows larger specific surface areas, the photocatalytic activity is lower than TiO_{2-x}N_x which might be due to the different routes of visible-light-driven photocatalysis.

Based on the characterizations (Table 1), there are sufficient reasons to attribute the different activities to the quantum efficiency. According to the photocatalytic activities, anion-doped TiO₂ is better than composite photocatalyst owing to its high quantum efficiency. That is to say, anion-doped TiO₂ directly narrows the band gap through the mixture of anion dopants to form a new energy band (Fig. 1(a)), which reveals a higher activity than composite photocatalyst. The low activity of the composite photocatalyst can be explained by the fact that the composite semiconductor decreases the efficiency of electron transfers between photosensitizer and TiO₂ phases, or because photosensitizer cannot effectively induce the electron of the valance band of TiO₂ to photosensitizer to form positive holes (Fig. 1(b)). As a result, anion-doped TiO₂ exhibits higher photocatalytic activity than composite photocatalyst.

4. Conclusions

It is effective to keep the N-doped TiO₂ (anion doped type) and

Fig. 9. Conversion rate of (a) different nitrogen concentrations of N-doped TiO₂ and (b) different weight ratios of MWCNTs–TiO₂.

Table 1. Characterization of N-doped TiO₂ Photocatalysts and MWCNTs–TiO₂ Composite Photocatalyst

Catalytic type	Crystal phase	Crystallite size	Specific surface areas	Conversion
TiO _{2-x} N _x	Anatase	8.4 nm	133 m ² /g	83.8%
MWCNTs–TiO ₂	Anatase	7.6 nm	153 m ² /g	57.5%
Degussa P25	A:75% R:25%	30 nm	55 m ² /g	23.9%

the MWCNTs–TiO₂ (composite photocatalyst type) with the same crystallite size by controlling pH value of sol during the sol–gel process. The results indicated that a low pH values show the fine crystallite size around 8 nm. Both of the N-doped TiO₂ and MWCNTs–TiO₂ are mainly in the anatase phase by calcining at 350°C. In anion doped type, the current work is no correlation between nitrogen-concentration and photocatalytic activity.

Previous studies have indicated that anion-doped TiO₂ was higher than cation-doped TiO₂ in photocatalytic activity; however, studies on composite photocatalysts are rare. The primary objective of the research was to investigate the efficiencies of various types of visible-light-driven photocatalysts and to find out the superior visible-light-driven photocatalysts for further modification and commercial exploitation. The experimental results showed that anion-doped TiO₂ exhibited higher photocatalytic activity than composite photocatalyst under visible light irradiation. It is possible that anion-doped TiO₂ directly forms a new energy band, which was needlessly induced to form electron/hole pairs by photosensitizers, revealing high activity. As a result, anion-doped TiO₂ demonstrated the superior potential for commercializing visible-light-driven photocatalysts owing to their (i) high activity, (ii) non-toxicity, and (iii) low cost for modification.

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