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Synergistic effect of N- and F-codoping on the structure and photocatalytic performance of TiO₂

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ARTICLE INFO

Article history:
Received 6 March 2014
Revised 4 June 2014
Accepted 13 June 2014
Available online 13 December 2014

Keywords:
TiO₂ hydrolysis
Anion doping
Photocatalyst
Nanoparticle

ABSTRACT

Three types of TiO₂ nanostructures were synthesized via a facile hydrolysis method at 195 °C. Effects of the preparation method and doping with N and F on the crystal structure and photocatalytic performance of TiO₂ were investigated. The nanomaterials were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, Brunauer-Emmett-Teller porosimetry, ultraviolet-visible diffuse reflectance spectroscopy and fluorescent emission spectra. Their photo-catalytic activity was examined by the photodegradation of methylene blue in aqueous solution under both ultra-violet and visible light irradiation. The results show that nitrogen and fluorine co-doped anatase TiO₂ had the characteristics of a smaller crystalline size, broader light absorption spectrum and lower charge recombination than pure TiO₂. Most importantly, more efficient photocatalytic activity under both ultra-violet and visible light was observed. The obtained N–F-TiO₂ nanomaterial shows considerable potential for water treatment under sunlight irradiation.

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Introduction

Over the past decades, TiO₂ has been widely used to treat water pollutants due to its low cost, nontoxicity, good stability and high photocatalytic activity. However, photocatalysis using TiO₂ usually requires ultraviolet light due to its large energy band gap (e.g., ~3.2 eV for anatase TiO₂), which limits its utilization under solar radiation in the decomposition of organic pollutants. In addition, severe recombination of photo-generated electron–hole pairs in TiO₂ restricts its large-scale application as well.

Extensive studies aimed at the production of efficient and visible-light responsive TiO₂ using simple methods have proved to be one of the most effective methods. The doped atoms can enter the lattice of TiO₂ or disperse on its surface, which could potentially affect the electronic structure and narrow the bandgap of TiO₂. TiO₂ doped with nonmetallic elements such as N, F, B and I has been successfully synthesized, and performed well under visible light irradiation (Wang et al., 2008; Sannino et al., 2013; Hirano and Sato, 2013). Doping of TiO₂ with metallic elements such as Fe, V and Cr has also been observed to result in higher photocatalytic activity than that of the pure TiO₂ under visible light irradiation (Zhang et al., 2012; Zheng et al., 2011; Zhang et al., 2010; Kuo et al., 2011). Zhang and Liu (2008) found that (N,Ni)-co-doped TiO₂ synthesized via a modified sol–gel method showed excellent photocatalytic activity under visible light illumination. Tryba et al. (2006) prepared Fe-C-TiO₂ nanoparticles by calcining a mixture of TiO₂ and FeC₂O₄, achieving much higher photocatalytic activity in phenol degradation than unmodified TiO₂. Liu and Chen (2008) prepared an S-doped TiO₂ photocatalyst using thiourea as the sulfur source to achieve good visible light activity in phenol degradation as well. Fan et al. (2010) and Zhang et al. (2010) also claimed positive effects of S doping on the photocatalytic properties of TiO₂ under visible light irradiation. Although the photocatalytic performance of TiO₂ has been enhanced to some extent, some critical problems remain unsolved. For example, the element doping techniques used for the TiO₂ catalysts are complicated and expensive, and the problems of large bandgap and severe recombination of electron–hole pairs have not been solved completely.

In this work, anatase TiO₂, rutile TiO₂ and anatase (N, F)-co-doped TiO₂ were prepared with a simple hydrolysis method at a low temperature, and were characterized in detail by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) porosimetry, diffuse reflectance UV–vis spectra (DRS) and fluorescent emission spectra (FES). Via the photodegradation of methylene blue (MB) in aqueous solutions, the photocatalytic activity of (N, F)-codoped TiO₂ and pure TiO₂ (in anatase and rutile phases) was investigated in detail.

1. Experimental

1.1. Synthesis of TiO₂ nanostructures

TiO₂ was synthesized by a simple hydrolysis method. Hydrochloric acid at 6.0 mol/L was added dropwise into a mixture of tetrabutyl titanate (Ti(OC₄H₉)₄) and ethylene glycol. After magnetic stirring for 10 min, three reaction mixtures were prepared with addition of the following chemicals: (1) absolute ethyl alcohol, (2) deionized water, (3) ammonium chloride and urea. The three different mixtures were heated to 195 °C, and maintained for 10 hr in a 50 mL reaction kettle. The obtained powders were thoroughly washed with deionized water and ethanol, and finally dried at 100 °C for 3 hr. Three types of TiO₂ samples, anatase TiO₂, rutile TiO₂ and (N, F)-co-doped TiO₂ in the anatase phase were obtained, which were denoted as A-TiO₂, R-TiO₂ and N–F-TiO₂, respectively.

1.2. Sample characterization

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained on a Philips Technai 20U-TWIN equipment (PHILIPS, Netherlands) transmission electron microscope with a linear resolution of 0.14 nm and a dot resolution of 0.19 nm. X-ray diffraction (XRD) measurements were taken on a Bruker D8 Advance X-ray diffractometer (BRUKER, Germany) (40 kW, 40 mA) using Cu Ka1 radiation (λ = 0.154 nm) in the 2θ range of 10° to 80°. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALABMKII X-ray photoelectron spectrometer (VG Scienta, USA) equipped with a monochromatic Al Ka X-ray source (1486.6 eV). The pressure in the chamber during the measurements was about 1 × 10⁻⁸ Pa. The analyzer was operated at a pass energy of 50 eV for high resolution scans and at a pass energy of 100 eV for survey scans. The binding energy of the C 1s peak at 284.6 eV was taken as a reference for the binding energy calibration. Background subtraction and peak fitting were done using an XPS peak fit program: (XPSPEAK41 by Prof. R. W. M. Kwok). Brunauer–Emmett–Teller (BET) tests were performed by a NAVA 2000e surface area analyzer (Quantachrome, USA) with nitrogen as an adsorbative gas. UV–vis diffuse reflectance spectroscopy (DRS) spectra of samples in the wavelength range of 200 to 800 nm were obtained on a UV-3101PC spectrophotometer: (SHIMADZU, Tokyo, Japan) using BaSO₄ as a reference. Fluorescent emission spectra (FES) of samples were made on a British FL5920 Steady/transient fluorescence spectrometer: (EDINBURGH, Edinburgh, England) with a slit width of 2.5 nm and a multiplication voltage of 700 V.

1.3. Photocatalytic measurements

The photocatalytic activity of all the samples was evaluated by the photodegradation of methylene blue (MB) in aqueous solutions under UV and visible light illumination, separately. Three 250 mL beakers were used as reactors, each containing 150 mL of 0.01 mmol/L MB solutions and a certain amount of the TiO₂ samples. The suspensions were magnetically stirred in the dark for 30 min to establish a MB adsorption/desorption equilibrium on the TiO₂. Then the photodegradation of MB in aqueous solution was carried out in ambient conditions under UV–vis light irradiation (250 nm < λ < 400 nm) and visible light (λ > 400 nm with a UV filter) from a 300 W high pressure–mercury lamp. The MB solution was stirred throughout the
process, and the MB was proved to be stable with or without UV or visible light illumination without the addition of catalysts. The distance from the lamp to the surface of the solution was 15 cm. For each reaction, at designated time intervals, six milliliter aliquots were withdrawn from the suspensions, which were centrifuged at 5000 r/min for 5 min. Then the concentrations of MB in the solutions were measured by monitoring the intensity of the peak of 664 nm, via a 722E spectrophotometer: (Shanghai INESA instrument co. LTD., Shanghai, China). The removal efficiency, $P$, was expressed as: $(C_0 - C_t) / C_0 \times 100\%$, where $C_0$ is the initial concentration of MB, and $C_t$ is the concentration at reaction time $t$ (Yu et al., 2011).

2. Results and discussion

The morphology of the three different TiO$_2$ samples was characterized by TEM and the results are shown in Fig. 1. As demonstrated in Fig. 1a and e, the particles of A-TiO$_2$ and
N–F–TiO$_2$ are nearly cubic in shape, while Fig. 1c shows that R–TiO$_2$ particles have a rod-like shape with a width of 20 nm and a length of 50–100 nm. As can be seen, the average size of the particles in N–F–TiO$_2$ (5–10 nm) is smaller than that of the particles in A–TiO$_2$ (18–23 nm) and R–TiO$_2$ (20–100 nm), indicating that the N and F dopants could inhibit the growth of the TiO$_2$ crystallites. Though agglomeration of the nanoparticles of N–F–TiO$_2$ was observed, the grain boundaries could be clearly distinguished. In addition, the lattice fringes of the nanoparticles can be clearly observed (Fig. 1b, d and f), suggesting the high crystallinity of these nanoparticles. From the fringes, the parallel interplanar spacing (d) of crystallites in A–TiO$_2$ and N–F–TiO$_2$ was estimated to be 0.35 nm, corresponding to the (101) crystal plane of anatase TiO$_2$. In contrast, the parallel interplanar spacing of 0.32 nm for the rutile (110) crystal plane was found for nanoparticles in R–TiO$_2$, demonstrating the presence of rutile TiO$_2$ in this sample.

Based on TEM results, it appeared that different phases of TiO$_2$ may exist in the three samples. The X-ray diffraction (XRD) results of the samples are shown in Fig. 2. The diffraction peaks of anatase TiO$_2$ are observed for A–TiO$_2$, without any diffraction peaks assignable to rutile TiO$_2$. Likewise, only anatase TiO$_2$ crystallites are observed in N–F–TiO$_2$ because all XRD peaks of this sample can be indexed to anatase, which reveals that the N and F doping promoted the formation of anatase. However, the width of the diffraction peaks of N–F–TiO$_2$ is greater than that of A–TiO$_2$, which would be caused by the decreased particle size. Additionally, it is assumed that the relatively broader XRD peaks of anatase in N–F–TiO$_2$ than in A–TiO$_2$ likely resulted from the entrance of dopant atoms into the crystal lattice of TiO$_2$, based on some previous reports. Lv et al. found that N atoms are uniformly doped into the lattice to form N–Ti–O bonds, rather than being distributed on the surface of TiO$_2$ crystals (Lv et al., 2011). Wang et al. (2011) also pointed out that N atoms are interstitially and substitutionally doped into TiO$_2$ lattices to form Ti–N–O, Ti–O–N and O–Ti–N bonds. Since N ions are larger than O ions, the presence of N ions in TiO$_2$ results in expansion and distortion of the crystal lattice (Jiang et al., 2011). Hence, we further calculated the cell parameters of the TiO$_2$ lattices of our three samples (Table 1). The lattice parameters of the three TiO$_2$ samples (Table 1) are 0.3789 nm/0.3789 nm/0.9512 nm (a/b/c) for A–TiO$_2$, 0.4593 nm/0.2951 nm/0.2951 nm (a/b/c) for R–TiO$_2$ and 0.3789 nm/0.3789 nm/0.9537 nm (a/b/c) for N–F–TiO$_2$; meanwhile, the parallel interplanar spacing (d) of the crystallites in A–TiO$_2$, R–TiO$_2$ and N–F–TiO$_2$ was calculated to be 0.3520, 0.3251 and 0.3251 nm, corresponding to the (101), (110), and (101) crystal planes of the three TiO$_2$ samples, respectively. These results are in good agreement with the TEM results. In R–TiO$_2$, the diffraction peaks of both anatase and rutile TiO$_2$ are found, and the rutile phase is clearly dominant because of the much stronger (110) rutile peak than (101) anatase peak. The relative content of rutile (X$_{R}$) could be calculated from the XRD patterns by the formula below.

$$X_R = \frac{100}{1 + \frac{i_{110}}{i_{101}}}$$  \hspace{1cm} (1)

where, $i_{101}$ and $i_{110}$ are the intensities of the (101) and (110) peaks, respectively. There is no observable rutile phase in A–TiO$_2$ and N–F–TiO$_2$, but the content of rutile phase is 98.8% in R–TiO$_2$. By the Scherrer formula (Liu and Chen, 2008), the crystalline size is 22.6 nm for A–TiO$_2$, 41.5 nm for R–TiO$_2$, and 9.2 nm for N–F–TiO$_2$, respectively (Table 1). The calculated particle sizes are in agreement with those observed in the TEM images.

The X-ray photoelectron spectroscopy (XPS) tests were performed to determine the chemical states and atomic concentrations of the constituent elements. As shown in Fig. 3, the samples of A–TiO$_2$ and R–TiO$_2$ predominantly contain Ti and O, and the sample of N–F–TiO$_2$ contains predominantly Ti, O, N, and F. This clearly proves that nitrogen and fluorine elements were successfully doped into TiO$_2$. The signal of carbon, which is seen in all samples, comes from contamination of the test environment. The peaks of 459 eV, 530 eV, 400 eV, 685 eV and 285 eV correspond to the binding energies of Ti 2p, O 1s, N 1s, F 1s and C 1s respectively (Mirabos et al., 2012). The high resolution N 1s and F 1s XPS spectra of the N–F–TiO$_2$ sample are shown in Fig. 4a and b. As shown in Fig. 4a, the peak of 396–404 eV is attributed to the nitrogen dopant, the two peaks corresponding to 399.3 eV and 404 eV in N–F–TiO$_2$ and R–TiO$_2$, respectively (Table 1). The F1s XPS spectra for N–F–TiO$_2$ and its fitting curves are shown in Fig. 4b. Two peaks were obtained based on the fitting of high resolution F 1s XPS spectra. The two peaks centered at 683.6 and 684.3 eV are assigned to oxyfluoride and F–Ti–O, respectively. The atom radius of F is similar to that of O, so that it substitutes for O in

<table>
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<tr>
<th>Sample</th>
<th>Crystal size (nm)</th>
<th>d (nm)</th>
<th>Lattice parameter (nm)</th>
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</thead>
<tbody>
<tr>
<td>A–TiO$_2$</td>
<td>22.6</td>
<td>0.3520 (101)</td>
<td>0.3789 0.3789 0.9512</td>
</tr>
<tr>
<td>R–TiO$_2$</td>
<td>41.5</td>
<td>0.3251 (110)</td>
<td>0.4593 0.2951 0.2951</td>
</tr>
<tr>
<td>N–F–TiO$_2$</td>
<td>9.2</td>
<td>0.3521 (101)</td>
<td>0.3789 0.3789 0.9537</td>
</tr>
</tbody>
</table>
some crystal lattices. The doped F atoms are directly connected to Ti atoms in the TiO₂ lattice and thus enhance the photocatalytic activity of the N–F-TiO₂ catalyst in the visible region (Li et al., 2011).

Based on TEM and XRD analysis, our three samples were found to be composed of TiO₂ crystallites of different sizes, and thus their specific surface areas should to be different. Fig. 5 presents the N₂ adsorption–desorption isotherms of the three TiO₂ samples. Their specific surface areas calculated from the BET equation are 47.3 m²/g for A-TiO₂, 33.8 m²/g for R-TiO₂, and 124.6 m²/g for N–F-TiO₂, respectively. The third sample has the largest specific surface area, consistent with the small size of the nanoparticles in the N–F-TiO₂ samples. Because the surface area plays an important role in heterogeneous catalytic reactions, excellent photocatalytic behavior for N–F-TiO₂ also could be anticipated.

According to the above characterization results, it can be deduced that N and F have been successfully doped into the lattice of TiO₂. Theoretically, N–F-TiO₂ shows response not only to incident light with a wavelength less than 387 nm, but also to visible light (Nguyen et al., 2003). UV–vis diffuse reflectance spectra (DRS) were measured to study the light absorption of undoped and doped TiO₂ (Fig. 6).

It is well known that the bandgap of anatase TiO₂ is 3.2 eV, and electrons in the valence band can be excited by incident photons with a wavelength below 387 nm (Kormann et al. 1988; Cao et al. 2010). Fig. 6 reveals that only N–F-TiO₂ shows a clear absorption in the visible light region, indicating that the bandgap has been narrowed due to the doping by N or F into the lattice. It is proposed here that the absorption in the visible light region is solely attributed to the doped N. The Fermi level is 5.83 eV for TiO₂ and 3.76 eV for N-TiO₂ (Wei et al., 2011). As the Fermi level (HOMO) drops, the bottom of the conduction band (LOMO) falls simultaneously to narrow the bandgap of TiO₂ and yield response to visible light (Wei et al., 2011). Irie et al. (2003) reported that in the TiO₂ lattice, N atoms could replace the O atoms to form a isolated narrow band in the valence band, and the impurity level was the main reason for the visible absorption of N-TiO₂. Asahi et al. (2001) concluded that the mixed orbital state was formed by replacing O 2p orbitals with N 2p orbitals, which formed Ti–N bonds and narrowed the TiO₂ bandgap (Li et al., 2005). On the other hand, the F atoms are doped into the surface of TiO₂ and mainly in the form of TiOF₂. The surface fluorination or formation of a surface fluorine compound was an important factor in the improvement of the photocatalytic performance of TiO₂ (Sun et al., 2011).

The red shift of the absorption edge of N–F-TiO₂ implies a decrease in the bandgap energy, which can be calculated by the Kubelka–Munk formula (Fang et al., 2007; Liu et al., 2008). The calculated results show that the bandgap of A-TiO₂ is 3.19 eV, in correspondence with anatase TiO₂, and the bandgap of R-TiO₂ is 3.11 eV, in accord with rutile TiO₂. The smallest bandgap is 2.75 eV for N–F-TiO₂, indicating a reduction in bandgap energy due to N and F atoms doped into the TiO₂ lattice.

The recombination rate of photo-generated electrons and holes also affects the photocatalytic activity of TiO₂, and this recombination yields detectable fluorescence emission, which provides a way to study the recombination process. A low fluorescence emission intensity indicates lower electron–hole recombination rates (Cai et al., 2007; Chen et al., 2008). The fluorescence emission spectra (FES) of the three samples are
shown in Fig. 7. The A-TiO$_2$ sample produces higher emission intensity than R-TiO$_2$, which means that the electrons and holes more easily recombine in the former than in the latter. It is seen that the fluorescence emission intensity of N–F–TiO$_2$ is the lowest, suggesting the N, F co-doped anatase TiO$_2$ has the smallest electron–hole recombination rate. This may be ascribed to the fact that doping with N and F in TiO$_2$ successfully inhibits the recombination of electrons and holes (Yang et al., 2013).

The photocatalytic activity of the three samples was evaluated by the photodegradation of MB in aqueous solutions under both UV and visible light irradiation. The degradation rates under UV light irradiation are presented in Fig. 8a. It can be seen that N–F–TiO$_2$ exhibits the highest catalytic efficiency of all the samples, and the MB is almost completely decolorized within 70 min. For A-TiO$_2$, lower photocatalytic activity could be observed and the MB in solution could be fully decomposed within 100 min. The high photocatalytic activity of these two samples is partially due to their small crystallite size, high specific surface area and anatase phase. The photocatalytic activity of R-TiO$_2$ is the worst of all the samples. The decolorization rate of MB is only 50% within 100 min, which should be attributed to the poor catalytic ability of the rutile phase (Hirano et al., 2003). From Fig. 8b, it can be deduced that the photocatalytic degradation of MB under UV light irradiation is a first-order reaction for all 3 catalysts. The degradation of MB follows the Langmuir–Hinshelwood model. The reaction rate constants ($k$) of the three reactions for N–F–TiO$_2$, R-TiO$_2$ and A-TiO$_2$ are 6.03 × 10$^{-2}$, 0.701 × 10$^{-2}$, and 4.85 × 10$^{-2}$ min$^{-1}$, respectively. The N–F–TiO$_2$ shows the highest photocatalytic activity of all the 3 kinds of TiO$_2$ under UV light.

The degradation results of all the samples under visible light irradiation are displayed in Fig. 9a. It can be observed that MB is barely decomposed by A-TiO$_2$ and R-TiO$_2$ under visible light irradiation, which agrees with the DRS results showing that the two samples show no response to visible light. In contrast, the N–F–TiO$_2$ exhibits significantly better performance in MB degradation under visible light, as evidenced by about 17% decomposition within 200 min.

Fig. 5 – N$_2$ adsorption–desorption isotherms of three TiO$_2$ samples.
Several reasons could account for the superior catalytic properties of N–F-TiO₂: (1) The N–F-codoped TiO₂ shows better response to visible light; (2) According to FES analysis, more charge separation sites should emerge in the N–F-TiO₂ sample, which greatly reduce the recombination of photo-generated electron–hole pairs (Xu et al., 2008); (3) The smaller crystallite size of N-F-TiO₂ should facilitate the rapid charge transfer from the bulk to the surface, which decreases the loss of charge in electron–hole recombination. Based on Fig. 9b it is also deduced that the degradation of MB under visible light is a first order reaction. The MB degradation by N-F-TiO₂ under visible light irradiation is in good agreement with the Langmuir–Hinshelwood model. All the reaction rate constants of the three samples are illustrated in Fig. 10. It is calculated that the reaction rate constant is $4.85 \times 10^{-2}$ min⁻¹ for A-TiO₂, $0.701 \times 10^{-2}$ min⁻¹ for R-TiO₂ and $6.03 \times 10^{-2}$ min⁻¹ for N-F-TiO₂ under UV irradiation, and 0 min⁻¹ for A-TiO₂, $0.0202 \times 10^{-3}$ min⁻¹ for R-TiO₂ and $0.968 \times 10^{-3}$ min⁻¹ for N-F-TiO₂ under visible light irradiation, respectively. This means that the photocatalytic activity of N-F-TiO₂ is superior to that of A-TiO₂ and R-TiO₂, especially under visible light irradiation. The enhanced photocatalytic activity indicates that N and F have been doped into the lattice of TiO₂, narrowing its bandgap and inhibiting the recombination of photogenerated electron–hole pairs.

3. Conclusions

In this work, we have demonstrated a simple hydrolysis method to prepare A-TiO₂, R-TiO₂ and highly efficient visible-light-driven N–F-TiO₂ photocatalysts. The N and F dopants inhibited the growth of TiO₂ crystals and promoted the formation of anatase TiO₂. Under UV light irradiation, both the TiO₂ (anatase) and the N-F-co-doped TiO₂ samples showed considerably high photoactivity, whereas the rutile TiO₂ sample displayed relatively low photoactivity. The N–F-TiO₂ nanoparticles showed stronger visible-light photocatalytic activity in degradation of MB than the other samples. The N-F-codopants could narrow the bandgap of TiO₂ and hinder the recombination of photo-generated electron–hole pairs, which made it active to visible light and increased the photo quantum efficiency. The above results suggest that the
obtained N-F-TiO₂ nanomaterial could perform as a potential visible-light-driven photocatalyst in water treatment under sunlight irradiation.

Acknowledgments

This work was financially supported by the Natural Science Foundation of China (No. 51376110), the Natural Science Foundation of Shandong Province (No. ZR2012BQ027), the Program for Youth Science and Technology Star Fund of Jinan (No. 20120123), the Excellent Young Scientist Foundation of Shandong Province (No. ZR2012BQ027), and the Program for Youth Science and Technology Star Fund of Shandong Province (No. ZR2012BQ027).

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