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Facile synthesis of C-decorated Fe, N co-doped TiO₂ with enhanced visible-light photocatalytic activity by a novel co-precursor method

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ABSTRACT

Lattice-doping and surface decoration are prospective routes to improve the visible-light photocatalytic ability of TiO₂, but the two techniques are difficult to combine into one preparation process because they are usually conducted under different conditions, which limits the efficiency of TiO₂ modification. In this study, TiO₂ was successfully modified by simultaneous lattice-doping and surface decoration, and the visible-light photocatalytic capacity was largely improved. Upon comparing the method reported here with previous ones, the most significant difference is that Fe(II)-phenanthroline was first used as the co-precursor of the introduced elements of C, N, and Fe. These three elements were simultaneously introduced to TiO₂ at high levels by this co-precursor method. The as-synthesized photocatalysts were systemically investigated and analyzed by several characterization methods such as XRD, FT-IR, XPS, Raman spectroscopy, EPR, UV-Vis DRS, photoluminescence spectra, photocurrent, electrochemical impedance spectra, TEM, and HRTEM. The photocatalytic degradation of 4-NP under visible-light irradiation was used to evaluate the photocatalytic activity of the photocatalysts. Based on the experimental data, a probable mechanism for the photocatalytic degradation by the photocatalysts is proposed. This is a novel method of using one source to simultaneously introduce metal and non-metal elements to TiO₂ at high levels, which may provide a new way to prepare highly effective TiO₂ photocatalysts.

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1. Introduction

Many efforts have been made to improve the visible-light photocatalytic capacity of TiO₂, mainly by changing two properties: narrowing the band gap and suppressing the recombination of photogenerated electron-hole pairs [1–4]. Of the

mentioned efforts, lattice and surface decoration are two important methods.

Lattice-doping is a method by which elements are doped into the TiO₂ lattice. This doping can sometimes create new

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conduction and valence bands that are narrower than the inherent ones of TiO_2 , resulting in a narrower band gap and improving the visible-light photocatalytic ability [5–11]. Metal elements and non-elements are usually used as dopants. Fe is a commonly used metal dopant because its ionic radius ($0.68 \text{ \AA}$ ($1 \text{ \AA} = 0.1 \text{ nm}$)) is nearly the same as that of Ti^{4+} ($0.64 \text{ \AA}$). Therefore, Fe^{3+} can be conveniently integrated into the TiO_2 matrix; moreover, its stable half-filled d^5 configuration can act as a charge-carrier trap and inhibit the recombination of photogenerated electron-hole pairs [7,12]. N is an important non-metal dopant, and because of its comparable atomic size to O, small ionization energy, metastable center formation, and stability, the substitution of N can alter both the electronic properties and structure of TiO_2 , which can enlarge the light-response range and accelerate the transfer of charge carriers [13]. Therefore, Fe and N were taken as the two dopants in this study.

Surface decoration is another technique used to improve the photoactivity of TiO_2 . It is different from lattice-doping because the introduced elements decorate the surface of TiO_2 but do not enter the TiO_2 lattice. Several studies have reported that surface C decoration can significantly improve the photocatalytic capacity of TiO_2 . For example, Wang *et al.* [14] reported that C materials modified on the TiO_2 surface can act as trapping centers to adsorb photogenerated electrons, which resulted in the acceleration of photogenerated electron-hole pair separation. Zabeck *et al.* [15] reported that surface C materials can play the role of sensitizers to sensitize TiO_2 , which enhanced TiO_2 catalytic activity under visible-light irradiation. Therefore, C was chosen as the surface decoration element for this study.

However, lattice-doping and surface decoration are difficult to combine into one preparation process, which limits the efficiency of TiO_2 modification to some extent. The main reason for this bottleneck is that C surface decoration is usually conducted under relatively mild conditions [14–16], while Fe, N-doping is always carried out under harsher conditions, such as calcination [17]. In order to search for clues to help solve this problem, we investigated the precursors of introduced elements in previous reports. We found that, most of the time, different substances were used as the respective sources for the different introducing elements. For example, Yu *et al.* [16] used graphite

Fig. 1. Structures of phenanthrene, phenanthroline, and Fe(II)-phenanthroline.

as the C source to prepare C quantum dot surface-modified TiO_2 . Larumbe *et al.* [17] used $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and urea as the sources of Fe and N, respectively, which were used to prepare Fe, N co-doped TiO_2 . It is known that strong interactions among different elements may result in synergistic effects. Based on this consideration, a co-precursor of lattice doping and surface-decorating elements was used in this study. That is to say, the elements that would be introduced into the TiO_2 lattice and onto the TiO_2 surface were contained into one molecular with chemical bonds among them. It was hoped that the synergistic effects among them would be helpful for the simultaneous lattice-doping and surface decoration of TiO_2 . A Fe(II)-phenanthroline complex was used as the co-precursor molecule in this study. Phenanthroline is an organic molecule containing C and N. Three phenanthrolines can coordinate with one Fe(II) to form a stable complex of Fe(II)-phenanthroline, whose structure is shown in Scheme 1 and Fig. 1. It can be seen that there are strong interactions among the elements of Fe, N, and C.

Four-nitrophenol (4-NP) was taken as the model contaminant by which to study the visible-light photocatalytic abilities of the as-prepared photocatalysts due to its recalcitrance [18] and high toxicity to the environment [19]. To the best of our knowledge, this is the first report where different elements, including metals and non-metals, were used to modify both the inner (lattice) and outer (surface) parts of TiO_2 by a common introducing source.

Scheme 1. Mechanism of formation of Fe, N co-doped TiO_2/C catalyst during preparation process.

2. Experimental

2.1. Catalyst preparation

All starting materials were obtained in an analytically pure form from Aladdin Chemical Reagent Co., Ltd., and used without further purification. Deionized water was used throughout this study. Scheme 1 illustrates the preparation procedure. In a typical synthesis, 0.06 g of phenanthroline (phen), 0.03 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 20 mL of ethanol, and 3 mL of titanium tetrabutoxide (TBOB) were mixed together and stirred for 40 min to form a uniform solution. In this case, the molar ratio of phen versus TBOB (denoted R) was 0.036. Then, 50 mL of deionized water was added dropwise, and the solution was continuously stirred for another 1 h. Then, the mixture was transferred to a Teflon[™]-lined stainless-steel autoclave and maintained at 180 °C for 24 h. After the mixture was slowly cooled to ambient temperature, the formed precipitant was collected by vacuum filtration and washed with deionized water and absolute ethanol in turn, and then dried at 80 °C for 4 h. Next, the product was calcined at 300 °C for 4 h. This product was denoted Fe, N co-doped TiO_2/C . For comparison, a TiO_2 -based nanocomposite with Fe, N, and C introduced by using respective sources was synthesized as a control using a similar process as follows. The structure of phenanthrene is similar to that of phenanthroline but does not contain N (the structures of phenanthrene, phenanthroline, and Fe(II)-phenanthroline are shown in Fig. 1). Phenanthrene was used as the source of C in the control. HNO_3 was used as the source of N [20]. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as the source of Fe. The molar ratios of C, N, and Fe versus TiO_2 were the same of those of Fe, N co-doped TiO_2/C . This control was denoted (Fe,N,C)- TiO_2 . Since this sample was prepared with respective sources of Fe, N, and C, it is obvious that there are no strong interactions among these elements when they are introduced to TiO_2 . In addition, N,C-modified TiO_2 (denoted N,C- TiO_2) was synthesized by adding only phenanthroline as a common source of N and C, and Fe-modified TiO_2 (denoted Fe- TiO_2) was synthesized by only adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as the source of Fe. The added amounts of the related sources were the same as those of Fe, N co-doped TiO_2/C . Bare TiO_2 was also prepared by the method described above without the addition of C, N, and Fe sources. For all these samples, their ability to photo degrade 4-NP was tested under visible-light irradiation.

2.2. Characterization

X-ray diffraction (XRD) patterns (Siemens D5000) were recorded on a D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation from 10° to 70° at a scan rate of 0.02°/s. Fourier transform-infrared spectroscopy (FT-IR) analyses were conducted on a Nicolet 380 (USA) instrument in the range 4000–400 cm^{-1} . The powders were analyzed by a scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS; FEI Quanta 200) at a pressure <5.0 MPa and an accelerating voltage of 20.00 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB 210 XPS system with a $\text{Mg K}\alpha$ (1253.6 eV) source. Ultraviolet-visible (UV-Vis) ab-

sorption spectra were obtained by UV-Vis diffuse reflectance spectrophotometry (Lambda 900). Electrochemical impedance and Mott-Schottky curve analysis were performed on a CHI660C electrochemical workstation (Shanghai Chenhua, China) with a standard three-electrode at room temperature. Photoluminescence spectra (PL) were recorded on an F-7000 fluorescence spectrophotometer (Hitachi, Japan). Electron-paramagnetic-resonance (EPR) spectra were recorded on an E500 EPR spectrometer (Bruker, Germany).

2.3. Photocatalytic experiments

The photocatalytic activities of prepared catalysts were evaluated by degradation of 4-NP under visible-light irradiation. A 500-W Xe illuminator (Perfectlight, Beijing, China) was used as the light source. A 400-nm cut-off filter was placed between the Xe illuminator and the reactor to completely remove light of wavelength shorter than 400 nm to provide visible light. In each experiment, 70 mg of catalyst was added into 70 mL of 4-NP solution (10 mg/L) with stirring. Prior to illumination, the suspension was stirred for 30 min in the dark to establish an adsorption-desorption equilibrium between the catalyst and 4-NP. The suspension was then exposed to visible-light irradiation with magnetic stirring. At given time intervals, the suspension was sampled, and the solution was separated using a filter membrane to remove the photocatalyst particles. The concentration of 4-NP in the solution was monitored by its absorbance intensity at 320 nm.

3. Results and discussion

The influence of added amounts of Fe(II)-phenanthroline in the preparation of Fe, N co-doped TiO_2/C was investigated, and the results are shown in Fig. S1(a) in the Supplementary Information. The results indicate that when the molar ratio of phenanthroline versus TBOB (denoted R) is 0.036, the as-synthesized Fe, N co-doped TiO_2/C exhibits the best performance. Therefore, $R = 0.036$ is determined to be the optimal ratio, and all the Fe, N co-doped TiO_2/C samples discussed in this study refer to this product, unless otherwise noted (the molar ratios of Fe^{2+} versus phen were kept at 1:3 in any case because every Fe^{2+} ion can coordinate with three phenanthrolines). Moreover, the effects of calcination temperature on Fe, N co-doped TiO_2/C were also investigated, and the details are shown in Fig. S1(b). The optimal calcination temperature was determined to be 300 °C. The photocatalytic performances of all prepared TiO_2 -based catalysts with different sources of introduced elements were evaluated by the degradation of 4-NP. Fig. 2 shows the related kinetics data over the catalysts under visible light. It can be seen that the regression curve of the natural logarithm of normalized 4-NP concentration versus reaction time was approximately linear, indicating that the kinetics of 4-NP degradation over the photocatalysts can be considered to be pseudo-first-order:

$$-\ln(C/C_0) = kt$$

where C is the concentration of 4-NP (mg/L) at time t (min), C_0 the concentration of 4-NP at $t = 0$ (min), and k the reaction rate

Fig. 2. Photodegradation of 4-NP over the TiO₂-based catalysts prepared with different sources of introduced elements.

Table 1

Values of k and R^2 of 4-NP over all catalysts.

Sample	K (min ⁻¹)	R^2
Fe, N co-doped TiO ₂ /C	0.00963	0.9822
N,C-TiO ₂	0.00803	0.9883
(Fe,N,C)-TiO ₂	0.00188	0.9942
TiO ₂	0.00164	0.9960
Fe-TiO ₂	-0.000461	0.5429

constant (min⁻¹). The rate constant k can be determined from the slope of the linear plot. The correlation coefficient R^2 and k values of 4-NP over all the catalysts are shown in Table 1. From the small absolute value of k of Fe-TiO₂, one can find that this catalyst has no photocatalytic activity toward 4-NP under visible light, indicating that using FeSO₄·7H₂O as the source of Fe to prepare Fe-doped TiO₂ in these experimental conditions reduces the activity of TiO₂ (the reason for the activity reduction is analyzed in the following). Except for Fe-TiO₂, other catalysts all showed improved photocatalytic activities compared with bare TiO₂. The k value of Fe, N co-doped TiO₂/C is the highest (0.00963 min⁻¹), which is approximately 5.9 times that of bare TiO₂ (0.00164 min⁻¹). N,C-TiO₂ has the second-highest k value (0.00803 min⁻¹), which is approximately 4.9 times of that of bare TiO₂. It is notable that there is a similarity in the preparation process of these two samples with relatively high performance. Fe(II)-phenanthroline or phenanthroline was used as a common source of introduced elements. Therefore, there are strong interactions among/between the introducing elements when introducing them to TiO₂. The result indicates that the synergistic effects of introducing elements with strong interactions could significantly improve the photocatalytic performance of TiO₂.

Fig. 3 shows the XRD patterns of pure TiO₂ and TiO₂-based catalysts. The diffraction peaks of pure TiO₂ observed at 25.3°, 37.8°, 48.0°, 53.9°, and 62.7° are consistent with anatase TiO₂ (101), (004), (200), (105), and (204) lattice planes (JCPDS Card No. 21-1272), which are denoted A(101), A(004), A(200), A(105), and A(204), respectively, in Fig. 3. The samples of Fe, N co-doped TiO₂/C, and N,C-TiO₂ show an obvious additional

Fig. 3. XRD patterns of TiO₂-based photocatalysts prepared with different sources of introduced elements.

peak at $2\theta = 30.8^\circ$, which corresponds to the (121) plane of brookite TiO₂ (JCPDS Card No. 29-1360), denoted B(121). This indicates that a new phase structure of brookite TiO₂ appears in these two samples, along with anatase TiO₂ phase. The XRD pattern of (Fe,N,C)-TiO₂ shows a faint peak at approximately $2\theta = 30.8^\circ$, indicating that the brookite crystalline phase of TiO₂ is very weak in this sample. There is no obvious peak at approximately 30.8° in the XRD pattern of Fe-TiO₂, which means there is no brookite phase of TiO₂ in this sample. These results indicate that using a co-source of introducing elements is beneficial for forming brookite TiO₂, and results in a mixed phase of anatase and brookite TiO₂ in the photocatalysts. The changes of crystalline phases suggest the lattice doping of Fe/N; furthermore, it has been reported that the mixture of different crystalline phases may improve the possibility of forming junction structures, which could induce enhanced photocatalytic activity [21,22]. The crystallite sizes of TiO₂, Fe-TiO₂, (Fe,N,C)-TiO₂, N,C-TiO₂, and Fe, N co-doped TiO₂/C calculated by the Scherrer formula [23] based on these XRD data are found to be approximately 10.2, 9.4, 10.0, 10.4, and 9.3 nm, respectively.

The UV-Vis diffuser reflectance spectra (DRS) of as-synthesized photocatalysts are displayed in Fig. 4(a). It can be seen that the absorption edges of all the photocatalysts shift to higher wavelength, and the intensities are enhanced in the visible region compared to bare TiO₂. The one with the largest redshift is Fe, N co-doped TiO₂/C, the onset of absorption of which is at approximately 416 nm; that with the smallest redshift is Fe-TiO₂, whose onset of absorption is at approximately 401 nm. In comparison, the onset of absorption of TiO₂ is at approximately 387 nm. The absorption edges of all modified TiO₂ photocatalysts enter the visible-light region, indicating that all of the samples can absorb visible light. It is known that a redshift of absorption edge would mean a reduction in band-gap energy, which is very likely to enhance the photocatalytic efficiency [24]. The band gaps of all photocatalysts were estimated by the plot of $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 4(b) [25]. The band-gap energies of Fe, N co-doped TiO₂/C, (Fe,N,C)-TiO₂, N,C-TiO₂, Fe-TiO₂, and TiO₂ are 2.89, 2.92, 2.94,

Fig. 4. (a) UV-Vis diffuse reflectance spectra of the as-prepared catalysts; (b) Band-gap energy (E_g) of the as-prepared catalysts.

3.00, and 3.17 eV, respectively. Fe, N co-doped TiO₂/C has the narrowest band energy gap.

As the production of photogenerated holes and electrons is the base of the photocatalytic ability of photocatalysts, the separation of photogenerated electron-hole pairs is important [26,27]. The separation efficiency of the photogenerated electron-hole pairs was investigated by photoluminescence (PL) spectroscopy. As shown in Fig. 5, all of the modified TiO₂ exhibits lower PL intensity compared to bare TiO₂, implying those modifications could effectively suppress the recombination of electron-hole pairs. Fe, N co-doped TiO₂/C is found to be the sample with the most suppressed recombination because it shows the lowest PL intensity. Subsequently, the photocurrent generation and electrochemical impedance spectra (EIS) of synthesized modified TiO₂ and bare TiO₂ were obtained to study the electron-excitation and charge-transport properties. As shown in Fig. 6, it is found that the photocurrent generated by Fe, N co-doped TiO₂/C is significantly higher than those of other samples, indicating that more electrons are generated in Fe, N co-doped TiO₂/C under visible-light irradiation. It is notable that Fe-TiO₂ has the lowest photocurrent generation, even lower than bare TiO₂ (inset of Fig. 6), indicating doping of Fe into TiO₂ under these experimental conditions is disadvantageous for electron excitation. This is one of the important reasons that Fe-TiO₂ is inactive compared with bare TiO₂ in the

photodegradation of 4-NP (Fig. 2). This is not an isolated case. Some examples of bad photocatalytic performance caused by Fe-ion doping have also been reported by others [28–31]. There is an interesting phenomenon that should be investigated. The sample of Fe, N co-doped TiO₂/C can be approximately considered to be an Fe-doping sample of N,C-TiO₂ because the former has only one additional element of Fe compared with the latter, except that the two samples were prepared by nearly the same process. We can see from the above analysis of Fe-TiO₂ activity that Fe-doping can be disadvantageous for photocatalytic performance in these experimental conditions. However, one can see from Fig. 2 that Fe, N co-doped TiO₂/C is more active than N,C-TiO₂, indicating that Fe-doping is beneficial in this case. We should note that Fe was doped in Fe, N co-doped TiO₂/C by the Fe(II)-phenanthroline complex, while Fe was doped in Fe-TiO₂ by FeSO₄·7H₂O. These results indicate that the synergistic effects of elements in the Fe(II)-phenanthroline complex could overcome the shortcomings of introducing Fe by using FeSO₄. Fig. 7 shows the EIS Nyquist plot, and that of Fe, N co-doped TiO₂/C has the smallest arc radius. The smallest arc radius indicates the fastest interfacial charge-transfer properties, which favor the subsequent photocatalytic reactions [21].

Fig. 5. PL spectra of as-synthesized modified TiO₂ and TiO₂.

Fig. 6. Photocurrent response under visible-light irradiation of as-synthesized modified TiO₂ and bare TiO₂; Inset, magnification of part in dashed-line rectangle.

Fig. 7. Electrochemical impedance spectroscopy of as-synthesized modified TiO₂ and bare TiO₂.

The two modified TiO₂ catalyst samples of Fe, N co-doped TiO₂/C and (Fe,N,C)-TiO₂ both have been introduced with elements C, Fe, and N, but these elements were introduced in different ways. In preparation of Fe, N co-doped TiO₂/C, Fe(II)-phenanthroline was used as the common source of Fe, N, and C. There are strong interactions between/among these elements when introducing them to TiO₂. In preparation of (Fe,N,C)-TiO₂, FeSO₄·7H₂O, HNO₃, and phenanthrene were used as the source of Fe, N, and C, respectively. There are no strong interactions between/among these elements when introducing them in this preparation. Although the two samples were prepared with similar methods, except for the difference in element sources, Fe,N co-doped TiO₂/C is significantly more effective than (Fe,N,C)-TiO₂. It is obvious that the difference of element sources has a close relationship with the reactivities. In order to investigate how this source difference affects the catalyst reactivity, Fe,N co-doped TiO₂/C, (Fe,N,C)-TiO₂, and bare TiO₂ were studied by Mott-Schottky plots and XPS analysis. Based on the Mott-Schottky plots of Fe,N co-doped TiO₂/C, (Fe,N,C)-TiO₂, and bare TiO₂ (Fig. 8), the calculated flat-band potentials (V_{fb}) of Fe,N co-doped TiO₂/C, (Fe,N,C)-TiO₂, and bare

Fig. 8. Mott-Schottky plots of Fe, N co-doped TiO₂/C, N,C-TiO₂, and bare TiO₂; inset, band XPS spectra of Fe, N co-doped TiO₂/C and (Fe,N,C)-TiO₂.

TiO₂ are -0.56 , -0.40 , and 0.36 eV versus SCE, i.e., -0.32 , -0.16 , and -0.12 eV versus SHE, respectively. These three catalysts are *n*-type semiconductors due to the positive slopes of their Mott-Schottky plots. In general, as an *n*-type semiconductor, the flat-band potential is equal to its Fermi level, and the conduction-band (CB) potential is approximately 0.2 times more negative than its Fermi level [21,32,33]. Therefore, the E_{CB} of Fe,N co-doped TiO₂/C, (Fe,N,C)-TiO₂, and bare TiO₂ are -0.52 , -0.36 , and -0.32 eV versus SHE, respectively. According to E_g values estimated by the results of DRS (the E_g value of Fe,N co-doped TiO₂/C is 2.89 eV, that of (Fe,N,C)-TiO₂ is 2.92 eV, and that of TiO₂ is 3.17 eV), the valence-band potentials (E_{VB}) of Fe,N co-doped TiO₂/C, (Fe,N,C)-TiO₂, and bare TiO₂ are 2.37, 2.56, and 2.85 eV, respectively, according to the empirical formula $E_g = E_{VB} - E_{CB}$. The band structures were also confirmed using band XPS spectra (inset of Fig. 8), and the corresponding valence-band potentials (2.34 eV for Fe,N co-doped TiO₂/C and 2.58 eV for (Fe,N,C)-TiO₂) were consistent with those obtained from the Mott-Schottky plots.

High-resolution XPS spectra of C, N, Ti, and Fe were also used to study Fe,N co-doped TiO₂/C, (Fe,N,C)-TiO₂, and bare TiO₂. The results are shown in Fig. 9. The binding energies (BEs) of the Ti 2p_{3/2} and Ti 2p_{1/2} peaks for the as-synthesized bare TiO₂ are 458.78 and 464.43 eV (Fig. 9(a)), respectively, which are identical to the typical values of TiO₂. Compared with TiO₂, the BE values of the Ti 2p peaks of Fe,N co-doped TiO₂/C and (Fe,N,C)-TiO₂ show a 0.13- and 0.05-eV shift toward lower BEs, respectively. Ti-N bonds are formed by the lattice incorporation of N, which result in the partial replacement of O²⁻ with N³⁻. Because the electronegativity of N atoms is smaller than that of O atoms, this partial replacement induces an increase of electron density on Ti. As a result, partial Ti⁴⁺ will be reduced to Ti³⁺ and cause a decrease of Ti 2p BE. This indicates the existence of Ti³⁺ and further confirms that N is incorporated into the lattice of TiO₂, and O is partially substituted by the incorporated N [14]. Fe, N co-doped TiO₂/C exhibits more shifted BE values than (Fe,N,C)-TiO₂, suggesting more N doping in Fe, N co-doped TiO₂/C. Fig. 9(b) shows that the O 1s peak of Fe, N co-doped TiO₂/C can be fitted into two peaks at 530.00 and 531.90 eV. The lower BE peak at 530.00 eV is ascribed to O 1s in the Ti-O linkages of TiO₂ [34–36]. The shift of this peak compared with TiO₂ is mainly due to the introduction of O vacancies into the TiO₂ lattice [37]. Oxygen vacancies can trap photogenerated electrons and promote the separation of h⁺/e⁻ to enhance photocatalytic ability. The existence of O vacancies was further confirmed by EPR studies as described in the following. The weak peak at 531.90 eV can be ascribed to an OH group [38–40]. Moreover, there is no O 1s peak ascribed to NO_x species at approximately 533 eV, indicating there are no surface-adsorbed N species in Fe, N co-doped TiO₂/C [14]. The O 1s peak at 529.90 eV of (Fe,N,C)-TiO₂ shows less of a shift from that of TiO₂ compared to Fe, N co-doped TiO₂/C, indicating fewer O vacancies were introduced in this sample than in Fe, N co-doped TiO₂/C.

Three typical states of C species are evidenced by the C 1s spectra in Fig. 9(c). Three peaks at 285.08, 286.38, and 288.88 eV exist for Fe, N co-doped TiO₂/C, and three peaks at 284.88,

Fig. 9. XPS spectra of samples. (a) Ti 2p, (b) O 1s, (c) C 1s, (d) N 1s, (e) Fe 2p.

286.28, and 288.78 eV exist for (Fe,N,C)-TiO₂. The peaks at approximately 285 eV are the binding energies of the sp²-hybridized C [15,36,41,42]. The peaks at approximately 286 and 289 eV are assigned to C–O and C=O bands, respectively [15,36,43]. The shift of the C 1s peak between Fe, N co-doped TiO₂/C and (Fe,N,C)-TiO₂ is caused by the different amount of C in these two samples. The signal related to the C–Ti bond (~281 eV) is not found, indicating that C does not dope into the TiO₂ lattice for both Fe, N co-doped TiO₂/C and (Fe,N,C)-TiO₂ [15,44]. These results indicate that all C species are modified on the surface of Fe, N co-doped TiO₂/C. The carbonaceous layer can be formed on the surface of TiO₂ via Ti–O–C and Ti–OCO bonds [36,42]. Carbon modified on the surface can work as a surface sensitizer to adsorb visible light and promote charge-carrier separation by taking up photogenerated electrons [45,46]. The existence of surface C in Fe, N co-doped TiO₂/C is further confirmed by Raman and FT-IR spectra, and is discussed in the following.

Fig. 9(d) shows the N 1s spectra. Three peaks at approximately 399.50, 400.40, and 401.30 eV are observed for Fe, N co-doped TiO₂/C, and three peaks at 399.48, 400.08, and 401.28 eV are observed for (Fe,N,C)-TiO₂. The peaks at approximately 399.50 and 399.48 eV can be attributed to the anionic N[−] in the O–Ti–N bond formed by the partial N replacement of O in the crystal lattice of TiO₂ [15,34,45–48]. The peaks at approximately 400.40 and 401.30 eV for Fe, N co-doped TiO₂/C, and at 400.08 and 401.28 eV for (Fe,N,C)-TiO₂, can be attributed to oxidized N. Since the presence of absorbed N species have been excluded by O 1s XPS spectra, these oxidized N atoms could be assigned to bonds like

Ti–O–N or Ti–N–O in TiO₂ [35,49], which come from the interstitial N [14]. Furthermore, the fact that no signal of N–H appears at approximately 402 eV further confirms that N species are not on the surface of the crystal [15].

The Fe XPS spectra of Fe, N co-doped TiO₂/C and (Fe,N,C)-TiO₂ are shown in Fig. 9(e). (Fe,N,C)-TiO₂ shows no obvious Fe XPS signals, indicating that no Fe was successfully introduced in this structure. Fe, N co-doped TiO₂/C shows a typical Fe 2p spectrum; furthermore, the spectrum is not symmetrical and can be resolved into two types of Fe 2p spectra by curve-fitting analysis. The first doublet comprises two peaks centered at 710.20 and 723.00 eV (Fe-1), which are attributed to the Fe 2p_{3/2} and Fe 2p_{1/2} peaks of Fe³⁺ in a segregated Fe₂O₃ phase or Fe-oxide cluster bonded at the surface. The second doublet of Fe 2p (Fe-2) is observed at 712.70 and 725.20 eV, which shows a shift to higher binding energy compared to the first doublet. This shift is because partial Ti⁴⁺ ions are replaced by Fe³⁺ ions in the TiO₂ lattice, resulting in the formation of Fe–O–Ti bonds and varying the electron density around the Fe³⁺ and Ti⁴⁺ atoms [11]. These results indicate that, during the course of impregnating-calcination, some Fe species accumulate on the surface probably because of the transfer of Fe from the inner part to the surface of TiO₂. This situation often occurs in Fe-doped TiO₂ materials, and has been reported by several other groups [11,50,51]. The relative atomic concentrations of C, N, and Fe in Fe, N co-doped TiO₂/C and (Fe,N,C)-TiO₂ estimated from the XPS data are shown in Table 2. It can be seen that the introduction of C is not significantly different in the two samples, but the amount of N introduced in Fe, N co-doped TiO₂/C is almost 3 times that in (Fe,N,C)-TiO₂, and Fe even

Table 2Element amounts of Fe, N co-doped TiO₂/C, (Fe,N,C)-TiO₂, and Cts/TiO₂-25.

Element	Fe, N co-doped TiO ₂ /C		(Fe,N,C)-TiO ₂		Cts/TiO ₂ -25*	
	Atomic conc. (%)	Mass conc. (%)	Atomic conc. (%)	Mass conc. (%)	Atomic conc. (%)	Mass conc. (%)
C	20.74	11.17	22.54	12.15	–	5.22
N	1.01	0.64	0.34	0.22	0.48	–
Fe	0.21	0.52	–	–	–	–

* Cts/TiO₂-25 is a sample of modified TiO₂ prepared using chitosan as a precursor in Ref. [43].

cannot be introduced in (Fe,N,C)-TiO₂. This clearly shows that introducing elements with strong interactions among each other in a co-precursor is significantly more effective than introducing elements isolated by respective sources. It is known that preparing N-doped TiO₂ with high N-dopant concentration is difficult work, especially when simultaneously introducing N and other elements [52]. Shao and co-workers [52] synthesized a N-doped and C-species-decorated TiO₂ by taking chitosan as a common precursor. The introduced amounts of C and N were 5.22 wt% and 0.48 at% in their material, which are only almost half of that in Fe, N co-doped TiO₂/C in this study (11.17 wt% for C and 1.01 at% for N). Chitosan is a polysaccharide derivative full of C and N atoms. The amounts of N and C introduced into TiO₂ using chitosan were relatively high, and the method was described by the authors as opening a new route to obtaining high-efficiency TiO₂-based photocatalysts. As a comparison, using the Fe(II)-phenanthroline complex in this study demonstrates significantly higher efficiency for the introduction of C and N. Furthermore, not only can non-metal elements be doped into TiO₂, but metal elements, i.e., Fe, also can, which is not achieved using chitosan.

The TEM images (see Fig. S2) indicate that the morphologies of Fe, N co-doped TiO₂/C and (Fe,N,C)-TiO₂ are not significantly different than that of bare TiO₂. These samples all show similar morphologies of irregular nanoparticles, which means that the preparation methods cannot obviously change the morphologies of TiO₂ particles. The HRTEM image of Fe, N co-doped TiO₂/C (Fig. 10(a)) shows lattice fringes with interplanar spacings of approximately 0.238, 0.352, and 0.29 nm, which match well with the (004) and (101) plane separation of anatase TiO₂ (denoted A(004) and A(101) in the figure) and the (121) plane separation of brookite TiO₂ (denoted B(121) in the figure), respectively. These results are consistent with the XRD results, indicating that Fe, N co-doped TiO₂/C is a significant crystal in the mixed phases of anatase and brookite TiO₂ (this was further confirmed by selected-area electron-diffraction (SAED) studies (Fig. S3)). These results indicate that a homostructure structure is formed by the introduction of Fe, N, and C in the Fe, N co-doped TiO₂/C sample [53–55]. Fig. 10(b) and 10(c) that show (Fe,N,C)-TiO₂ and TiO₂ are significant crystals in anatase TiO₂ with no homostructure formation, which is consistent with the XRD results as well. The nanoparticle sizes of these three samples are approximately 10 nm from the HRTEM images, which correspond to the results calculated from the Scherrer formula by XRD.

The corresponding Raman spectra of Fe, N co-doped TiO₂/C and bare TiO₂ are shown in Fig. 11. That of bare TiO₂ indicates the typical modes of anatase; that is, three *E_g* peaks (144, 193, and 635 cm⁻¹), one *B_{1g}* mode (400 cm⁻¹), and *A_{1g}*+*B_{1g}* modes centered approximately 516 cm⁻¹ [14]. Oppositely, three new peaks at 243, 318, and 364 cm⁻¹ appear in the spectrum of Fe, N co-doped TiO₂/C. These bands are assigned to the presence

Fig. 10. HRTEM images of as-synthesized (a) Fe, N co-doped TiO₂/C, (b) (Fe,N,C)-TiO₂, and (c) TiO₂ (right-hand images are corresponding enlargements of marked locations on the left, respectively).

Fig. 11. Raman spectra of Fe, N co-doped TiO₂/C (1) and TiO₂ (2).

Fig. 12. FT-IR spectra of Fe,N co-doped TiO₂/C (1) and TiO₂ (2).

of brookite TiO₂ nanocrystals [56], which is consistent with the XRD and HRTEM results. The spectra ranging from 1000 to 1600 cm⁻¹ is magnified and shown in the inset of Fig. 11, clearly showing that there are several new peaks appearing in the spectrum of Fe, N co-doped TiO₂/C compared with that of bare TiO₂. It has been reported that peaks in this range indicate the existence of amorphous C atoms with some degree of graphic ordering [57–61]. Therefore, the remaining C on the crystalline surface should be present as a graphite-like carbonaceous species. These results are consistent with the XPS results, and confirm that there are carbonaceous species on the surface of the crystal.

Fig. 12 shows the collected FT-IR spectra of Fe, N co-doped TiO₂/C and bare TiO₂. In the spectrum of Fe,N co-doped TiO₂/C, the peaks at 3417 and 1632 cm⁻¹ are assigned to the stretching vibration of the H–O–H bond from the surface-adsorbed H₂O, OH, or COOH groups [62]. The peak at 589 cm⁻¹ is attributed to the vibration of Ti–O–Ti [62]. Compared with the spectrum of bare TiO₂, there are several new peaks appearing in that of Fe,N

co-doped TiO₂/C. The peak at 1425 cm⁻¹ is attributed to the symmetric stretching vibration of an arylcarboxylate group [63]. The peak at 1196 cm⁻¹ is attributed to the vibration of the C–C skeleton [64]. The peak at 1130 cm⁻¹ is attributed to the asymmetric stretching vibration of C–O–C, and the peak at 1050 cm⁻¹ is attributed to the symmetric stretching vibration of C–O–C [64]. These results are in accordance with the XPS and Raman analyses conducted to confirm the carbonaceous species on the surface of TiO₂.

In order to understand the reason for the improved photocatalytic ability of Fe, N co-doped TiO₂/C, identification of the active species for the photodegradation is important [65,66]. e⁻, h⁺, •OH radicals, and O₂^{•-} radicals are the well-known active species that play important roles in the photocatalytic reaction process. According to the results of Mott-Schottky curves (Fig. 8), the *E*_{CB} value of Fe,N co-doped TiO₂/C is approximately -0.52 eV versus SHE, which is more negative than the standard redox potential of O₂/O₂^{•-} (-0.33 V versus SHE) [52]; the *E*_{VB} value of Fe, N co-doped TiO₂/C is approximately 2.37 eV versus SHE, which is less positive than the standard redox potential of •OH/OH⁻ (2.38 V versus SHE) [52]. As a result, O₂ can be reduced to O₂^{•-} by the photogenerated e⁻, while OH⁻ cannot be oxidized to •OH by h⁺ when Fe, N co-doped TiO₂/C is irradiated with visible light. As a detection method, the EPR spin-trapping technique with DMPO is also used to detect the •OH and O₂^{•-} radicals. It can be seen in Fig. 13(a), upon irradiation by visible light, a strong and obvious peak of DMPO–O₂^{•-} species can be found in the spectrum of Fe, N co-doped TiO₂/C, indicating that O₂^{•-} radicals can be produced by Fe, N co-doped TiO₂/C. In contrast, there are no obvious signals of DMPO–OH• species appearing in Fig. 13(b), indicating that •OH cannot be generated over Fe,N co-doped TiO₂/C by visible-light irradiation. These results are consistent with the calculated results. We performed trapping experiments by using K₂S₂O₈ as an e⁻ scavenger, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) as a photogenerated hole (h⁺) scavenger, and 1,4-benzoquinone (BQ) as an O₂^{•-} scavenger to determine the major reactive spe-

Fig. 13. EPR spectra of (a) DMPO•O₂^{•-} and (b) DMPO•OH of Fe,N co-doped TiO₂/C samples under visible-light irradiation for 5 min (mixtures of 2-mg Fe,N co-doped TiO₂/C and 500-μL DMPO (0.04 mol/L) were freshly prepared in different solvents on the basis of the targeted radical; Water and methanol were used for hydroxyl radical and superoxide radical anion trapping, respectively).

Fig. 14. Removal rate of 4-NP over Fe, N co-doped TiO₂/C after addition of different scavengers.

cies in the photocatalytic oxidation of 4-NP over Fe,N co-doped TiO₂/C. As shown in Fig. 14, the photodegradation efficiency of 4-NP dramatically decreases with the addition of EDTA-2Na and BQ, indicating that h⁺ and O₂^{•-} are the major active species responsible for the degradation of 4-NP. After the addition of K₂S₂O₈, the photocatalytic activity increases initially, but approximately equals that of the no-scavenger experiment in the end. These results illustrate that the photogenerated e⁻ do not affect the photoreduction rate. However, at the initial phase of the photoreaction, the scavenging of e⁻ can increase the separation rate of e⁻ and h⁺ and, hence, increase the photocatalytic rate.

Fe, N co-doped TiO₂/C was also examined by EPR spectroscopy to determine the paramagnetic species. As shown in Fig. 15, the signal at $g = 2.032$ is assigned to paramagnetic VO[•] [49,67], which refers to the radicals generated by trapping one electron in an O vacancy. Because the formation of VO[•] results from the partial substitution of O by N, the presence of VO[•] ensures the lattice incorporation of N [49,68]. The electrons left in the O vacancies can reduce adjacent Ti⁴⁺ to Ti³⁺ [37]. As a result, a new band that is below the conduction band is formed. These are the 3d states of Ti³⁺, which can act as the color center re-

Fig. 15. X-band EPR spectrum of the N-TiO₂/C sample recorded at room temperature.

Scheme 2. Proposed photocatalytic mechanism over the Fe, N co-doped TiO₂/C nanocomposites.

sponsible for its visible-light adsorption. The existence of Ti³⁺ can be confirmed by the EPR signal at $g = 1.961$ [34,35]. The existence of the O vacancies and Ti³⁺ in the structure of Fe, N co-doped TiO₂/C is important in the improvement of the photocatalytic reactivity under visible light.

Based on the above results, a probable degradation mechanism is proposed in Scheme 2. It is well known that Fe or N incorporation into the TiO₂ lattice can introduce new doping band levels. The Fe incorporation leads to an Fe doping level below the conduction band of TiO₂, mainly by the overlap of Fe 3d and Ti 3d bands, and the N incorporation leads to an N doping level above the valence band of TiO₂ mainly due to the overlap of N 2p and O 2p bands. These new doping levels narrow the band gap of TiO₂ and shift the optical absorption to the visible-light region [69–76]. Furthermore, N doping converts some Ti⁴⁺ to Ti³⁺ by charge compensation. The 3d orbital of the Ti³⁺ states is lower than the conduction band [14], and it also overlaps with the Fe 3d band to form a donor energy together with the Ti⁴⁺ 3d band, which contributes to the visible-light absorption in the photocatalyst. However, the C modified on the surface of TiO₂ can acts as a sensitizer to enhance the visible-light absorption and reduce the reflection of light (the color of Fe, N co-doped TiO₂/C is dark, as shown in Fig. S4). Furthermore, the C on the surface can also absorb the photogenerated electrons, favoring the separation of the h⁺/e⁻ pairs to keep them highly effective [42,77]. Under the irradiation of visible light, Fe, N co-doped TiO₂/C can be excited to produce charge carriers (Eq. (1)). Then, the generated electrons participate in the production of O₂^{•-} radicals (Eqs. (2)). Finally, those active species react with contamination molecules and degrade them (Eq. (3)), while the C species on the surface are protected by the previous electron transfer:

4. Conclusions

Fe, N co-doped TiO₂/C photocatalysts were successfully synthesized by an improved hydrothermal-calcination process by using a Fe(II)-phenanthroline complex as a common source of Fe, N, and C. The results indicate that metal and non-metal

elements were successfully and simultaneously introduced at high levels. The introduced amounts of N and C almost doubled compared with the results of the previous method. A homocrystalline phase was formed, and the crystalline phase of the photocatalyst was a mixed phase of anatase and brookite TiO₂. Moreover, the light absorption of the photocatalyst can be expanded to visible light. Compared with the bare TiO₂, Fe,N-TiO₂, (Fe,N,C)-TiO₂, and Fe-TiO₂, the Fe, N co-doped TiO₂/C showed the highest photocatalytic performance in the degradation of 4-NP under visible-light irradiation, which indicated that introducing Fe, N, and C into TiO₂ by a co-precursor was more beneficial for improving the photocatalytic ability.

The approach addressed here is considered to provide a simple, green, and low-cost method of synthesizing TiO₂-based photocatalysts with high visible-light photocatalytic reactivity.

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Graphical Abstract

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Facile synthesis of C-decorated Fe, N co-doped TiO₂ with enhanced visible-light photocatalytic activity by a novel co-precursor method

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Inner and outer parts of TiO₂ were simultaneously modified to significantly improve its visible-light photocatalytic performance. This complicated modification was facily fulfilled by a novel co-precursor method.

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通过一种新型共前驱体的方法简单合成能增强 TiO₂ 可见光光催化活性的 C 修饰及 Fe, N 共掺杂的 TiO₂ 材料

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摘要: 为了提高 TiO₂ 的可见光光催化活性, 研究者做了很多努力. 晶格掺杂和表面修饰是提高 TiO₂ 可见光光催化活性的两种重要方法, 但由于这两种方法实施的条件不一样, 所以很难将它们在同一个制备过程中统一起来. 为了解决这个问题, 我们通过邻菲罗啉与 Fe²⁺ 络合形成 Fe(II)-phenanthroline 配合物, 然后以这种配合物作为 Fe, N, C 的共同来源, 通过水热-煅烧的方法合成 Fe, N 共掺杂且 C 表面修饰的 TiO₂ 材料 (Fe, N co-doped TiO₂/C). 通过其在可见光照射下降解 4-NP 来评估材料的性能, 同时也以 XRD, FT-IR, XPS, EPR 等手段对材料进行表征, 结合实验结果推测了其可能的光催化机理. 由可见光光催化降解动力学数据可知, Fe, N co-doped TiO₂/C 表现出来的性能最佳, 其反应速率常数为 0.00963 min⁻¹, 约是纯 TiO₂ 的 5.9 倍, 约是以三种单独来源分别引入 Fe, N, C 三种元素样品 ((Fe,N,C)-TiO₂) 的 5.1 倍. 这说明不同引入元素之间的强烈相互作用可以协同地提高 TiO₂ 光催化能力. HRTEM 图片显示 Fe, N co-doped TiO₂/C 中存在异质结构, 它是锐钛矿和板钛矿的混合晶相, TiO₂ 的这种混合晶型有利于增强其光催化性能. 结合 Fe, N co-doped TiO₂/C 的 XPS、拉曼和 FT-IR 数据进行分析, 结果显示 C 元素是修饰在 TiO₂ 晶体表面, N 元素是完全掺杂到 TiO₂ 晶格中, Fe 元素大部分掺杂到晶格中, 少部分修饰在晶体表面 (这在 Fe 掺杂 TiO₂ 的研究中较常见). 另外, 从 XPS 元素相对含量分析可知, 用邻菲罗啉作为 C, N 的共同来源同时引入 C, N, 引入量比以往的报道提高了 2 倍左右, 这表明我们报道的这种方法可以高水平地同时向 TiO₂ 引入 C 和 N 元素, 为同时高水平地向 TiO₂ 中引入这两种元素提供了新的思路. 结合 EPR, 时间-电流图, 电化学阻抗图谱 (EIS), 光致发光图谱, Mott-Schottky 图谱, XPS 导带分析, 活性自由基中间体捕获实验等多种表征的结果, 我们推测 Fe, N co-doped TiO₂/C 的光催化机理如下: 在可见光照射下, Fe, N co-doped TiO₂/C 被激发而产生电子与空穴 (h⁺), 电子与氧气反应形成 O₂⁻, 然后 O₂⁻ 和 h⁺ 把污染物分子氧化并降解它们, 而材料表面所修饰的 C 物质受之前所转移过来电子的保护, 而不至于被强烈氧化. 本研究实现了 TiO₂ 晶格掺杂与表面修饰在同一制备过程的结合, 为制备高性能无机-有机元素共掺杂, 内部-外部共改性的 TiO₂ 光催化材料提供了新的思路.

关键词: 晶格掺杂; 表面修饰; TiO₂; 光催化; 降解 4-NP

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