Fe + N Noncompensated Codoping TiO$_2$ Nanowires: The Enhanced Visible Light Photocatalytic Properties

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The Fe + N codoped nanowire samples are prepared by hydro-thermal method and annealed in NH$_3$ atmosphere. The XRD (X-ray diffraction), SEM (Scanning electron microscope), UV-vis absorption spectroscopy, and BET (Brunauer, Emmett, and Teller) results indicate that the samples are pure anatase nanowires. The Fe + N codoped samples have the highest specific surface area, the largest red-shift, and the largest absorption enhancement in the visible light range compared with Fe doped, N doped, and undoped nanowires. The measurements of XPS (X-ray photoelectron spectroscopy) show that N content of Fe + N codoped TiO$_2$ is about two times as large as that of the N doped TiO$_2$. It is assumed that nitrogen doping plays a very important role for the photocatalytic activity increase and hence the Fe + N codoped nanowire TiO$_2$ shows the most effective photocatalytic activity under the visible light irradiation.

1. Introduction

Due to the strong photocatalytic activity, anti-photo-corrosion ability, biologic compatibility, and chemical stability of TiO$_2$, it has become the most promising photocatalysis [1–3]. However, the wide band gap of TiO$_2$ (3.2 eV for the anatase phase and 3.0 eV for the rutile phase) needs ultraviolet (UV) light for electron-hole separation, which is only 5% of the natural solar light [4]. It is of great significance to enlarge the TiO$_2$ absorption to visible light range and to improve the photocatalytic efficiency of it that can be used in visible light irradiation.

Recently, it was recognized that compared with metal ions (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) [5], transition metal ions (Fe$^{3+}$, Cr$^{6+}$, Co$^{3+}$, Mo$^{5+}$ [6–9]), rare earth cations (La$^{3+}$, Ce$^{3+}$, Er$^{3+}$, Pr$^{3+}$, Gd$^{3+}$, Nd$^{3+}$, Sm$^{3+}$) [10], and nonmetal doping (C [11, 12], S [13], F [14, 15], N [16, 17]), metal-nonmetal doped TiO$_2$ exhibited a valid process for narrowing the band gap and have been demonstrated to be more appropriate for extending the photocatalytic activity of TiO$_2$ into the visible region, such as Bi + C(N) codoping [18], Mo + C codoping [19], Mo + N codoping [20], Pr + N codoping [21], and Cd + N codoping [22]). As a result, it was found that the monodoping can generate the recombination center inside the TiO$_2$, which goes against the light-induced charge carriers' migration to the surface [19, 23]. In compensated n-type + p-type dopant systems, the defect bands can be passivated and will not be effective as carrier recombination centers [19, 24]. And the coulombic attraction between the n-type and p-type dopants with opposite charge substantially can enhance doping concentration of nonmetal [25]. Recently, noncompensated codoping was proposed by Romero-Gomez et al. [26], for its distinctive merit of ensuring the creation of intermediate electronic bands in the gap region and enhancing photoactivity manifested by efficient electron-hole separation in the visible-light region. Macak et al., Shankar et al., and Allam and El-Sayed pointed out that the morphology, crystallinity, composition, and illumination geometry of nanotube arrays were critical factors in their performance as photoelectrodes [27–29]. TiO$_2$ nanostructure materials displayed high performance for their potential in improving photocatalytic activity because of their high surface area.

In this work, the Fe + N noncompensated codoping nanowires are prepared by hydrothermal method and its
photocatalytic activities are evaluated by the degradation of methyl blue under visible light irradiation.

2. Experiments

Titanium isoproxide (Alfa Aesar company, 99.5%) was used as a starting material. Titanium foils (0.6 mm thick, 99.5% purity, cut in $1 \times 2 \, \text{cm}^2$) were prepared. First, 10 mL titanium isoproxide solutions were dissolved in 62.5 mL absolute ethanol solutions. The solutions were then poured into 625 mL de-ionized water and stirred for 24 h. Then, ammonium hydroxide solution was added dropwise to keep the solution’s pH value at 8. Then, the white gel precipitates were formed. The precipitates were collected by centrifuge and dried in an oven at 50°C for 24 h. Then the obtained powder was put into a Teflon bottle with a titanium foil at the bottom. The bottle was filled with 10 M NaOH and reacted at 180°C for 24 h. When the reaction was completed, the samples were purified by 0.1 M HNO$_3$ to remove the sodium ions. Finally, the samples were dried in an oven at 50°C for 12 h. The nitrogen-doped samples were obtained by annealing the samples in an ammonia atmosphere at 500°C for 2 h. For preparing the Fe-doped samples, firstly, 36 mg of iron nitrate hydrate was added into de-ionized water to obtain a doping concentration of 1 mol% in TiO$_2$. Then, the solution of iron nitrate hydrate and the solution of titanium isoproxide were prepared. Secondly, 36 mg of iron nitrate hydrate was added into de-ionized water to obtain a doping concentration of 1 mol% in TiO$_2$. Then, the solution of iron nitrate hydrate and the solution of titanium isoproxide were dissolved in absolute ethanol and stirred for 24 h. Following the same procedure as that for pure samples and N doped samples, we can get Fe doped and Fe + N codoped samples. X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8 Advance diffractometer using Cu $K_\alpha$ radiation at room temperature. The morphologies were recorded by scanning electron microscope (SEM, FEI Sirion Field Emission Gun). X-ray photoelectron spectroscopy (XPS) with Mg Ka radiation was applied to investigate the surface composition and modifications on the chemical valence of the doping ions. The UV-visible absorption spectra were measured using a Cary 5000 UV-Vis-NIR spectrophotometer; BaSO$_4$ was used as a reflectance standard in a UV-visible diffuse reflectance experiment. The BET spectra were measured by specific surface area analyzer (V-sorb 2800P).

The photocatalytic activities under the visible light irradiation were evaluated by the degradation of methyl blue irradiated by a 450 W xenon lamp. In the process, the TiO$_2$ nanowire powder was immersed into a quartz colorimetric cuvette filled with 120 mL 10 mg/L methylene blue (MB) solution and placed below xenon lamp. The distance between the solution and the lamp was 10 cm distance. And the intensity of the light incident on the samples was about 900 mW/cm$^2$. The solution in the photoreactor was placed in the dark for 30 minutes to reach the absorption-desorption equilibrium.

3. Results and Discussion

Figure 1 shows the XRD patterns of Fe + N codoped, Fe doped, and undoped TiO$_2$ nanowires. As it can be seen from Figure 1, for all the samples, there are nine characteristic diffraction peaks that appear at 25.36°, 37.88°, 47.99°, 53.93°, 55.06°, 62.69°, 68.80°, 70.32°, and 75.10°, which are in well accordance with the (101), (004), (200), (105), (211), (204), (116), (220), and (215) diffraction peak positions of anatase TiO$_2$ [JCP2.2CA: 21-1272]. No peaks of impurities (such as rutile, FeTiO$_3$, or Fe cluster) are detected. That is to say that all the samples are pure anatase phase. According to the Bragg equation, with a binary line regression fitting [30] using the (101), (004), (200), (105), and (211) characteristic peaks, the lattice constants $a$ and $c$ and the lattice volumes are estimated and listed in Table 1. It can be seen that, for Fe doped samples, the lattice constants $a$ and $c$ are smaller than that of the undoped samples, in accordance with that reported by Van Minh et al. [31]. As it is known that the atomic radius of Fe$^{3+}$ (0.069 nm) is smaller than that of Ti$^{4+}$ (0.075 nm), so after Fe$^{3+}$ doping into Ti$^{4+}$ site, the cell parameter will decrease. While for the Fe + N codoped samples, the lattice constants $a$ and $c$ are almost the same with the undoped samples.

Table 1: Lattice constants, volume of the unit cell, and average crystallite sizes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>Volume (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>0.3781</td>
<td>0.9510</td>
<td>0.1360</td>
</tr>
<tr>
<td>Fe doped</td>
<td>0.3775</td>
<td>0.9486</td>
<td>0.1352</td>
</tr>
<tr>
<td>Fe + N codoped</td>
<td>0.3782</td>
<td>0.9512</td>
<td>0.1362</td>
</tr>
</tbody>
</table>

Figure 1: XRD patterns of Fe + N codoped, Fe doped, and undoped TiO$_2$ nanowires.
Figure 2: SEM images of pure (a) and Fe + N codoped (b) TiO₂ nanowires.

Figure 3: BET specific surface area of pure and Fe + N codoped TiO₂ nanowires.

Doping of Fe and N elements may restrain the growth of nanowires, which is similar to the report in papers [32, 33].

The specific surface area is a macroscopic parameter which can be helpful to adjust the photocatalytic activity of photocatalyst. The specific surface areas gained from BET experiment measurements are 141.04 m³/g, 145.151 m³/g, 151.82 m³/g, and 153 m³/g for undoped, Fe doped, N doped, and Fe + N codoped TiO₂ nanowires, respectively. The specific surface area spectra of pure and Fe + N codoped TiO₂ nanowires are shown in Figure 3. It is believed that the specific surface area increase for Fe + N codoped TiO₂ nanowires comes from the decreased diameter size compared with undoped samples, as it can be seen from the SEM results.

In order to get the chemical states and the composition information, XPS measurements of Fe + N codoped nanowires were performed and the results are shown in Figure 4. Figure 4(a) shows the XPS survey spectrum of Fe + N codoped nanowires, where the peaks at 458.15, 530.67, 710.90, and 396.02 eV correspond to the binding energy of Ti 2p₃/₂, O 1s, Fe 2p₃/₂, and N 1s, respectively. The C 1s peak observed at 284.71 eV is a signal of adventitious elemental carbon. There are no other impurity element observed in Figure 4(a), which confirms the existence of N element and Fe element in the Fe + N codoped samples lattices within the limits of instrumental error. The Fe 2p core level XPS spectrum of Fe + N codoped nanowires is showed in Figure 4(b). As we can see, there are two XPS peaks locating at 710.46 eV and 723.61 eV, close to the binding energy of the core level for Fe 2p₃/₂ and Fe 2p₁/₂ of Fe³⁺ ion, respectively [34]. The result provides the direct evidence for the conclusion that the valence of Fe ion is +3, occupies the Ti⁴⁺ site, and induces the cell parameter decrease. The calculation result by the Fe 2p core level spectrum shows that Fe content is 1.03%. Figure 4(c) shows the N 1s core level XPS spectra of N doped and Fe + N codoped nanowires. For N doped samples, there is one peak at the binding energy of 400.17 eV (labeled as N₈), while for Fe + N codoped samples, there are two peaks with similar intensity at the bonding energies of 396.02 eV and 400.17 eV (labeled as N₈ and N₆), respectively, which is also reported by Drera et al. [35]. Normally, the peak position of N₈ (at about 396 eV) reflects the formation of N–Ti–O bonds, indicating the substitution of N ions for O ions [36–38]. The peak position of N₆ (at about 400 eV) can be assigned to molecular nitrogen bonded to surface defects or the N atoms bonding to O sites in TiO₂, forming Ti–O–N bonds.

It is noticed that a new XPS peak (N₆ peak) appears for Fe + N codoped samples compared with N doped samples, the larger N₁s peak area of Fe + N codoped samples may indicate that Fe + N codoping can enhance the N doping content on substituting sites. To confirm the suggestion, the N content is calculated from the N 1s core level spectra. The results show that the N contents are 1.87 mol% and 3.93 mol% for N-doped and Fe + N codoped samples. It verifies that codoping N with Fe increases the solubility of N in TiO₂, as reported in another paper [39].

Figure 5(a) illustrates the UV-vis absorption spectroscopy of the pure, Fe doped, N doped, and Fe + N codoped TiO₂ samples. The pure TiO₂ nanowire exhibits the characteristic spectrum of TiO₂ with its fundamental absorption sharp edge around 380 nm (3.2 eV band gap). Compared with the pure samples, the absorption edge of Fe doped, N doped, and Fe + N codoped samples is shifted towards visible light range and the absorptions significantly enhance in visible
light range. The spectrum of Fe + N codoped samples has the largest red-shift and the absorption enhancement in the visible light range. Figure 5(b) shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ deduced from Figure 5(a). The band gap of each sample is determined by fitting the absorption spectra data according to the equation $(\alpha h\nu)^2 = B(h\nu - E_g)$ ($\alpha$ is the absorption coefficient; $h\nu$ is the photoenergy; $B$ is a constant number; and $E_g$ is the absorption band gap energy). As it can be seen that the band gaps are 3.21 eV, 3.05 eV, 3.03 eV, and 3.02 eV of the pure, Fe doped, N doped, and Fe + N codoped TiO$_2$, respectively, which are similar to those reported in [40, 41], but much higher than the values calculated by Romero-Gomez et al. [26]. In this work, the contents of Fe element are about 1% for Fe doped and Fe + N codoped samples, and the contents of N element are about 1.87 mol% and 3.93 mol% for N-doped and Fe + N codoped samples. The reason for this deviation may be the lower doping content of N ions and Fe ions in experiments compared with the theoretical model.

As to the origin of the visible-light sensitivity by Fe doping, N doping, and Fe + N codoping, the possible mechanism can be put forward, similar with our previous work in [42]. It is known that doping with some nonmetal or metal elements in TiO$_2$ would tailor the band gap. Herein, for the Fe doping, the absorption edge red-shift could be understood by the band gap narrowing, which is the result of the induced sub-band-gap transition corresponding to the excitation of 3d electrons of Fe$^{3+}$ to TiO$_2$ conduction band [41, 43]. For N doping, the doped N ions could induce an added shoulder on the edge of the valence band maximum and the localized N 2p states above the valence band [40]. At the
same time, it is known that the valence state of N is lower than that of O so that the incorporation of N must promote the synchronous formation of oxygen vacancies for the charge equilibrium in TiO$_2$ [44]. Therefore, after N doping the band gap narrows resulting in the newly formed oxygen vacancies in TiO$_2$ lattices which cannot be neglected. As a result, after N doping, the visible light response is attributed to both oxygen vacancies and the N 2p states. For Fe + N codoping, after N ions dope into the TiO$_2$ lattices, the Fe ions are introduced into the lattice of TiO$_2$ as the oxidation state of Fe$^{3+}$ confirmed by the XPS results. Here Fe-doping is a p-type doping and it can increase the oxygen vacancies induced by the holes doping of N, similar to [44]. Consequently, the codoped TiO$_2$ results in the best visible-light and the largest red-shift because of the synergistic effect of Fe ions and N ions codoping.

The MB degradation experiments were carried out in an aqueous solution under visible light irradiation by inserting a filter ($\lambda \leq 400$ nm) between the Xe-lamp and the samples. Figure 6 shows the photocatalytic degradation curves of MB catalyzed by the samples. The photocatalytic activity is in the order of the Fe + N codoped TiO$_2$ > N-doped TiO$_2$ > Fe-doped TiO$_2$ > undoped TiO$_2$. The Fe + N codoped TiO$_2$ nanowires exhibit the best photocatalytic activity, and the removal of MB is about 59% after 4 hours of irradiation under visible light. For nitrogen doped samples, density functional theory (DFT) calculations [45] have shown a large decrease in the formation energy for oxygen vacancies as a result of the presence of nitrogen atoms in the lattice and the neglected band narrowing is seen. While for Fe + N codoped samples, compared with the N doped TiO$_2$, Fe-doping is a p-type doping and it can increase the oxygen vacancies induced by the hole doping of N, similar to [44].

It has been reported that oxygen vacancies induced by N-doping, Fe-doping, or self-doping play an important role in the photocatalytic activity of TiO$_2$ nanowires by trapping the photoinduced electron and acting as a reactive center for the photocatalytic process [46, 47]. As a result, the Fe + N codoped nanowires gain the best visible-light response. At the same time, after Fe + N codoping the Fe + N codoped nanowires yield the highest specific surface area. Therefore, it is not surprising that the Fe + N codoped nanowires show the best photocatalytic activity by visible light irradiation.

4. Conclusions

The Fe + N codoped nanowire samples are prepared by hydrothermal method in 10 M NaOH and annealed in NH$_3$ atmosphere at 500°C. The XRD and SEM results show that the Fe + N codoped samples are pure anatase nanowires with 40 nm diameter, which is smaller than the pure TiO$_2$ nanowires whose average diameter is about 50 nm. The UV-vis absorption spectroscopy and BET results indicate the highest specific surface area, the largest red-shift, and the largest absorption enhancement in the Fe + N codoped nanowires compared with that in Fe doped, N doped, and undoped nanowires in visible light range. The measurements of XPS show that the N doped samples have the N content of 1.87 mol%, while Fe + N codoped TiO$_2$ have the N content of 3.93 mol%, which is about two times as large as that of the N doped TiO$_2$. It was assumed that the iron and N codoping can rapidly increase the N content in TiO$_2$. Hence, the Fe + N codoped nanowires show the most effective photocatalytic activity under visible light irradiation for doubled N content and the synergistic effects of codoped nitrogen and iron ions.
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