A Mild in-Situ Method to Construct Fe-Doped Cauliflower-Like Rutile TiO₂ Photocatalysts for Degradation of Organic Dye in Wastewater

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Abstract: A mild in situ method was developed to construct an iron doped rutile TiO₂ photocatalyst like cauliflower for degradation synthetic textile dye-methyl orange. The synthesized photocatalysts presented distinguished photocatalytic activity. At the optimal Fe concentration (0.5%), the decomposition rate of methyl orange (MO) was about 90% under 40 min of ultraviolet (UV) light irradiation. Whereas, to our knowledge, only 70% of the decomposition rate of MO was achieved by commercial photocatalyst P25 under the similar reaction condition. Additionally, the rutile preparation temperature did not exceed 100°C, which was much lower than the traditional preparation calcination temperature (e.g., 600°C). The specific surface area of Fe doped catalysts was bigger than that of the control sample and the catalyst characterization indicated that the doped iron was incorporated into the rutile TiO₂ lattice and resulted in the lattice disorder. The lattice disorder would have generated surface defects in the crystal structure, which was in favor of the photocatalytic reaction. The UV-Vis diffuse refection characterization and Density Functional Theory (DFT) calculation suggested that doping a small amount of Fe into the lattice of rutile would lead to a narrower band gap and the formation of a doping energy level between conduction and valence bands of TiO₂. This further increased the degradation efficiency of synthetic textile dyes in wastewaters. Our study has provided a relatively easy operation for synthesis Fe doped rutile TiO₂, which is a benefit to decrease the cost in wastewater treatment process.

Keywords: photocatalysts; TiO₂; wastewater; degradation; organic dye

1. Introduction

Fresh water is one of the significant natural resources for human beings. However, fresh water only accounts for 3% of the total water resource on earth. Since the 19th century, with the rapid development of the chemistry industry, limited and precious fresh water resources have been seriously polluted. The dyeing industry is one of the main pollution sources of fresh water; the discharged wastewaters containing dyes are toxic to human beings, aquatic life and microorganisms [1–3].

Scientists and researchers have made great efforts to degrade dyes in wastewaters. The most common methods used in industries are physical techniques, such as adsorption by ultrafiltration, reverse osmosis, activated carbon, ion exchange on synthetic adsorbent resins, coagulation by chemical agents, etc. [4–9]. These methods have only succeeded in accumulating contaminative...
organic compounds from water and becoming solid-wastes, which will require regeneration of the adsorbent and further treatment of solid-wastes. To overcome such drawbacks, scientists and researchers have developed biochemical techniques, such as enzymatic decomposition, biodegradation, microbiological, ozonation, and advanced oxidation processes, H₂O₂/UV processes, for dyes removal from wastewaters [10–14].

Unfortunately, due to the chemical stability of pollutants in wastewaters, all those aforementioned wastewater treatment technologies have proven to be ineffective for processing wastewater containing synthetic textile dyes. In one investigation, researchers found that 61% of selected dyes were practically untreated [15].

Photocatalysis has been proven to have the ability to distinguish decomposing organic compound in wastewaters, which arouse the great interest of scientists for studying the removal of dyes from wastewaters [16–20]. Photocatalysis is a photoinduced reaction, which is accelerated by the presence of a catalyst [21]. Generally, semiconductors (such as ZnO, TiO₂, CdS, Fe₂O₃, and ZnS) were chosen as catalysts for photo-catalysis [22]. Semiconductors are materials containing a valence band and conduction band which are separated by a band-gap. An electron–hole pair is generated by two steps: (1) A semiconductor molecule absorbs photons with enough energy which is equal or greater than its band-gap; (2) the electrons in the valence band are excited by the energetic photons and jump up into the conduction band. The generated electron–hole pairs can either interact separately with other molecules or can recombine. For the photocatalytic reaction, the less recombination of electron–hole pairs the better.

Because of its photochemical stability, non-toxic nature and low cost, titanium dioxide (TiO₂) is widely utilized as a photocatalyst [23,24]. Anatase and rutile phases are the two important phases of TiO₂ in photocatalysis. Anatase TiO₂ exhibits a higher photocatalytic activity compared to rutile TiO₂ [25,26]. Therefore, anatase TiO₂ has been the most investigated photocatalysts in the past decades. Compared to anatase TiO₂, rutile TiO₂ has a higher positive conduction band edge potential and faster recombination rate of electron-hole pairs, which leads to its lower photocatalytic activity [27–29].

Nevertheless, Rutile TiO₂ has proven to be the most stable phase, which can bear strongly acidic or basic environments. Hence, rutile TiO₂ has potential applications in optical communication, energy resources and photosensitive reactions, etc. [30,31]. In addition, rutile TiO₂ has smaller band gap energy (Rutile: 3.0 ev, Anatase: 3.2 ev), lower production cost, better chemical stability and higher light scattering efficiency in contrast with anatase TiO₂ [29]. Therefore, rutile TiO₂ as a photocatalyst has gradually attracted the interest of scientists due to its unique advantages.

So far, the disadvantage of TiO₂ is the relatively large band gap energy, which results in the low photocatalytic efficiency. Large band gap energy signifies the narrow light-response range and low separation probability of the photoinduced electron-hole pairs in TiO₂ photocatalysts [32,33].

In order to increase the photocatalytic activity of TiO₂, various methods have been developed, for instance, optimization of particle sizes, increasing its surface to volume ratio, dispersion of TiO₂ species in zeolite cavities, coupling of TiO₂ with other semiconductor particles, doping with metal or non-metal ions into TiO₂ [34,35]. The introduced transition metal ions can lead to the formation of a doping energy level between conduction and valence bands of TiO₂. Additionally, dopant ions may act as a trap for holes or electrons, which increases the catalytic activity of TiO₂ [36–38].

Iron has been viewed as a suitable candidate due to its low cost among the numerous transitional metals. In addition, the radius of Fe³⁺ (0.65 Å) is similar to that of Ti⁴⁺ (0.61 Å), so Fe³⁺ can be doped into the crystal lattice of TiO₂ easily [39–42]. Additionally, because the energy level of Fe²⁺/Fe³⁺ lies close to that of Ti³⁺/Ti⁴⁺, Fe³⁺ can provide a shallow trap for a photo-generated hole and electron, which is of benefit to the separation of the photo-generated electron-hole pair, and finally leads to the increment of quantum yield [43].

Traditional synthetic methods to produce rutile TiO₂ is calcination either amorphous titania or anatase TiO₂ at high temperature (e.g., 600 °C) [44,45]. However, high temperature calcination could result in agglomeration, which leads to small surface areas and large particle sizes. A study indicated
that, in comparison with rutile TiO$_2$ prepared at a high temperature, the rutile produced at a low temperature exhibited better photocatalytic performance [46]. Researchers have reported a number of methods to prepare rutile TiO$_2$ at relatively low temperatures. However, these methods usually need to introduce acids, solvents or other chemicals, which finally increase synthesis complexity and cost [47,48].

In this paper, a mild in situ method has been proposed to construct an iron-doped rutile TiO$_2$ photocatalyst for the degradation of organic dye in wastewater. The synthesized photocatalysts samples were characterized by Transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS), and nitrogen adsorption–desorption methods. Methyl orange (MO, see Figure 1) is a common contaminant in industrial wastewater and cannot be photodegraded in the absence of photocatalyst under light irradiation. Hence, the photocatalytic performances of synthesized photocatalysts were evaluated by degrading MO with UV light irradiation. Finally, the reason for the photocatalytic activity increment of Fe doped rutile TiO$_2$ was tentatively discussed.

![Figure 1. Molecular structure of MO.](image)

**2. Results**

Four photocatalysts have been synthesised, among which one is the control sample (0.0%Fe-TiO$_2$), the other three are Fe-doped rutile TiO$_2$ photocatalysts. The iron mass fraction of doped rutile TiO$_2$ photocatalyst was 0.5% (0.5%Fe-TiO$_2$), 1.0% (1.0%Fe-TiO$_2$) and 2.0% (2.0%Fe-TiO$_2$), respectively.

### 2.1. Phase Analysis of Synthesised Photocatalyst

According to the JCPDS NO.21-1276, the diffraction peaks at $2\theta = 27.4^\circ$, 36.0$^\circ$, 41.3$^\circ$, 54.5$^\circ$, 62.9$^\circ$, 69.1$^\circ$ correspond to the (110), (101), (111), (211), (220), (301) facets of rutile TiO$_2$, respectively.

As displayed in Figure 2, the XRD spectrum of four synthesized photocatalysts was well matched with the standard rutile TiO$_2$ XRD patterns. It should be noted that no crystalline phase ascribed to iron oxide could be found in the XRD patterns. There are two reasons responsible for this result: (1) Fe content in the synthesized photocatalysts was below the detection limit of this technique; (2) Fe$^{3+}$ ions might have substituted Ti$^{4+}$ ions and incorporated into the crystal lattice of TiO$_2$, because the radius of Ti$^{4+}$ was similar to the Fe$^{3+}$ ions (Fe$^{3+}$: 0.65Å, Ti$^{4+}$: 0.61Å) [49,50]. More, accurately, the XRD spectrum was in favour of the second reason. The introduction of Fe$^{3+}$ would slightly affect the crystal structure of synthesized photocatalyst, which would lead to the peak slightly shifting. The position of the facet (110) peak slightly shifted from 27.2$^\circ$ to 27.4$^\circ$ (see Figure 3), which probably indicated that Fe$^{3+}$ ions were incorporated into the TiO$_2$ lattice.

![Figure 2. XRD patterns of synthesised photocatalysts.](image)
were assembled in irregular slices and lattice fringes were clearly visible as showed in Figure 6. All the lattice plane of rutile TiO\(_2\)
photocatalyst was like a cauliflower bud at Nano-size. The synthesised nanoflower photocatalysts
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Catalysts
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Figure 3. Partial enlarged detail of XRD patterns of synthesised photocatalysts.

The Raman spectrum of synthesised photocatalysts was reported in Figure 4. The rutile structure had two TiO\(_2\) molecules in the unit cell with the space group \(D_{4h}^{14}\) (P4\(_{2}/\)mm). The frequencies of the Raman bands observed were located at \(~143\ \text{cm}^{-1}\) (\(B_{1g}\)), \(~447\ \text{cm}^{-1}\) (\(E_g\)), \(~612\ \text{cm}^{-1}\) (\(A_{1g}\)) and \(~235\ \text{cm}^{-1}\) (anomalously), which were well in agreement with previous published work [51–53]. The Raman spectrum further demonstrated that the synthesized photocatalyst was Rutile phase. The strong anomalously broad band about 235 cm\(^{-1}\) of Rutile has been extensively investigated, and is generally assigned as a multi-photon process [54]. The introduction of Fe didn’t significantly affect the lattice structure of Rutile TiO\(_2\) as displayed in Figure 4. Nevertheless, a slightly blue-shift of the Raman peak (\(E_g\)) was observed. In addition, the intensity of the \(E_g\) peak decreased and full width at half maxima (\(E_g\) and \(A_{1g}\)) increased with the increase of Fe content. The \(E_g\) mode was much more sensitive to oxygen vacancies as they were related to planar O–O interactions [51]. Combining the broadening and shifting of the characteristic diffraction peaks of d110, this indicates that the iron ions appeared to be doped into the lattice structure of TiO\(_2\), which leads to the generation of oxygen vacancies in order to compensate for the charge [39,55].

![Raman spectrum of synthesised photocatalysts.](image)

Figure 4. Raman spectrum of synthesised photocatalysts.

2.2. The Morphology of Synthesised Photocatalysts

Figure 5 shows the representative SEM images of synthesised photocatalyst. The morphology of photocatalyst was like a cauliflower bud at Nano-size. The synthesised nanoflower photocatalysts were assembled in irregular slices and lattice fringes were clearly visible as showed in Figure 6. All the synthesised photocatalysts contained the lattice fringe spacing 0.324 nm, which corresponded to the (110) lattice plane of rutile TiO\(_2\). Though the SAED pattern of Fe, doped photocatalysts demonstrated
the existence of (211) lattice facets, the HRTEM images did not clearly show them. It is probably because of their narrow fringe spacing (0.169 nm). In addition, the electron diffraction results insets in Figure 6 (a-2, b-2, c-2, d-2) indicated that all samples were highly crystalline, which was consistent with the XRD results.

![HRTEM images of synthesized photocatalyst. (0.0%Fe-TiO$_2$: a-1, a-2; 0.5%Fe-TiO$_2$: b-1, b-2; 1.0%Fe-TiO$_2$: c-1, c-2; and 2.0%Fe-TiO$_2$: d-1, d-2).](image)

**Figure 6.** TEM and HRTEM images of synthesized photocatalyst. (0.0%Fe-TiO$_2$: a-1, a-2; 0.5%Fe-TiO$_2$: b-1, b-2; 1.0%Fe-TiO$_2$: c-1, c-2; and 2.0%Fe-TiO$_2$: d-1, d-2).

### 2.3. The Performance of the Synthesized Photocatalyst

The performances of synthesized photocatalysts were evaluated by the decomposition of methyl orange (MO) under the UV light irradiation. The degradation curves of MO as a function of irradiation time are shown in Figure 7. Compared to the control experiment (without photocatalyst, green line), the concentration of MO demonstrated a downward trend with the increase of irradiation time. The photocatalyst 0.5%Fe-TiO$_2$ presented the highest activity, the degradation rate of MO...
was about 90% under 40 min of UV light irradiation. The photocatalyst 1.0% Fe-TiO$_2$ and 2.0% Fe-TiO$_2$ exhibited degradation rates of 77% and 73% under 40 min of UV light irradiation, respectively. The degradation rate of MO for 0.0%Fe-TiO$_2$ was about 62% under the same irradiation time, which was the lowest among the four synthesized photocatalyst. Introduction of iron element into rutile TiO$_2$ seemed beneficial to the degradation of MO. However, the photocatalytic performance of synthesized photocatalyst was decreased with the increase of Fe concentration; the optimal concentration of Fe was 0.5%. The MO photo-degradation kinetic study was presented in Figure 8. The reaction rate constants were in order: 0.5% Fe-TiO$_2$, 1.0% Fe-TiO$_2$, 2.0% Fe-TiO$_2$ and 0.0%Fe-TiO$_2$. The sequence of the reaction rate constants was in line with the activity of the synthesised photocatalyst.

![Figure 7. Photo-degradation rate of MO as a function of UV light irradiation time.](image1)

![Figure 8. Kinetic plots for photo-degradation of MO.](image2)

It is difficult to compare the results reported in the literature, because the catalyst preparation methods and the experimental conditions were usually different. Tong et al. [56] reported a Fe-doped Anatase for the degradation of MO. In their work, at the optimal doping levels of Fe$^{3+}$ (0.1%) and 6h UV light irradiation, the degradation rate of MO was 79%; under the same reaction condition, the degradation rate of MO by commercial photocatalyst P25 was only 70%. Leong et al. prepared a Ni(OH)$_2$ decorated rutile TiO$_2$ photocatalyst and the highest removal rates of model compound tetracycline was 68% under 2 h visible light irradiation [29]. So far, our photocatalyst seems to have presented the prominent photoactivity for a decomposing organic compound in wastewater.
3. Discussion

The Fe doped cauliflower-like rutile TiO$_2$ photocatalysts could significantly increase the photo-degradation rate of MO under the UV irradiation. In this section, we tentatively discussed the reason for the incremental photocatalytic activity of Fe-doped rutile TiO$_2$ photocatalyst.

The nitrogen adsorption-desorption and pore diameter distribution is shown in Figure 9. All the samples could be categorized as isotherms of type IV, indicating the presence of mesoporous materials according to the International Union of Pure and Applied Chemistry classification [57]. H3-type hysteresis loops were obtained, which implied the formation slit-like pores that were associated with nanobeam aggregation [58].

Figure 9. N$_2$ adsorption-desorption and pore diameter distribution of synthesized photocatalysts; (a): 0.0% Fe-TiO$_2$, (b): 0.5% Fe-TiO$_2$ (c): 1.0% Fe-TiO$_2$ (d): 2.0% Fe-TiO$_2$.

As indicated in Table 1, the specific surface areas of the Fe-doped photocatalysts were larger than that of the control sample (0.0% Fe-TiO$_2$). A bigger and more specific surface area benefitted the adsorption of reactants, because it offered more active sites for photocatalytic reaction. It is worth noting that the specific surface area of Fe-doped photocatalysts decreased with the increment of Fe concentration. Other researchers have also observed a similar phenomenon. They consider the reason for this increased surface area of Fe-doped TiO$_2$ may be explained as follows: The decreased lattice spacing of TiO$_2$ resulting from Fe dopant changes the pore diameter and pore volume of synthesized photocatalysts, which further increases the surface area of Fe-doped TiO$_2$ [56,59].
Table 1. Physicochemical properties of the photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%Fe-TiO₂</td>
<td>69.2</td>
<td>0.36</td>
<td>26.2</td>
</tr>
<tr>
<td>0.5%Fe-TiO₂</td>
<td>120.4</td>
<td>0.26</td>
<td>10.8</td>
</tr>
<tr>
<td>1.0%Fe-TiO₂</td>
<td>115.6</td>
<td>0.24</td>
<td>10.3</td>
</tr>
<tr>
<td>2.0%Fe-TiO₂</td>
<td>107.2</td>
<td>0.21</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Due to the small doped Fe concentration, no crystalline phase attributed to iron oxide could be found in the surface of rutile TiO₂ by the aforementioned catalysts characterization. Hence, X-ray photoelectron spectroscopy (XPS) measurements were carried out to study the chemical composition and the elemental valence state on the surface of the synthesized photocatalysts. As expected, O1s and Ti2p peaks could be clearly observed, but no obvious Fe2p peak could be found (see Figure 10). XPS measurement suggested that the introduced iron element did not exist on the surface of the synthesized photocatalyst.

![Figure 10. The XPS spectra of Fe-doped photocatalysts.](image)

In order to investigate the presence of Fe, EDX and HAADF-STEM characterization of 0.0% Fe-doped TiO₂ and 0.5% Fe-TiO₂ were carried out (see Figure 11). It was found that there was no energy spectrum of Fe in 0.0% Fe-doped TiO₂ (Figure 11a), while a small amount of Fe element existed in the spectrum of 0.5% Fe-TiO₂ sample (Figure 11b). The high angle on the annular dark field image of
scanning transmission electron microscope (HAADF-STEM shown in Figure 11c–f) also demonstrated the presence of the Fe element.

Figure 11. EDX spectrum of 0.0% Fe-TiO₂ (a) and 0.5% Fe-TiO₂ (b); The HAADF-STEM image of the observed area of 0.5% Fe-TiO₂ (c), and the corresponding energy-dispersive X-ray spectroscopy (EDX) elements mapping of 0.5% Fe-TiO₂: Ti (d: yellow), O (e: purple) and Fe element (f: orange).

Therefore, it is reasonable to speculate that the introduced iron element was incorporated into the crystal lattice of rutile TiO₂. The radius of Fe³⁺ (0.65Å) was similar to that of Ti⁴⁺ (0.61Å), so less Fe³⁺ ions could be easily doped into the crystal lattice of TiO₂ and have caused the slight disorder of the rutile phase structure. This slight disorder was demonstrated by XRD measurement (see Figure 3). The lattice disorder would have generated surface defects (e.g., oxygen vacancies) in the crystal structure, which was in favour of the photocatalytic reaction.

It is generally accepted that the introduction of transition metal ions can result in lattice disorder, which further leads to a narrower band gap and the formation of a doping energy level between conduction and valence bands of TiO₂ [60,61]. We carried out the UV-Vis diffuse reflection characterization to confirm the decrease of band-gap of Fe-TiO₂ samples. All the samples exhibited absorption in the ultraviolet and visible range. For Fe-TiO₂ samples, an obvious red shift at 400–500 nm was observed in Figure 12a. The band gap decreased from 3.04 eV for 0.0% Fe-TiO₂ to 2.98 eV for 2.0% Fe-TiO₂ as showed in Figure 12b. This further proved that Fe had been doped into the TiO₂ lattice.

This view was further demonstrated by our density functional theory (DFT) calculation. A new energy level and narrower band gap signified high separation probability of the photoinduced electron-hole pairs in the TiO₂ semiconductor photocatalysts. The band gaps of synthesized photocatalysts were calculated by the VCA approach based on DFT. The calculation suggested that the introduction of Fe into the TiO₂ lattice could narrow the band gap of TiO₂ (see Figure 13) and with an increase in the Fe dopant concentration, the calculated band gap at G (gamma point) decreased accordingly. This was caused by the conduction band minimum (CBM), which moved down. It should be noted that extremely narrow band gap implied the high recombination rate of photo-hole pairs, which was also averse to the photocatalytic reaction. Therefore, there was an optimal band gap energy
value that corresponded to the highest photocatalytic activity. Namely, an optimal introduced Fe concentration needed to be determined for the optimal band gap energy, which corresponded to the highest photocatalytic activity. In this study, the optimal introduced Fe concentration was 0.5%wt.

![Figure 12](image1.png)

**Figure 12.** (a) Uv-vis diffuse reflection spectra of synthesised photocatalyst; (b) Band gap derived from Uv-vis diffuse reflection spectra.

![Figure 13](image2.png)

**Figure 13.** Band structures synthesised photocatalyst. (a) 0.0%Fe-TiO2; (b) 0.5%Fe-TiO2; (c) 1.0%Fe-TiO2; (d) 2.0%Fe-TiO2.

There was a disparity that existed between the result of the DFT calculation and that of the experiment. However, this difference was also observed by other researchers [62–66]. The disparity can be explained by not considering the discontinuity in the exchange-correlation potential in the DFT calculation [63,67]. Nevertheless, the DFT calculation results were still advisable for qualitative characterization to confirm the decrease of band-gap of Fe-TiO2 samples. All the samples exhibited accordingly. This was caused by the conduction band minimum (CBM), which moved down. It should increase in the Fe dopant concentration, the calculated band gap at G (gamma point) decreased from 3.04 eV for 0.0% Fe-TiO2 to 2.98 eV for 2.0% Fe-TiO2 as showed in Figure 12b. This further proved that Fe had been doped into the TiO2 lattice.

There was an in-situ redox process which could be easily doped into the crystal lattice of TiO2 and have caused the slight disorder of the lattice. This slight disorder was demonstrated by XRD measurement (see Figure 3). The Uv-vis diffuse reflection spectra of synthesised photocatalyst is shown in Figure 12a.

The doping mechanism of in-situ synthesis was also proposed as below. In the catalyst synthesis process, Ti2O3 nanostructure was first formed via TiCl3 hydrolysis in acidic aqueous solution containing excessive Cl−, which had a strong reducing ability. According Fe3+[φ=0.777v] → Fe2+[φ=0.447v] → Fe, electrode potential of Fe3+ → Fe was φ = 0.0367v. The electrode potential of Ti4+ → Ti3+ was −0.37v. Once the Fe3+ ions were in contact with Ti2O3 deposit in acidic environment, they were easily reduced to Fe.
by Ti<sub>2</sub>O<sub>3</sub>. Meanwhile, corresponding Ti<sub>2</sub>O<sub>3</sub> was oxidized into TiO<sub>2</sub>. Oxygen vacancies, described by standard Kröger-Vink notation, were created during this chemical reduction [52]. The oxygen vacancies would slowly disappear when the material was exposed to air. However, Fe<sup>3+</sup> acted to stabilize oxygen vacancies. This mild in-situ redox process could be described by the following formula [49, 52]:

\[
3\text{Ti}_2\text{O}_3 + 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}^{0} + 6\text{TiO}_2 + 6\text{H}^+
\]

\[
\text{Ti}_2\text{O}_3 + \frac{1}{2}\text{O}_2 = 2\text{TiO}_2 \quad (2)
\]

\[
\text{O}^\times_{O} \xleftrightarrow{\text{TiO}_2} \text{V}_O + \frac{1}{2}\text{O}_2(g) + 2e' \quad (3)
\]

\[
2\text{Fe} + \frac{3}{2}\text{O}_2 = \text{Fe}_2\text{O}_3 \quad (4)
\]

\[
\text{Fe}_2\text{O}_3 \xrightarrow{\text{TiO}_2} 2\text{Fe}^{'} + 3\text{O}^\times_{O} + \text{V}_O \quad (5)
\]

\[
\text{Fe}_2\text{O}_3 + \frac{1}{2}\text{O}_2(g) + 2e' \xrightarrow{\text{TiO}_2} 2\text{Fe}^{'} + 4\text{O}^\times_{O} \quad (6)
\]

where \(V^\times_O\) represents an \(O^{2-}\) ion in the oxygen lattice site, \(V_O\) is an oxygen vacancy, \(\text{Fe}^{'}\) indicates \(\text{Fe}^{3+}\) ion in the titanium lattice site, which can stabilize the oxygen vacancies as ionic charge-compensating species. Alternatively, the \(\text{Fe}^{3+}\) acceptor can be compensated by a decrease in the concentration of free electrons in the TiO<sub>2</sub>.

Other researchers have used the similarly method to synthesize the photocatalyst [69]. However, in their study, the introduced metals were loaded on to the surface rather than doped into the TiO<sub>2</sub> lattice. The probably reason is that, in their work, the radii of selected metals (Pt, Au, Ru, etc.) ions are much larger than that of Ti<sup>4+</sup>. Hence, selected metal ions couldn’t substitute the Ti<sup>4+</sup> in the rutile TiO<sub>2</sub> lattice.

4. Materials and Methods

4.1. Photocatalysts Synthesis

Four photocatalysts have been synthesised, among which one is the control sample, the other three are Fe-doped rutile TiO<sub>2</sub> photocatalysts. The iron mass fraction of doped rutile TiO<sub>2</sub> photocatalyst was 0.5% (0.5% Fe-TiO<sub>2</sub>), 1.0% (1.0% Fe-TiO<sub>2</sub>) and 2.0% (2.0% Fe-TiO<sub>2</sub>), respectively.

For control sample synthesis, first, 20 g TiCl<sub>3</sub> solution (Alfa Aesar, Haverhill, MA, USA, 20% in 3% hydrochloric acid aqueous solution) was mixed with 60 g of 30 wt% NaCl aqueous solution. Then, the mixed solution was heated at 100 °C for 12 h under N<sub>2</sub> atmosphere to get the blue deposit (Ti<sub>2</sub>O<sub>3</sub>). This process could be described by the following equation:

\[
\text{Ti}^{3+} + \text{H}_2\text{O} = \text{Ti(OH)}_3 + 3\text{H}^+ \quad (7)
\]

\[
2\text{Ti(OH)}_3 \doteq \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} \quad (8)
\]

Next, the blue deposit was quickly washed by deionized water several times to remove the unreacted TiCl<sub>3</sub>. The existence of TiCl<sub>3</sub> (purple) was identified by the colour of washed deionized water (purple to colourless). Afterwards, the washed blue deposit was re-dispersed in deionized water under an acidic environment and exposed to the air at room temperature for 24 h, which could oxide the blue deposit (Ti<sub>2</sub>O<sub>3</sub>) and turn it into white deposit (rutile TiO<sub>2</sub>). The auto-oxidation process could be described according to the Kröger-Vink formula [70]:

\[
\text{Ti}_2\text{O}_3 + \frac{1}{2}\text{O}_2 = 2\text{TiO}_2 \quad (9)
\]
Finally, the white deposit (rutile TiO$_2$) was separated by filtration, the Cl$^-$ ions were washed off by deionized water. The existence of Cl$^-$ ions was identified by AgNO$_3$ solution (0.1mol/L). The synthesized sample was vacuum-dried at 80 °C for 24 h and was used as a control sample.

For the Fe doped photocatalyst, the first two steps were the same as the control sample synthesis steps. Third step, the washed blue deposit (Ti$_2$O$_3$) was re-dispersed in deionized water and the suspension was heated to 80 °C with N$_2$ atmosphere protection in a water bath. Fourth step, the calculated amount of 0.01 mol/L FeCl$_3$·6H$_2$O (AR, Alfa Aesar, Haverhill, MA, USA) aqueous solution was subsequently added into the blue suspension (Ti$_2$O$_3$) at 80 °C. After being maintained at 80 °C for 3 h, the mixture was naturally cooled to room temperature and exposed to air for 24 h. Finally, the white deposit (rutile TiO$_2$) was separated by filtration, the Cl$^-$ ions were washed off by deionized water. The existence of Cl$^-$ ions was identified by AgNO$_3$ solution (0.1mol/L). The synthesized samples were vacuum-dried at 80 °C for 24 h and were used as the Fe-doped photocatalyst.

4.2. Photocatalysts Characterization

X-ray powder diffraction (XRD) patterns were measured on a PANalytical/Empyrean diffractometer at room temperature. The patterns were recorded over the angular range 10–80° (2θ), using a scanning step 2°/s and Cu(K$_α$) radiation (λ = 1.5418 Å) with working voltage and current of 40 kV and 200 mA, respectively. Raman spectra were obtained on a RENISHAW (Staffordshire, UK). The wavelength of the laser was 532 nm and scanning range was 100–1000 cm$^{-1}$. Exposure time was 1 s. Scanning electron micrographs (SEM) were recorded with a Hitachi S-3400N (Tokyo, Japan), which was used to determine the morphology of the sample. Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) energy-dispersive X-ray spectroscopy (EDX) and High angle annular dark field image of scanning transmission electron microscope (HAADF-STEM) were performed with a FEI TECNAI F30 microscope (Hillsboro, OR, USA). The control voltage was 300 kV, and samples were dropped on a holey carbon-coated copper 400-mesh grid (2SPI, Shanghai, China). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Shimadzu/CRATOS AMICUS X-ray photoelectron spectrometer (Kyoto, Japan) with an AlK$_α$ (1486.67 eV) excitation source, which determines the existence and valence states of synthesised photocatalysts. UV-Vis diffuse reflection was carried on a Perkin Elmer UV/VS/NIR Lambda 750s spectrometer (Waltham, MA, USA) to confirm band-gap of Fe-TiO$_2$ samples. The BET surface areas ($S_{BET}$) and pore diameter distribution of the synthesized photocatalysts were determined by the N$_2$ adsorption-desorption test performed on a Micrometrics ASAP2020 analyser (Norcross, GA, USA).

4.3. Photocatalysts Evaluation

The photocatalytic performance of synthesized photocatalysts was evaluated in a homemade setup, which was equipped with a 300 W mercury lamp. Methyl orange (MO, see Figure 1) was selected as the model compound, which was illuminated by UV light (λ ≤ 420 nm).

A synthesized photocatalyst (25 mg) was suspended into a quartz tube, which contained 50 mL of MO aqueous solution (6 mg/mL). The suspension mixture was magnetically stirred for 120 min in the dark to attain the adsorption-desorption equilibrium for MO and dissolved oxygen on the surface of synthesized photocatalyst surface. Subsequently, the obtained suspensions were illuminated with UV light (λ ≤ 420 nm) under magnetic stirring. During the reaction, 1.5 mL of suspensions was collected at a regular interval. The collected sample was centrifuged to separate the photocatalyst from the suspension sample. The supernatant was transferred into a transparent cuvette and the concentration of MO was measured with a UV–vis absorption spectrometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China).

The degradation rate of MO was calculated using the following equation: Degradation rate = 100% × (C$_{MO}$ − C)/C$_{MO}$, where C$_{MO}$ is the initial concentration of MO, and C is the MO concentration at the given time of irradiation, respectively. The photocatalytic degradation of MO follows the pseudo-first order decay kinetics, which can be assumed to be calculated using the following
formula: \( \ln(C_{\text{MO}}/C) = k_{\text{app}} \times t \) [38]. In this equation, \( k_{\text{app}} \) is the apparent pseudo-first order degradation rate constant (min\(^{-1}\)), which can be used to measure the efficiency of the degradation of MO and the photocatalytic performance of samples.

4.4. DFT Calculation Details

The DFT calculations were performed using the plane wave based periodic DFT method as implemented in the CASTEP module of Materials Studio [71]. The electron exchange and correlation energies were treated within the Generalized Gradient Approximation in the Perdew–Burke–Ernzerhof functional (GGA-PBE). The plane wave basis was set up to 400 eV, and the Monkhorst–Pack scheme K-point sampling was set as \( 4 \times 4 \times 3 \). The calculated Rutile TiO\(_2\) had a tetragonal structure with lattice parameters \( a = b = 4.594 \, \text{Å}, \ c = 2.959 \, \text{Å} \). A VCA approach was used to simulate our Fe-doped photocatalysts. This method allowed us to replace each atom of a certain type in the unit cell with a fictitious element with a non-integer atomic number [72]. For Fe-doped rutile TiO\(_2\), Ti atoms were replaced with virtual pseudo-potentials, Ti-Fe atoms with different Fe contents \( (x) \), as 
\[
V_{\text{VCA}}^{ps} [x] = xV_{Fe}^{ps} + (1 - x)V_{Ti}^{ps}
\]
but maintained the rutile crystal structure [73–76].

5. Conclusions

A mild in situ method was developed to construct an iron-doped rutile TiO\(_2\) photocatalyst for the degradation of organic dye in wastewater. The synthesized photocatalysts were like cauliflower bud at Nano-size. XRD and Raman spectrum confirmed the rutile phase of TiO\(_2\). The Fe-doped photocatalysts presented distinguished photocatalytic activity. At the optimal Fe concentration (0.5%), the degradation rate of the methyl orange was 90% under 40 min of UV light irradiation. The specific surface area of Fe doped catalysts was bigger than that of the control sample. EDX and HAADF-STEM characterization suggested that there was no energy spectrum of Fe in 0.0% Fe-doped TiO\(_2\), while a small amount of Fe element existed in the spectrum of 0.5% Fe-TiO\(_2\) sample. However, XPS indicated that the introduced iron element didn’t exist on the surface of the synthesized photocatalyst. Due to the radius of Fe\(^{3+}\) (0.65 Å) being similar to that of Ti\(^{4+}\) (0.61 Å), it was reasonable to speculate that less Fe\(^{3+}\) ions could be easily doped into the crystal lattice of TiO\(_2\) and cause the slight disorder of rutile phase structure. This slightly disorder was demonstrated by the slight shift of position of the facet (100) peak in the XRD measurement. The UV-Vis diffuse reflection characterization and DFT calculation further suggested that doping small amount of Fe into the lattice of rutile would lead to a narrower band gap, formation of a doping energy level between conduction and valence bands of TiO\(_2\), which is favourable for photo-decomposing the organic pollutants in waste water.

The novelty of this study can be emphasized as follows:

1. This study provided a mild and low cost method for the synthesis the Fe-doped rutile TiO\(_2\). The rutile preparation temperature did not exceed 100 °C, which was much lower than the traditional preparation calcination temperature (e.g., 600 °C). TiCl\(_3\) was used as a titanium source other than expensive Ti(OC\(_4\)H\(_9\))\(_4\). To our knowledge, doping Fe into rutile TiO\(_2\) using this method was reported first in this paper.

2. The synthesized photocatalysts presented the prominent photoactivity for decomposing organic dye in wastewater. It is difficult to compare with those results reported in the literature, because the catalysts preparation methods and the experimental conditions were usually different. Tong et al. [58] reported a Fe-doped Anatase for the degradation of MO. In their work, at the optimal doping levels of Fe\(^{3+}\) (0.1%) and 6 h UV light irradiation, the degradation rate of MO was 79%; under the same reaction condition, the degradation rate of MO by commercial photocatalyst P25 was only 70%. Leong et al. prepared a Ni(OH)\(_2\) decorated rutile TiO\(_2\) photocatalyst and the highest removal rates of model compound tetracycline was 68% under 2 h visible light irradiation [59]. So far, our photocatalyst seems to have presented the prominent photoactivity for decomposing organic compounds in wastewater.
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