Effect of Fe doping on the photocatalytic activity of TiO\textsubscript{2} hollow fibers under LED light irradiation

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Abstract. Fe-doped TiO\textsubscript{2} hollow fibers (Fe-THF) were prepared using a template replication method with kapok as the template. The Fe concentration was varied by adjusting the amount of iron (III) nitrate from 0 to 5 mol\%. The effect of Fe doping on morphology, crystal structure, bandgap energy, and photocatalytic activity was investigated and discussed. Based on the characterization results, it was found that all samples possessed a hollow structure with anatase as the main crystalline phase. The rutile phase began to be observed with high-level doping. Bandgap energy decreased significantly from 3.02 to 2.12 eV as the Fe concentration increased, owing to the formation of intermediate energy level. The photocatalytic activity was probed using the degradation of methylene blue under light-emitting diode (LED) irradiation. We found that the photocatalytic activity of Fe-THF was inferior to undoped THF and decreased with increasing Fe concentration. This result indicated that Fe dopant could act as the recombination centers in the lattice system, thus inhibiting the photocatalytic activity of THF.

1. Introduction
Since 1972, TiO\textsubscript{2} has been found to be a promising photocatalyst material for the photo-electrochemical water splitting [1]. By absorbing the photons from a light source, the generation of electron–hole pairs in TiO\textsubscript{2} can accelerate chemical redox reactions. Owing to its unique optical properties and low cost, TiO\textsubscript{2} has significant potential for use in energy and environmental applications, such as dye-sensitized solar cells [2], wastewater treatment [3], and H\textsubscript{2} production [4]. However, the photocatalytic performance of TiO\textsubscript{2} is limited by its wide bandgap (3.0–3.2 eV) and high recombination rate of photogenerated electrons and holes. The enhancement of photocatalytic performance for TiO\textsubscript{2} is based on three strategies, as follows: (i) narrowing bandgap energy by creating impurity levels near the valence or conduction band through metal or non-metal doping [5], (ii) reduction of recombination rate by decorating the surface with noble-metal nanoparticles [6], and (ii) designing specific shapes and structures to enhance light scattering and absorb more incident photons [7]. Therefore, the rational design and integration of TiO\textsubscript{2} based on these strategies remains challenging and may provide the unexpected results.

In our previous work, we successfully synthesized TiO\textsubscript{2} hollow fibers (THF) using a template replication method with the use of kapok as biotemplate [8]. THF calcined at 450 °C showed the best photocatalytic activity on paraquat degradation under ultraviolet (UV) light exposure. In a further effort to improve the photocatalytic activity of THF, narrowing the bandgap by metal doping has been the
focus of this work. Fe was selected as dopant since the ionic radius of Fe\(^{3+}\) ion (0.064 nm) is nearly similar to Ti\(^{4+}\) ion (0.068), which can allow easy incorporation into TiO\(_2\) lattice [9]. The effect of Fe doping on morphology, crystal structure, and bandgap energy were investigated and discussed based on the following characterization techniques: scanning electron microscopy (SEM), X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS). Moreover, the photocatalytic activity of Fe-doped THF on the degradation of methylene blue (MB) was evaluated by measuring the change in absorption under light-emitting-diode (LED) irradiation.

2. Experimental

2.1. Synthesis of Fe-doped TiO\(_2\) hollow fibers (Fe-THF)

A certain amount of Fe(NO\(_3\))\(_3\)·9H\(_2\)O ranging (1, 3, and 5 mol\%) was mixed with 150 mL of ethanol under vigorous stirring at room temperature for 1 h. Then, 3 mL of titanium butoxide (8.7 \(\times\) 10\(^{-3}\) mol) was slowly dropped into the mixture by keeping vigorous stirring for 1 h. Dried kapok fibers (1 g) were immersed in the precursor for 1 h and dried 18 h at room temperature. The calcination was carried out at 450°C with a heating rate of 5°C/min under air atmosphere for 1 h in order to remove the kapok template and crystallization of TiO\(_2\). White fluffy product was obtained for undoped THF. The products with Fe doping were light yellow, and became more yellow as the Fe concentration increased. THFs prepared by using Fe(NO\(_3\))\(_3\)·9H\(_2\)O of 1, 3, and 5 mol\% were named 1-Fe-THF, 3-Fe-THF, and 5-Fe-THF, respectively.

2.2. Characterization

Phase structures were identified using X-ray diffractometer (Rigaku, SmartLab) with Cu K\(_\alpha\) radiation (\(\lambda = 1.54056\) Å) at 40 kV and 40 mA. Morphology was observed with a scanning electron microscope (JEOL, JSM-7600F) operated at an accelerating voltage of 5 kV. Moreover, the elemental compositions were investigated by energy dispersive spectrometer (Oxford Instrument). Bandgap energy was estimated by UV-vis diffuse reflectance spectrometer (Shimadzu, UV-2550) and Tauc plot.

2.3. Photocatalytic activity measurement

5 ppm of MB solution was prepared and stirred in the dark for 24 h. 50 mg of the sample was suspended in 50 mL of MB solution and stirred under dark conditions for 1 h to obtain adsorption–desorption equilibrium. After that, the suspensions were stirred under white LED irradiation (20 W Phillips) for 6 h. 3 mL of suspension was collected hourly and centrifuged to collect only irradiated MB solutions. The MB degradation was evaluated with an UV-vis spectrometer (Shimadzu, UV-1700) through the change in absorption at 663.5 nm.

3. Results and discussion

SEM images of the THF and Fe-THF are illustrated in Figure 1. Clearly, all samples exhibited a hollow fiber structure with a diameter of about 20–30 µm. No obvious difference in morphology was observed regardless of Fe concentration. The presence of Fe dopant in THF was also confirmed by energy dispersive spectroscopy (EDS) measurement. It was found that the chemical composition of Fe-THFs comprised of only Ti, O, and Fe. The Fe concentration was found to be 0.22, 0.64, and 0.96 at% for 1-Fe-THF, 3-Fe-THF, and 5-Fe-THF, respectively.

![Figure 1](image_url)
The XRD patterns of all samples are shown in Figure 2(a). All diffraction peaks of THF and 1-Fe-THF were associated with the anatase phase (JCPDS card no. 21-1272) without other crystalline phase. However, a small diffraction peak at 27.7° corresponding to the rutile phase (JCPDS card no. 21-1276) was observed for 3-Fe-THF (indicated with an arrow) and was stronger for 5-Fe-THF. The emergence of the rutile phase was likely due to the fact that Fe doping resulted in lower phase transformation temperature of TiO\(_2\) to turn anatase into the rutile phase \cite{10}. Moreover, there were no detectable diffraction peaks of the secondary phase (i.e., Fe\(_2\)O\(_3\)), even at high Fe concentration. This result is evidence that Fe\(_{3+}\) ion has been incorporated or replaced in the TiO\(_2\) lattice due to the nearly similar ionic radii of Fe\(_{3+}\) (0.064 nm) and Ti\(_{4+}\) (0.068 nm).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) XRD patterns and (b) absorption spectra of all samples. The corresponding Tauc plots between \((uhv)^{1/2}\) versus \(h\nu\) are shown in the inset of (b).}
\end{figure}

UV-vis absorption spectra of all samples in the wavelength range of 300–800 nm are demonstrated in Figure 2(b). It was seen that the absorption band edge shifted significantly toward longer wavelengths with increasing Fe concentration, indicating the redshift phenomenon. In other words, the absorption of Fe-THFs was extended from UV to the visible-light region. Furthermore, the bandgap energy \((E_g)\) can be calculated using the Tauc plot of \((uhv)^{1/2}\) for indirect allowed transition versus energy \((h\nu)\), as shown in the inset of Figure 2(b). The bandgap energy of the samples was obtained by extrapolation of the linear line to intercept the \(h\nu\)-axis. The bandgap energy was estimated to be 3.02, 2.92, 2.49, and 2.12 eV for THF, 1-Fe-THF, 3-Fe-THF, and 5-Fe-THF, respectively. The reduction of bandgap energy at higher Fe concentration is attributable to the formation of an impurity state below the conduction band, which can thus enable visible-light absorption.

The photocatalytic activity of all samples was further evaluated by the degradation of MB under LED irradiation. Figure 3a presents the change in the absorption spectrum of MB solution in the presence of 1-Fe-THF at different irradiation times. It was evident that the absorption of MB solution decreased continuously with prolonged irradiation time, indicating its photocatalytic degradation. Figure 3b displays the relative concentration \((C/C_0)\) as a function of irradiation time for all samples. Note that \(C_i\) and \(C_0\) are the concentrations of MB at the given reaction and initial times, respectively. There was no noticeable reduction in the absorption of MB in the absence of samples, suggesting that MB was not self-degraded by LED. Under dark conditions for 1 h, MB adsorption was observed about 12% on THF and decreased to about 1% for 5-Fe-THF. Further adsorption on the sample surface did not occur after 1 h. The decrease in MB adsorption on the sample surface may be due to the decrease in surface area and a difference in surface chemistry at high Fe concentration. After LED irradiation for 6 h, MB was degraded by 67%, 66%, 55%, and 49% for THF, 1-Fe-THF, 3-Fe-THF, and 5-Fe-THF, respectively. From these results, although Fe doping could narrow bandgap energy of THF to be responsible in the visible light region, the photocatalytic activity of Fe-THF was not improved. Rather, the opposite
occurred. This finding was similar to the previous works reported by Li et al. [9] and Moradi et al. [10] showing that excess Fe doping led to poor photocatalytic activity. The adverse effect of Fe doping on photocatalytic activity can be ascribed to the fact that overly high levels of Fe dopants can serve as a recombination center for electrons and holes, instead of electron scavenger sites, thus inhibiting photocatalytic activity [9,10].

![Figure 3](image_url)

**Figure 3** (a) UV–vis absorption spectra of MB solution at the presence of 1-Fe-THF at different irradiation times. (b) Plot of $C_t/C_0$ versus irradiation time for all samples.

4. Conclusions
In summary, Fe-THFs with different Fe concentrations (0.22–0.96 at%) have been successfully synthesized via the biotemplate method. Anatase was found as the main crystalline phase in Fe-THFs, while rutile phase was formed at high Fe concentrations. The Fe-THFs revealed a redshift phenomenon, which extended their absorption to visible light region, resulting in a significant reduction of bandgap energy. Despite narrow bandgap energy, the photocatalytic activity of Fe-THFs was inferior to undoped THF and became worse at higher Fe concentration. Poor photocatalytic activity of Fe-THFs in this work could be attributed to too much Fe dopant in the lattice structure, which in turn led the formation of recombination centers, thereby inhibiting electron–hole pair separation. The results obtained in this work suggested that more detailed investigations are necessary to seek the optimum Fe concentration for enhancing the photocatalytic activity of THF. Surface area and chemical bonding state of dopant must also be considered for comparison in future work.

5. References
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