Controllable synthesis of Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O as a highly efficient heterogeneous Fenton-like catalyst

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Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O has been successfully synthesized by a simple hydrothermal process. The effects of hydrothermal temperature and pH value on the morphologies and sizes of the Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O particles were investigated. The Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O photocatalyst showed lower photocatalytic activity for the degradation of methylene blue under visible light irradiation. But the heterogeneous Fenton-like Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O with H$_2$O$_2$ showed highly efficient photocatalytic activity in the photocatalytic decomposition of methylene blue. Effective electron transfer from the visible light-excited dyes to Fe(III), which leads to regeneration of Fe(II) and an easy cycle of Fe(III)/Fe(II), results in much faster degradation and mineralization of methylene blue in the photo-Fenton reaction under visible light irradiation.

1. Introduction

Fenton and photo-Fenton reactions have proven to be effective methods to treat organic pollutants in wastewater, and the mechanism and kinetics have been studied by many researchers.\(^1\)\(^-\)\(^10\) However, the Fenton process has significant disadvantages: iron ions have to be separated from the system at the end of the process by precipitation, which is expensive in labor, reagents and time; it is limited by a narrow pH range; and iron ions might be deactivated due to complexation with some iron complexing reagents.\(^11\)\(^,\)\(^12\) To overcome these disadvantages of the homogeneous Fenton process, heterogeneous Fenton and Fenton-like catalysts have recently received much attention.

To date, investigations have mainly focused on three types of materials: an iron–oxygen series of compounds;\(^13\)\(^-\)\(^16\) Fe-immobilized materials;\(^17\)\(^-\)\(^31\) and natural Fe-containing materials.\(^12\)

These heterogeneous Fenton and Fenton-like catalysts were demonstrated to be useful to treat various organic pollutants in water over a wide applicable pH range. However, many of them did not show favorable catalytic activity.\(^12\) In this sense, it is a challenging issue to develop novel heterogeneous Fenton-like catalysts with higher catalytic activity.

In this paper, Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O were controllably synthesized with tunable morphology by a simple hydrothermal method. The influence of reaction parameters (pH value and hydrothermal temperature) on the Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O morphology, structure and the relationship between the morphology and photocatalytic activity were investigated. The heterogeneous Fenton-like Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O with H$_2$O$_2$ showed highly efficient photocatalytic activity in the photocatalytic decomposition of methylene blue. The aim of this research was to enrich the available methods for the preparation of novel heterogeneous Fenton-like catalysts with high catalytic activity.

2. Experimental section

2.1. Materials

Methylene blue of analytical reagent grade quality was used without further purification. Other chemicals were commercial products of analytical grade or reagent-grade. All the solutions were prepared with distilled water.

2.2. Preparation of Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O

In a typical synthesis procedure, Fe(NO$_3$)$_3$·6H$_2$O (5 mmol) was completely dissolved in deionized water (14 ml). Under vigorous agitation, an aqueous solution (14 ml) containing Na$_3$PO$_4$·6H$_2$O (5 mmol) was added into the above solution at room temperature. The pH value of the mixture was adjusted with 10 M NaOH and HNO$_3$ (68%). Then, the mixture was transferred into a Teflon-lined steel autoclave of 40 ml, and the autoclave was heated under autogenous pressure at 180 °C for 24 h. Afterward, the autoclave was cooled to room temperature gradually. The yellowish green precipitate was washed with distilled water three times. Then, it was dried at 60 °C in air.

2.3. Characterization

The degradation rates of methylene blue (MB) solutions were scanned by a Hitachi U-3010 spectrophotometer periodically...
and the maximum absorption wavelength of the MB solution was identified as 664 nm. The UV-vis spectra data were recorded in the range from 200 to 800 nm. The UV-vis diffuse reflectance spectra (UV-vis DRS) of the samples were obtained on a UV-vis spectrophotometer (UV-3010, Shimadzu) using an integrating-sphere accessory. The fluorescence data were recorded on a Hitachi F-7000 Fluorescence spectrophotometer. BaSO₄ was used as a reflectance standard. The pH value was measured by Model PHS-7A pH meter. X-ray diffraction (XRD) experiments were carried out using a Rigaku DMAX-2400 diffractometer with Cu-Kα radiation. The size and morphology of Fe₅(PO₄)₄(OH)₃·2H₂O particles were characterized with the aid of a JEOL JEM-6700F field emission scanning electron microscope (SEM) and LEO-1530 field emission scanning electron microscope.

2.4. Photocatalytic oxidative degradation

The photocatalytic activities of the Fe₅(PO₄)₄(OH)₃·2H₂O were evaluated by MB decomposition under visible-light irradiation. In the case of visible-light irradiation, a 500 W xenon lamp (λ > 290 nm, the Institute of Electric Light Sources, Beijing) was focused through a window. A 420 nm cutoff filter was placed onto the window face of the cell to ensure the desired irradiation condition. The average light intensity was 40 mW cm⁻². The radiant flux was measured with a power meter (the Institute of Electric Light Sources, Beijing).

A cylindrical double-layer glass photochemical reactor with an internal diameter 70 mm, external diameter 80 mm, and height 80 mm was utilized for the photocatalysis reaction. A distance of 12 cm between the lamp and reactor was maintained. Running water was piped into the layer in order to keep the temperature constant.

The photocatalytic degradation of MB in aqueous solution was studied by using Fe₅(PO₄)₄(OH)₃·2H₂O as the photocatalyst at room temperature and normal atmospheric pressure. Fe₅(PO₄)₄(OH)₃·2H₂O (50 mg) and 100 ml MB (1 × 10⁻⁵ M) aqueous solution were added into the reactor, and then stirred with a magnetic stirrer prior to irradiation by a xenon lamp at room temperature. Prior to irradiation, the solution was put in the dark for 60 min to ensure equilibrium of the working solution. After the reaction, the sample solution was put in a centrifuge to remove Fe₅(PO₄)₄(OH)₃·2H₂O from solution. The solution obtained this way was extracted into a quartz cell. The fluorescence of the samples was measured in the quartz cell every 60 min. By comparison of the fluorescence intensity with that of a known concentration of TAOH, the amount of TAOH produced was determined. The amount of OH formed in Fe₅(PO₄)₄(OH)₃·2H₂O photocatalysis was estimated from that of TAOH by adopting the trapping factor.

3. Results and discussion

3.1. Controlling the synthesis of Fe₅(PO₄)₄(OH)₃·2H₂O

The pH value of the starting precipitate precursors had crucial effect on the formation of Fe₅(PO₄)₄(OH)₃·2H₂O. The precursor suspensions were adjusted to the desired pH values by adding NaOH solution and HNO₃ solution, and then were hydrothermally treated at 180 °C for 24 h. Fig. 1 shows the XRD patterns of Fe₅(PO₄)₄(OH)₃·2H₂O samples prepared by the hydrothermal procedure at different pH values. The diffraction peaks of all the samples could be easily indexed as a pure, orthorhombic crystalline phase Fe₅(PO₄)₄(OH)₃·2H₂O, which is in good agreement with the standard card (JCPDS Card number: 45-1436). As seen from the XRD patterns, the high crystallinity could be obtained at a relatively high pH value. When the pH value was increased to 5, it changed to a mixture.

The microstructures of the as-prepared samples were then investigated with SEM. Fig. 2a shows a TEM micrograph of the sample prepared at pH = 1, from which one can see that the sample was bottle gourd in shape with diameters of 5 μm. It looks like a small sphere grew at the surface of a large sphere, and the
surface of the sphere was very smooth (Fig. 2b). As the pH value was adjusted to 1.5, many horns grew on the surface of the sphere (Fig. 2c). When the pH value was increased to 2, all spheres evolved into cerioid-asteroid particles with a size of 10 μm (Fig. 2d and 2e). It was like many lance-points agglomerated together. The microstructure was nearly unchanged while pH value rose to 2.5 (Fig. 2f). When the pH value was adjusted to 3 or 4, to our great surprise, many cruciate flowers existed in the resulting product (Fig. 2g and 2h). It was clear that each cruciate flower was composed of a crosslike trunk and many branches, and the branches were perpendicular to their trunk. Besides the trunk and branches, some tubers grew on the trunk and were perpendicular to branches. When the pH value was 3, there were many particles covering the surface of the cruciate flower. When the pH value increased to 4, the particles disappeared, and only pure cruciate flowers could be found. The pH value played an important role in the formation of Fe₅(PO₄)₄(OH)₃·2H₂O. When the pH value was 1, there was less OH⁻ in solution. So the nucleation and growth of Fe₅(PO₄)₄(OH)₃·2H₂O were restrained. Fe₅(PO₄)₄(OH)₃·2H₂O grew isotropically and the morphology of Fe₅(PO₄)₄(OH)₃·2H₂O presented microspheres. As the pH value increased, the amount of OH⁻ also increased in the solution. The nucleation and growth of Fe₅(PO₄)₄(OH)₃·2H₂O were accelerated, so Fe₅(PO₄)₄(OH)₃·2H₂O grew anisotropically. The crystalline surface of the preferential growth direction grew faster; it caused microspheres to transform into cerioid-asteroid particles; finally the cerioid-asteroid particles turned into cruciate flowers.

On varying the reaction time with the temperature fixed at 180 °C, the Fe₅(PO₄)₄(OH)₃·2H₂O crystalline phase appeared only after 14 h hydrothermal treatment, which is shown in Fig. 3. When the Fe₅(PO₄)₄(OH)₃·2H₂O crystalline phase appeared, the cruciate flowers appeared at the same time (Fig. 4b). Before the Fe₅(PO₄)₄(OH)₃·2H₂O crystalline phase formed, only particles could be found (Fig. 4a). In addition, the temperature also had a significant influence on the formation of Fe₅(PO₄)₄(OH)₃·2H₂O. When the temperature was below 160 °C, the Fe₅(PO₄)₄(OH)₃·2H₂O phase could not form (Fig. 5). The cruciate flower was broken by degrees as the temperature increased to 220 °C (Fig. 6). It meant the cruciate flower morphology could not be obtained at high temperature, as high as 220 °C, under identical solution conditions. This suggests that Fe₅(PO₄)₄(OH)₃·2H₂O might lose the water like Ca₁₀(PO₄)₆(OH)₂ as high as 220 °C. This process was reversible, so it did not affect the properties of Fe₅(PO₄)₄(OH)₃·2H₂O, but the cruciate flower morphology would be destroyed.

3.2 Optical properties and photocatalytic activity

The optical absorption of the Fe₅(PO₄)₄(OH)₃·2H₂O nanoplates was measured using a UV-vis spectrometer. The optical absorption of all the samples was nearly the same. Fig. 7 showed typical diffuse reflection spectra of Fe₅(PO₄)₄(OH)₃·2H₂O obtained after synthesis at different pH values and different temperatures. The bandgap of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different pH values are shown in Table 1. The steep shape of the spectra indicated that the visible light absorption was not due to the transition from the impurity level but was due to the bandgap transition (Table 1). The band at 400–450 nm could be assigned to Fe–O charge transfer transitions.

Methylene blue was used as a probe in the heterogeneous photocatalysis, and decoloration and decomposition could be
Monitored via the visible-light absorption signature. Fig. 8 shows the degradation of MB using Fe₅(PO₄)₄(OH)₃·2H₂O samples synthesized at different pH values. The first-order linear relationship was revealed by plots of ln(C/C₀) vs. irradiation time (t), where C was the concentration of MB at the irradiation time t and C₀ was the concentration in the adsorption equilibrium of the photocatalysts before irradiation. Via the first order linear fit, the determined reaction-rate constants k were 0.0769, 0.0903, 0.1015, and 0.0975 h⁻¹, respectively, for the samples synthesized at different pH values. Among these samples, the photocatalytic activity increased as the pH value increased. The surface area of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different pH values is shown in Table 2. The photocatalytic activity was not in accordance with the surface area. This means the surface area has no obvious effect on the photocatalytic degradation of MB in aqueous solution. The sample obtained at low pH was not highly

<table>
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<th>4</th>
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<td>bandgap (hυ/eV)</td>
<td>2.686</td>
<td>2.676</td>
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crystalline, which was confirmed by the XRD result. A lot of defects could act as an electron–hole recombination center, resulting in a low photocatalytic activity. Fig. 9 shows the first-order plots for the photocatalytic degradation of MB using Fe₅(PO₄)₄(OH)₃·2H₂O samples synthesized at different temperatures. The reaction rate constant \( k \) was 0.09233, 0.10318, 0.08909, 0.09751 and 0.10942 h⁻¹, respectively, for the 240, 220, 200, 180 and 160 °C samples. The surface area of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different temperatures is shown in Table 3. The surface area of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different temperatures was similar. This means the temperature has no obvious effect on the surface area. When the pH value was 4, the activity of the sample prepared at 160 °C was the highest. The photocatalytic activity was not in accordance with surface area. It was mainly attributed to a better crystalline phase which was consistent with the XRD.

### 3.3. Photocatalytic activity of the Fenton-like reaction and the reaction mechanism

The degradation process of MB catalyzed by Fe₅(PO₄)₄(OH)₃·2H₂O obtained at 160 °C with various \( \text{H}_2\text{O}_2 \) concentrations is shown in Fig. 10. The first-order linear relationship was obtained, as showed by the plots of \( \ln(C/C_0) \) versus reaction time (the inset of Fig. 10). The reaction rate constant \( k \) was 0.34252, 0.40664, 0.27864 and 0.37608 h⁻¹, respectively, for the 240, 220, 200, 180 and 160 °C samples. The reaction rate constant \( k \) was 0.09233, 0.10318, 0.08909, 0.09751 and 0.10942 h⁻¹, respectively, for the 240, 220, 200, 180 and 160 °C samples. The surface area of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different temperatures is shown in Table 3. The surface area of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different temperatures was similar. This means the temperature has no obvious effect on the surface area. When the pH value was 4, the activity of the sample prepared at 160 °C was the highest. The photocatalytic activity was not in accordance with surface area. It was mainly attributed to a better crystalline phase which was consistent with the XRD.

The mechanism of the Fenton-like reaction is shown in Scheme 1.⁴⁴,⁴⁵

Fig. 10 also shows that the spectral band at 664 nm blue-shifts during the course of the photodegradation. As weak electron-donor substituents, methyl groups could facilitate attack on MB by OH⁻ in the demethylation process; this is also likely to be a major step in the photocatalytic oxidative degradation of MB.⁴⁶ Examination of the spectral variations in Fig. 10 suggests that MB is N-demethylated in a stepwise manner (methyl groups are removed one at a time as confirmed by the gradual peak wavelength shifts toward the blue region), with cleavage of the MB chromophore ring structure occurring concomitantly. N-demethylation, deamination and oxidative degradation takes place during the photocatalyzed degradation of MB.⁴⁶ Mixtures of N-demethylated intermediates yield spectra with broad absorption bands in the visible range. To examine the process in detail, the neutral intermediates were also identified by LC/MS (Fig. S1†). The suggested structures of the intermediates based on the LC/MS results are shown in Table 1 of the supporting information.‡ The result is consistent with the UV-vis spectral result.

Fig. 11 shows the fluorescence spectra observed for a solution of the Fe₅(PO₄)₄(OH)₃·2H₂O suspension containing 16 mM disodium terephthalate irradiated for various duration times. Since the observed fluorescence spectra were identical to that of TAOH, it was concluded that TAHO was generated from TA by the reaction with OH⁻ where OH⁻ formed in the Fe₅(PO₄)₄(OH)₃·2H₂O photocatalysis. Fig. 11 represents the fluorescence intensity as a function of the duration of irradiation. Since the fluorescence intensity increases with irradiation time until 5 h of visible light irradiation, the amount of OH⁻ formed in the Fe₅(PO₄)₄(OH)₃·2H₂O photocatalysis reaches an equilibrium after this duration under visible light irradiation.

### Table 2 The BET results of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different pH values

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<th>4</th>
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<td>BET surface area/m² g⁻¹</td>
<td>23.31</td>
<td>0.27</td>
<td>0.75</td>
<td>1.65</td>
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### Table 3 The BET results of Fe₅(PO₄)₄(OH)₃·2H₂O obtained at different temperatures

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<th>Temperature/°C</th>
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<th>200</th>
<th>220</th>
<th>240</th>
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<td>BET surface area/m² g⁻¹</td>
<td>1.65</td>
<td>1.08</td>
<td>1.27</td>
<td>0.51</td>
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**Fig. 9** First-order plots of the photocatalytic degradation of MB using Fe₅(PO₄)₄(OH)₃·2H₂O samples synthesized at different temperatures.

**Fig. 10** The UV-vis spectral changes of MB (Fe₅(PO₄)₄(OH)₃·2H₂O: 0.5 g l⁻¹; \( \text{H}_2\text{O}_2 \): 9.8 mM; MB: \( 1 \times 10^{-5} \) M). Inset: the first-order linear relationship for the photocatalytic degradation of MB using various \( \text{H}_2\text{O}_2 \) concentrations.
The mechanism of the Fenton-like reaction.

Degraded product  \[ \text{dye} \rightarrow \text{dye}^- \]

**Scheme 1** The mechanism of the Fenton-like reaction.

**Fig. 11** The changes in the fluorescence spectra of the irradiated Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O (0.5 g L$^{-1}$) suspension containing 40 mM disodium terephthalate and 9.8 mM H$_2$O$_2$ at various irradiation periods.

4. Conclusions

In conclusion, the photocatalytic properties of Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O were investigated under visible light irradiation in detail. The Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O was first tested and used as a heterogeneous Fenton-like catalyst. It was found that Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O possessed high catalytic activity towards the degradation of MB in the presence of H$_2$O$_2$. The high catalytic activity could be attributed to an interesting mechanism, that is, the activation of H$_2$O$_2$ by Fe(III) in Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O by a Fenton-like pathway.

Acknowledgements

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References