

Synthesis of shape-controlled $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystal via one-step hydrothermal method

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The aim of this study was to look for a simple and easy method to prepare $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystal with various morphologies. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were employed as raw materials without any surfactant assistance to synthesise $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystal by one-step hydrothermal method. The effect of reactant concentration on the morphology of the product was systematically studied. The results indicate that with increasing concentration of reactants, morphology of the product could be converted from dendrite shape to flower shape and sphere. The corresponding FePO_4 with various morphologies was also easily prepared by heating the $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ precursor at the optimum temperature. This work provides an effective method to synthesise $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ and FePO_4 microcrystal with various morphologies which could meet the demands of lithium-ion battery material and catalyst material.

1. Introduction: In recent years, iron phosphate has gradually attracted the attention of scientists, not only because of their excellent physical and chemical properties but also their wide application ranging from selective catalyst [1] to electrode materials in lithium batteries [2–4]. Owing to these intriguing properties and application, their structures with various morphologies, such as spherical particles [5], porous and mesoporous particles [6, 7], nanotubes [8], ultrafine nanopowder [9] and nanosphere [10], have been the subject of intensive research.

Iron hydroxyl phosphate ($\text{Fe}_x(\text{PO}_4)_y(\text{OH})_z \cdot n\text{H}_2\text{O}$), such as giniite $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ with rich crystal chemistry, is well known as the main precursors of iron phosphate and lithium iron phosphate which can be used in lithium batteries as a promising electrode material. Recently, some spontaneous growth processes and mechanisms have been studied during the synthesis of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ crystals. For instance, Song *et al.* [11] have synthesised $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ mesoporous microspheres by hydrothermal method, which are considered to be constructed by polyhedral nanocrystals. Yang *et al.* [12] have synthesised a hierarchical $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microflower, with self-prepared $\beta\text{-FeOOH}$ nanorod as raw material by a hydrothermal reaction. Han *et al.* [13] have reported a new cathode material in lithium-ion batteries by a one-pot hydrothermal approach, using 3D graphene aerogel and $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microspheres as raw materials. It shows an excellent specific capacity of 155 mAh g^{-1} after 300 cycles at a current density of 50 mA g^{-1} . $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ single-crystalline dendrites were synthesised by Li *et al.* [14]. The amount of H_2O_2 solution, types of iron precursors and pH values in the reaction system are the major factors affecting the morphology and size of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ products. A biocompatible hyperbranched $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ with single crystallinity in nature which can be used for highly selective capture of phosphopeptides was prepared via a simple solution method [15]. Therefore, controlling chemical composition, morphologies and sizes of iron phosphate-based materials is an effective means of improving their properties, and is important for their application in catalysis and electrode materials in lithium batteries. However, little attention has been paid to transformation of various morphologies of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ crystals.

Here, a simple and easy method to prepare $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystal with various morphologies

was demonstrated. $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystal converted from dendrite shape to flower shape and sphere were synthesised without any surfactants by a simple hydrothermal reaction. The shape control was achieved just by adjusting the reactant concentration. Moreover, the formation mechanism of different morphology of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystals was discussed. Finally, on this basis, we have successfully prepared a variety of morphologies of iron phosphate by anneal treatment of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ precursor at 750°C in air for 2 h.

2. Experimental: $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystals with various morphologies were synthesised by a hydrothermal treatment of FeCl_3 with $\text{NH}_4\text{H}_2\text{PO}_4$ as additives at 220°C . By adjusting the concentrations of FeCl_3 solution and $\text{NH}_4\text{H}_2\text{PO}_4$ solution, $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystals with varied morphology were produced.

In a typical experimental procedure for preparing $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystal, 0.2 mL of FeCl_3 aqueous solution (0.5 M), 0.2 mL of $\text{NH}_4\text{H}_2\text{PO}_4$ aqueous solution (0.5 M) and 59.6 mL deionised water were mixed. After magnetic stirring for 30 min, the mixture was transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL and maintained at 220°C for different time for hydrothermal treatment. After the autoclave was cooled down to room temperature naturally, the yellow-white precipitate was separated by centrifugation, then washed several times with deionised water and absolute ethanol and dried at 80°C . The obtained product was labelled S1. After a simple adjustment of the reactant concentration, the different morphology of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ was prepared. For sample S2, 0.5 mL of FeCl_3 aqueous solution (0.5 M) and 0.5 mL of $\text{NH}_4\text{H}_2\text{PO}_4$ aqueous solution (0.5 M) were used. Also, 1 mL, 3 mL of FeCl_3 aqueous solution (0.5 M) and 1 mL, 3 mL of $\text{NH}_4\text{H}_2\text{PO}_4$ aqueous solution (0.5 M) were used for the preparation of samples S3 and S4, respectively. Information relating to synthesising and processing conditions of all samples were shown in Table 1. All the reagents were analytical purity and purchased from Sigma-Aldrich Chemical, Co. and used as raw material without further purification.

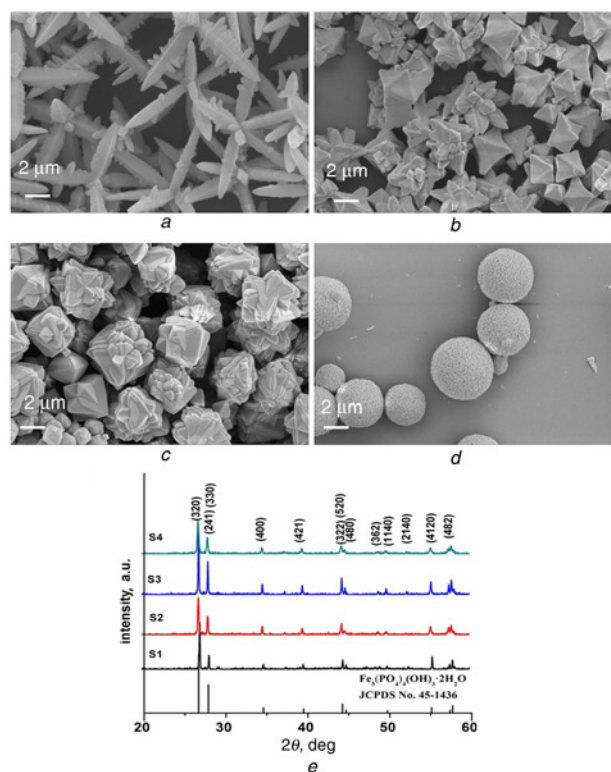
The morphology of the microcrystal was characterised by scanning electron microscope (SEM; Zeiss Supra 40). The phases of the microcrystal were verified by X-ray diffractometer (XRD; Bruker D8 Advanced Diffractometer System, $\text{Cu K}\alpha$, $\lambda = 1.5418 \text{ \AA}$). Thermogravimetric analysis (TGA/DSC) was conducted

Table 1 Process parameters of all samples

Sample	FeCl ₃ aqueous solution (0.5 M), mL	NH ₄ H ₂ PO ₄ aqueous solution (0.5 M), mL	Deionised water, mL
S1	0.2	0.2	59.6
S2	0.5	0.5	59
S3	1	1	58
S4	3	3	54

between 30 and 900°C, with a heating rate of 10°C/min by Q600 thermogravimetric analyser (TA Instruments, USA).

3. Results and discussion: To study how the concentrations of reactants affect the morphologies and the structures of the product, a series of experiments were carried out. In the hydrothermal reaction, the Fe₅(PO₄)₄(OH)₃·2H₂O microcrystal was prepared with different concentration combination of FeCl₃ aqueous solution and NH₄H₂PO₄ aqueous solution as raw material at 220°C for 48 h. The morphologies and the phases of the as-prepared products were investigated by SEM and XRD as shown in Fig. 1. From Fig. 1e, showing X-ray diffraction (XRD) patterns of the samples, we can see that all of the peaks of the products can be well indexed to a pure orthorhombic Fe₅(PO₄)₄(OH)₃·2H₂O (JCPDS Card No. 45-1436) without any impurities. This means that the reactant concentration has no effect on the phase of product. All the diffraction peaks are very sharp and strong which indicate that the as-synthesised products are well crystallised. However, the morphology of the products is diverse from each other when varying the reactant concentration.

**Fig. 1** SEM images

- a S1
- b S2
- c S3
- d S4
- e XRD patterns of the Fe₅(PO₄)₄(OH)₃·2H₂O microcrystal

Figs. 1a–d. display typical SEM images of the Fe₅(PO₄)₄(OH)₃·2H₂O sample synthesised with different amount of reactants at 220°C for 48 h. The effect of reactant concentration on the morphology of the product can be clearly observed. When 0.2 mL of FeCl₃ aqueous solution (0.5 M) and 0.2 mL of NH₄H₂PO₄ aqueous solution (0.5 M) were added in the reaction system, a large number of 6–10 μm dendritic structures existed in the final product (Fig. 1a). It is clear that each dendrite is composed of five or six branches, with a large number of jagged structures on these branching stems. As the amount of reactants was adjusted to 0.5 mL of FeCl₃ aqueous solution (0.5 M) and 0.5 mL of NH₄H₂PO₄ aqueous solution (0.5 M), peculiar angular morphological features can be seen in the resulting products. These angular bodies can combine into a flower or octahedral with sizes of 4–8 μm. When the amount of reactants was increased to 1 mL of FeCl₃ aqueous solution (0.5 M) and 1 mL of NH₄H₂PO₄ aqueous solution (0.5 M), the morphology of the resulting product evolved into a number of flower structures with sizes of 2–4 μm (Fig. 1c). Each flower is composed of some flakes. The microstructure of products was changed into a great deal of sphere structures with diameters of 2–4 μm while the amount of reactants rose to 3 mL of FeCl₃ aqueous solution (0.5 M) and 3 mL of NH₄H₂PO₄ aqueous solution (0.5 M) (Fig. 1d). It is indicated that the morphology of Fe₅(PO₄)₄(OH)₃·2H₂O products can be affected by the concentration of reactants. With increasing concentration of reactants, morphology of the product could be from dendrite-shaped converted to be flower-shaped and sphere. Although these Fe₅(PO₄)₄(OH)₃·2H₂O samples have different morphologies, their physical phases are identical, as demonstrated by the X-ray diffraction patterns (Fig. 1e). The synthesis of single-crystalline Fe₅(PO₄)₄(OH)₃·2H₂O with various morphologies enriches the micro- and nanostructure of iron hydroxyl phosphates. It is of great significance to the more and more widely growing field of giniite application.

To elucidate the formation and evolution mechanism of Fe₅(PO₄)₄(OH)₃·2H₂O microcrystal, we also carried out a series of time-dependent experiments at 220°C but with different reaction times (0.5, 1, 3, 12, 24 and 48 h, respectively). The reaction products at different stages were collected from the reaction mixture during the reaction process, and then their morphologies and phases were investigated by SEM and XRD, respectively. XRD patterns of as-synthesised samples at different reaction times were shown in Fig. 2i. When the reaction time was 0.5 h, broad diffraction peaks were observed. According to the main diffraction peak locations, the products could be indexed to the orthorhombic crystalline phase Fe₅(PO₄)₄(OH)₃·2H₂O. With the increase of the reaction time, all diffraction peaks became sharp, indicating the growth of the Fe₅(PO₄)₄(OH)₃·2H₂O crystallites. No peaks of any impurities are detected in the patterns.

The morphologies of sphere products with various reaction times (hours) are shown in Figs. 2a–h. Fig. 2a shows the microstructures of the as-prepared samples with reaction time of 0.5 h, from which one can clearly see that the sample is composed of large-scale nanoparticles and a small amount of microspheres with the average diameter of ~2 μm. The morphology of microspheres is not uniform. The high-magnification SEM image of nanoparticles is presented in Fig. 2b. We can see that the size of the particles is widely ranging from tens of nanometres to ~100 nm. It implies that the Ostwald ripening process occurs at 0.5 h. When increasing the reaction time to 1 h, all the nanoparticles disappear, only the microsphere structure left as shown in Fig. 2c. The diameter of the microspheres is widely ranging from 0.5 to 3 μm, with a nearly smooth surface (Fig. 2d). When extending the reaction time to 3 h, the smooth surface of microsphere becomes uneven and a little rough. However, the sphere size does not change. When the reaction time is further increased to 24 h, the sphere morphology of particles remain unchanged but the surface becomes noticeable rougher (Fig. 2f). Finally, when the reaction time reaches 48 h,

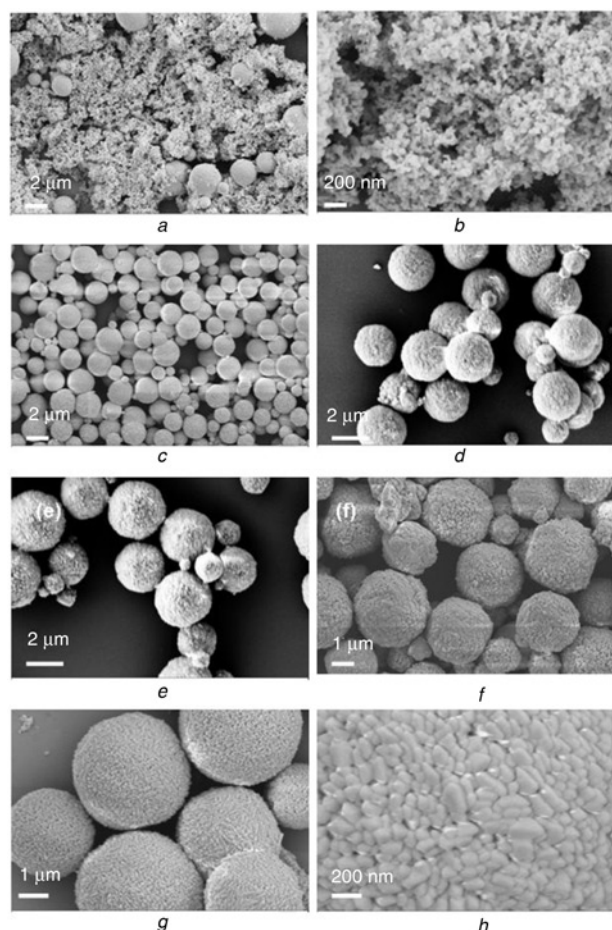


Fig. 2 Low- and high-magnification SEM images of S4 sample with different reaction times
a and b 0.5 h
c 1 h
d 3 h
e 12 h
f 24 h
g and h 48 h
i XRD patterns of the S4 sample with different reaction times

perfect and well-crystallised $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microspheres are obtained. Most of them are uniform microspheres of $\sim 3 \mu\text{m}$ in diameter as presented in Fig. 2g. At the same time, it can be seen that the average diameter of the microspheres is getting bigger and bigger and the surface of the microspheres becomes coarser with increasing reaction time, which is probably due to the prolonged reaction time and growth of crystals. High-magnification SEM image in Fig. 2h clearly show some detail structural information of rough surface of the microspheres. The surface of the microspheres is not flat and smooth. A lot of

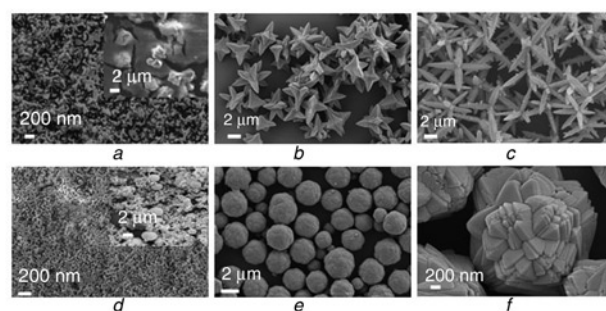
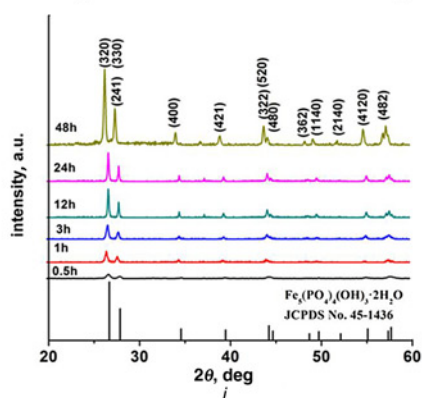


Fig. 3 SEM images of S1 sample with different reaction times
a 0.5 h
b 1 h
c 12 h
S3 sample with different reaction times
d 0.5 h
e 1 h
f 12 h

small nanoparticles appear on the peripheral surface of the microspheres. Moreover, the porous structure resulting from the aggregation of the nanoparticle can also be clearly observed. Finally, we can sum up the formation and evolution mechanism of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microsphere. As shown in Figs. 2g and h, as the extension of the reaction time, the morphology of the products changed from amorphous nanoparticle to mesoporous microsphere structures, showing the gradually growth of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ from small nanoparticles produced at early stage to the bigger and rougher microspheres.

Figs. 3a–c show the evolution process of the morphology of the products gradually changed from particle structure to dendrite fractal structure with the increase of the reaction time. Before the $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ crystalline phase formed, only nanoparticles could be observed. When the reaction time was 0.5 h, with the $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ crystalline phase appeared, the cerioid-asteroid particles appeared at the same time, which is shown in Fig. 3a. As the reaction time was prolonged to 1 h, all the nanoparticles disappear, and what we can see are cerioid-asteroid particles with a size of 2–4 μm (Fig. 3b). It was like many lance-points agglomerated together. When the reaction time was 12 h, to our great surprise, some dendrite fractal structure existed in the final product (Fig. 3c). Each dendrite was composed of some well-defined hyperbranched microstructures. It is shown in Figs. 3d–f, the formation of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microflower structure is also dependent on the reaction time. At first, the sample after heating for 0.5 h maintains a basic shape of a microsphere and a large amount of nanoparticles. It means that the Ostwald ripening process also occurs at 0.5 h. Then, increasing the sample heating time to 1 h, the nanoparticles disappeared, and a small amount of horns occurred on the surface of microsphere. Finally, when the reaction time was further prolonged to 12 h, the horns became bigger and bigger, and the morphology of the products changed from similar microsphere to microflower structure. In brief, from the information obtained at the different reaction stages, it can be deduces that some nanoparticles would be produced at the primary stage and the novel rough microsphere structure may grow from these small particles and then anisotropically develop microflower structure at the right time.

To find out the optimum temperature for the preparation of FePO_4 , the thermal analysis kinetics of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ precursor was studied. A combined thermogravimetry/differential scanning calorimetry (TG/DSC) analysis curve of the $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystal was shown in Fig. 4e. At first, a little weight loss in the TGA curve before 200°C can be observed, which is due to the removal of physically water adsorbed in the sample. The weight loss of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$

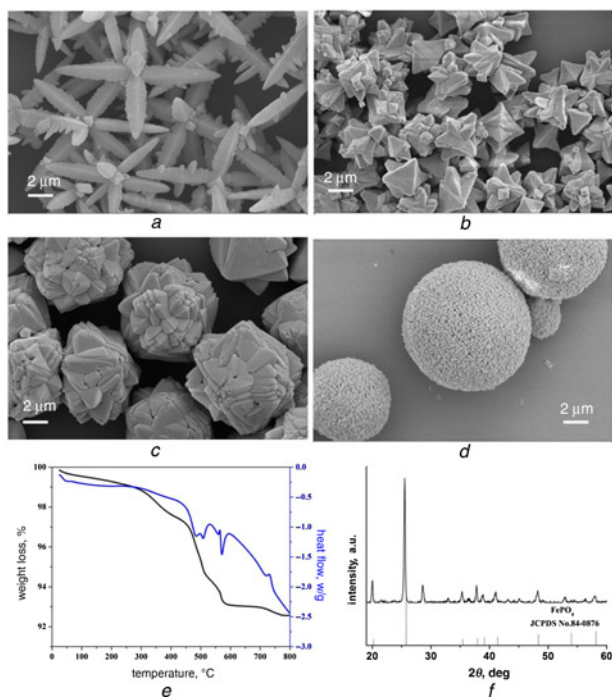
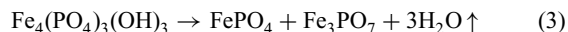
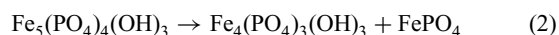
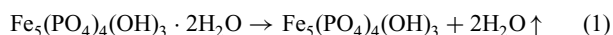


Fig. 4 SEM images of FePO_4 obtained after anneal treatment
a S1
b S2
c S3
d S4 at 750°C in air for 2 h
e TG/DSC curve of the S4 at a heating rate of $10^\circ\text{C}/\text{min}$
f XRD pattern of FePO_4 obtained after anneal treatment S4 at 750°C in air for 2 h

microcrystal between 200 and 750°C is $\sim 8\%$. It can be attributed to the loss of crystalliferous water and the phase transformation from $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ precursor to FePO_4 . At the same time, the DSC analysis reveals that when the temperature is $>750^\circ\text{C}$, there is no endothermic peak or thermopositive peak appeared. Therefore, to ensure the complete transformation from $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ precursor to FePO_4 , the temperature of 750°C was chosen as the heat treatment temperature of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$. According to the TGA results, the evolution mechanism of FePO_4 was proposed and shown in (1)–(3)



The XRD pattern of the $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ heated at the temperature 750°C in air for 2 h was shown in Fig. 4f. The major peaks are in good agreement with those of the standard FePO_4 as PDF-840876. The sharp peaks indicate that the growth of the FePO_4 microcrystal gains is good. In addition, there are a small amount of impurity phase appears in the product. Figs. 4a–d show the SEM images of as-prepared FePO_4 obtained from $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ after heat treatment at 750°C for 2 h. We can see that the morphology of the FePO_4 microcrystal is inherited from $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$. From the outside, they look exactly the same. It means that thermal treatment only induces the conversion of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ to FePO_4 , and has no influence on the morphology of the final products.

4. Conclusions: In conclusion, these results suggest that we have successfully synthesised orthorhombic $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microcrystals with various morphologies by a facile one-step hydrothermal reaction only with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ as raw material. Shape control of microcrystal was successfully conducted by simply adjusting the concentration of reactants without the aid of any surfactant or template. With increasing concentration of reactants, morphology of the product could be from dendrite-shaped converted to be flower-shaped and sphere. At the same time, various morphologies of FePO_4 can be easily obtained by calcining $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ precursor at 750°C , which is optimised by TG/DSC analysis. This work provides a simple and easy method for preparing various morphologies of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ and FePO_4 microcrystal which is required for lithium-ion battery material and catalysts with high catalytic activity.

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6 References

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