Synthesis of Hexagonal Mesostructured $FePO_4$ Using Cationic Surfactant as the Template

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An effective, fast, easy approach was reported for the first time to synthesize highly-ordered hexagonally mesostructured iron phosphate using cationic surfactant as the template.

Mesoporous materials have attracted much attention since it was first reported in 1992,[1] for its promise applications as high surface area catalysts, adsorbents, hosts for inclusion compounds, and electrochemical devices.[2] This method has been extended to prepare mesoporous metal phosphate,[3–9] which can be used as catalysts, adsorbents, and iron exchangers. Materials containing phosphate moiety would provide an attractive area of investigation on new cathode or anode materials.[10] Iron phosphate has been reported to be used not only as good catalyst,[11,12] but also as cathode material for lithium secondary batteries.[13] The mesoporous structure will benefit not only catalytic performance but also the cathode performance, for it facilitating the penetration of the liquid electrolyte into the electrodes. Therefore, the preparation of the materials with an ordered mesoporous structure would be of significant interest. Mesoporous iron phosphate was first reported by Yan[6] in 2001 by employing anion surfactant, sodium dodecyl sulfate, as the template. However, only disordered mesoporous iron phosphate has been detected from the TEM image. After that, lamellar structured iron phosphate was claimed to be made using poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer (p123) as the template.[9] As the best to our knowledge, no ordered-hexagonal mesostructured iron phosphate has been declared to be prepared up to date. Here we present for the first time a very effective, fast, easy approach to synthesize highly-ordered hexagonally mesostructured iron phosphate using cationic surfactant as the template.

The mesostructured materials were synthesized employing cationic surfactant, cetyltrimethylammonium chloride (CTMACl, $C_{16}H_{33}$ NMe_3Cl) as the template. Usually, 0.2-g CTMACl was dissolved in 7 mL of water. A transparent solution of 0.4-g $Fe_2(SO_4)_3$ and 0.4135-g H_3PO_4 mixture dispersed in 1 mL of deionized water was added into the above solution as a batch. Followed by adding 0.12 mL of HF, 0.40 g of $LiOOCCH_3$ dissolved in 1.5-g distilled water was then added dropwise under vigorous stirring. The solution mixture was stirred for another 12 h period at room temperature, then transferred into a Teflon-lined stainless-steel tube. The synthesis gel was initially heated at 323 K for 24 h. The precipitation was collected through filtration and washed with a large amount of water. Highly ordered mesostructured iron phosphate was observed from XRD shown in Figure 1 using CTMACl as surfactant. The XRD of the as-synthesized product shows four well-resolved peaks in $2^\circ < 2\theta < 6^\circ$, corresponding to a hexagonal unit cell as (100), (110), (200), and (210). These peaks can be indexed in to Bragg reflections of *P6mm* space group together with TEM mages. The first intense reflection corresponds to a *d* spacing 4.18 nm, which agrees with that of MCM-41[1] using the same surfactant as the template. The calculated lattice constant is 4.82 nm. The distinct presence of higher order (110), (200), and (210) reflections observed in the XRD patterns indicates the great textual uniformity in the material. No sharp wide-angle diffraction peaks are observed in Figure 1 (inset) which indicated the walls of the iron phosphate mesostructured materials are amorphous.

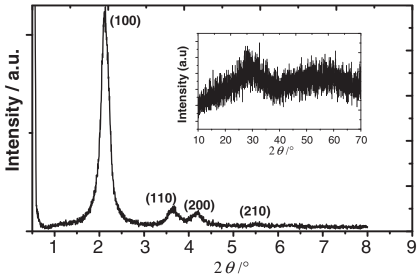


Figure 1. Small angle XRD pattern and wide angle XRD pattern (inset) of mesostructured iron phosphate.

The highly ordered hexagonal phase was further confirmed by TEM analysis. Figure 2 (left) shows a TEM images of the regular hexagonal array of uniform channels with a *d* spacing of 4.18 nm of the hexagonal phase. Figure 2 (right) shows a TEM images parallel to the pore channel direction. EDX and radiofrequency inductively coupled plasma (ICP) elemental analysis were used to characterize the chemical composition of the resultant, which reveal the existence of Fe, P, O and the molar ratio of Fe to P being almost 1. TEM result is in a good agreement with that obtained from XRD patterns.

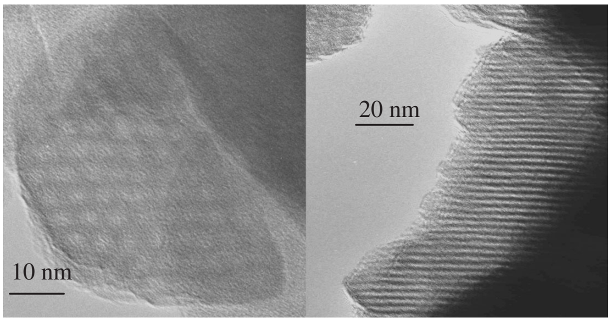


Figure 2. TEM images of mesostructured iron phosphate, perpendicular (left) and along to the direction of the hexagonal pore arrangement (right).

TG-DTA measurement in air for the as-synthesized sample reveals that the weight of the surfactant in the sample is about 45 wt %, which is almost equal to that in the silica MCM-41, much larger than that in non-siliceous materials (such as vanadium oxide-based materials.[11]) The amount of the surfactant inside the materials is so large, from this it follows that the structure should be unstable and thus a removal of the template by extraction has so far proved to be unsuccessful. Removal of the template by extraction was attempted using supercritical fluid extraction, only 50 wt % of surfactant can be removed. It is possible to perform partial template extraction with ethanol. This is probably due to the strong interaction between the walls and the surfactant in the pores. Investigation into template removal by other method, such as supercritical fluid extraction with other cosolvent is under investigation. Detail characterization is under way.

On the basis of the experimental results, the formation mechanism of the mesostructured materials can be explained as $I^+X^-S^+$ (I^+ being metal cations, X^- anion, S^+ a cationic surfactant) miceller assemblies process. Usually, highly charged clusters are needed to drive the assembly process, which rely on strong electrostatic interactions between the polycharged clusters and polycharged surfactant micelles in solution. The phosphate and sulfate are believed to complex the metal oxopolymers, and also to interact with the positively charged headgroup of the surfactant. The excess PO_4 ions are believed to be present to balance the unit positive charge on the framework. The choice of inorganic precursor is very important for the formation of the ordered hexagonal mesostructure. If $FeCl_3$ or FeAA (iron acetylacetonate) was used as the inorganic precursor, overlapped peaks of [200] and [110] were observed for the sample in the XRD as indicated in Figure 3, the (210) peak cannot be detected for both of the samples, only mesostructured iron phosphate with less-ordered structure was detected from TEM image; if $Fe(NO_3)_3$ was employed as the inorganic precursor, a very broad peak was observed from small-angle XRD, the (200) peak was not distinct. Therefore, Cl^- or AA is easier to interact with the positively charged headgroup of the surfactant comparing with the ionic of NO_3^-.

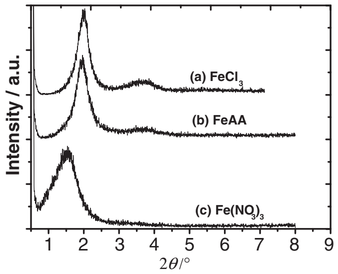
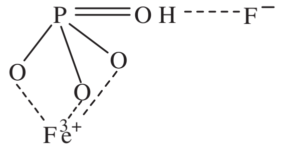


Figure 3. Small-angle XRD patterns of mesostructured $FePO_4$ employing $FeCl_3$, FeAA, and $Fe(NO_3)_3$ as the precursors.

The role of HF in the formation of the mesoporous structure was also examined. HF has been reported to be employed in a strategy that is designed to enhance host–guest interactions and also promote the effective communication between different interaction sites.[14] The presence of F^- ion inside the resultant material was detected by EDX in our case, the similar phenomenon was also observed in the preparation of mesostructural aluminophosphates by Stucky.[14] That means F^- ion participates in the assemble process. Considering the growth process, it is believed that the adding of the adequate HF is an important step prior to mix with $LiOOCCH_3$. The function of added $LiOOCCH_3$ lies in adjusting the pH of the reaction to have the precipitation. The use of hydrothermal treatment was proved to be successful in the formation of the ordered mesostructured materials. Just as Stucky reported, postsynthesis treatment can enhance the quality of the hexagonal mesostructured phase.[14] We suggest a structure model as described as below (Scheme 1):



Scheme 1. Proposed formation mechanism of mesostructured $FePO_4$.

As illustrated in Scheme 1, Coulomb attraction existed between the headgroups of the $CTMA^+$ molecules and the F^- anions, and extended the attraction by hydrogen-bonding between ion pairs [$FePO_4$] and [$H^+F^-CTMA^+$] fragments. Charged inorganic cluster precursors are prearranged as a mesoscopic salt with surfactant molecules of the opposite charge. It is a surfactant templating self-assembling process.

In conclusion, a novel method was reported for the first time to prepare highly-ordered hexagonal mesostructured iron phosphate with high structural uniformity. The approach as well as the great useful of $FePO_4$ in the application in lithium second battery and catalytic area provides promise method to fabricate this type of mesoporous materials.

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References and Notes

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