Iron hydroxyl phosphate microspheres: Microwave-solvothermal ionic liquid synthesis, morphology control, and photoluminescent properties

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ABSTRACT

A variety of iron hydroxyl phosphate ($NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$) nanostructures such as solid microspheres, microspheres with the core in the hollow shell, and double-shelled hollow microspheres were synthesized by a simple one-step microwave-solvothermal ionic liquid method. The effects of the experimental parameters on the morphology and crystal phase of the resultant materials were investigated. Structural dependent photoluminescence was observed from the double-shelled hollow microspheres and the underlying mechanisms were discussed.

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1. Introduction

Iron hydroxyl phosphates are well-known minerals with rich crystal chemistry and magnetic properties [1]. Their synthetic products are of particular interest in applications such as catalysis [2] and lithium batteries [3]. Among them, $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ (spheniscidite) is known as a mineral which is isotypic with $KFe_2(PO_4)_2OH \cdot 2H_2O$ (leucophosphite) [4,5]. Synthetic $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ was obtained by a hydrothermal process [6] and its antiferromagnetism and thermal properties were investigated [7,8]. Another mineral of interest is $Fe_5(PO_4)_4(OH)_3 \cdot 2H_2O$ [9,10]. To the best of our knowledge, however, morphological studies and photoluminescence properties of these materials have not been reported yet.

The microwave-solvothermal ionic liquid (MSIL) method is a recently developed route to the synthesis of inorganic materials in a closed system. Ionic liquids are a new kind of environmentally friendly reaction media and have excellent microwave absorbing ability. An application of microwave irradiation prompts a high reaction rate, allowing rapid synthesis of materials at elevated temperatures in a pressurized system. Therefore, the MSIL method combines the advantages of microwave chemistry and properties of ionic liquids with solvothermal growth conditions [11–13].

Nanostructures with hollow interiors are currently drawing intensive research interest due to their unique properties and potential applications that differ from those of non-hollow-structured materials [14]. Among the many hollow structures, hollow microspheres represent an important class of materials with broad applications in catalysis, drug delivery, chemical storage, light fillers, photonic crystals, and low dielectric constant materials [15–20]. Up to now, single-shelled hollow spheres have been widely investigated. Very recently, double-shelled or multi-shelled hollow spheres were also synthesized using hard templates [21], soft templates [22], and intermediate-templates via phase-transformation processes [23]. Double-shelled hollow spheres such as ZnS were also obtained through the Ostwald ripening process [24]. In addition, a medicine-inspired solution-phase approach was used to prepare double-shelled hierarchical ferrihydrite hollow spheres [14]. However, the synthesis of double-shelled hollow microspheres through a fast, one-step, microwave-solvothermal ionic liquid method remains to be explored.

Herein, we report on the successful synthesis of a variety of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ microspheres using a fast, one-step, microwave-solvothermal ionic liquid method. One of the advantages of this method is that $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ microspheres with various structures such as solid microspheres, microspheres with the core in hollow shell and double-shelled hollow microspheres, can be synthesized. These distinguished structures are obtained by using simple reagents $Fe(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_2HPO_4$ in the mixed solvents of deionized water and

ionic liquid 1-n-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF$_4$]) under microwave-solvothermal conditions. The rich morphologies of NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O obtained by the present synthetic method enable the investigation of structural dependent properties such as photoluminescence (PL), which is important for numerous applications, especially in light emitting diodes. Much effort has been made to acquire luminescent materials by incorporating organic dyes into crystalline porous structures or doping with metal activators [25,26]. Photoluminescence from the dye-free, double-shelled hollow microspheres of NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O was observed in this study while the other nanostructures did not show PL. The underlying mechanisms are discussed in terms of the size effect of the nanoparticles possibly formed on the inner surfaces of the double-shelled hollow microspheres.

2. Experimental section

2.1. Preparation of double-shelled hollow microspheres of NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O

In a typical synthetic procedure, 0.101 g Fe(NO$_3$)$_3$·9H$_2$O and 0.050 g (NH$_4$)$_2$HPO$_4$ were added into mixed solvents of 15 mL deionized water and 5 mL [BMIM][BF$_4$] under magnetic stirring. The resultant solution was loaded into a 60 mL-Teflon autoclave and microwave heated to 433 K for 60 min at this temperature. The microwave oven used for sample preparation was a microwave-solvothermal synthesis system (MDS-6, Sineo, Shanghai, China). After cooling down to room temperature, the product was collected and washed by centrifugation–redispersion cycles with deionized water and ethanol several times, and then dried to a powder at 333 K. Other samples were prepared following a similar procedure. See Table 1 for the detailed preparation conditions.

2.2. Characterization of samples

X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Rigaku D/max 2550 V, Japan) with high-intensity CuKα radiation ($\lambda = 1.54178$ Å). Scanning electron microscopy (SEM) images were taken with a field-emission scanning electron microscope (JEOL JSM-6700F, Japan). Transmission electron microscopy (TEM) micrographs were obtained with a field-emission transmission electron microscope (JEOL JEM-2100F, Japan). The thermogravimetric (TG) curve was taken with a heating rate of 10 K/min in flowing air with an STA 409/PC simultaneous thermal analyzer (Netzsch, Germany). Photoluminescence was excited by the 325 nm line of a He–Cd laser. The emission light was focused onto the entrance of a monochromator and recorded by a CCD detector.

3. Results and discussion

Fig. 1a–d shows the XRD patterns of the as-prepared samples 1–4. The diffraction peaks can be indexed to a single phase of well-crystallized NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O with a monoclinic structure (JCPDS no. 82-1164), indicating the formation of iron hydroxyl phosphates under the present experimental conditions. The TG curve of a typical sample (sample 4) is shown in Fig. 1e, which is similar to that reported in the literature [1,8]. The first weight loss corresponds most likely to the loss of the "free" H$_2$O.
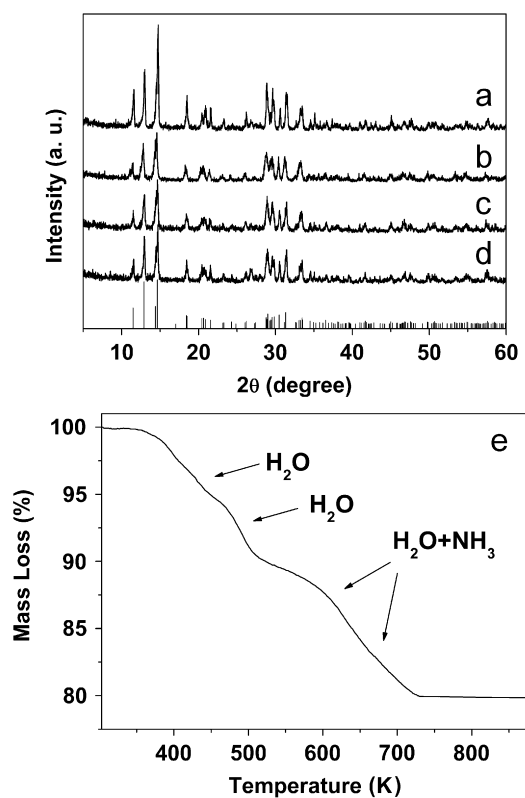

Fig. 1. XRD patterns: (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4, and (e) TG curve of sample 4.

Table 1
Experimental parameters for the preparation of typical samples by the microwave-solvothermal ionic liquid method at 433 K.

Sample no.	Solution	t (min)	Phase of product	Morphology of product	Size (μm)
1	0.202 g Fe(NO$_3$)$_3$·9H$_2$O+0.100 g (NH$_4$)$_2$HPO$_4$ +15 mL H$_2$O+5 mL [BMIM]BF$_4$	5	NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O	Solid microspheres	2–2.5
2	Same as sample 1	30	NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O	Microspheres with the core in hollow shell	2–2.5
3	0.101 g Fe(NO$_3$)$_3$·9H$_2$O+0.050 g (NH$_4$)$_2$HPO$_4$ +15 mL H$_2$O+5 mL [BMIM]BF$_4$	5	NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O	Microspheres with the core in hollow shell	1–1.5
4	Same as sample 3	60	NH$_4$Fe$_2$(PO$_4$)$_2$OH·2H$_2$O	Double-shelled hollow microspheres	1–1.5
5	0.101 g Fe(NO$_3$)$_3$·9H$_2$O+0.050 g (NH$_4$)$_2$HPO$_4$+20 mL H$_2$O	30	Fe$_5$(PO$_4$)$_4$(OH)$_3$·2H$_2$O	Star-like structures	–
6	0.101 g Fe(NO$_3$)$_3$·9H$_2$O+0.100 g (NH$_4$)$_2$HPO$_4$+15 mL H$_2$O+5 ml [BMIM]BF$_4$	30	–	Flower-like structures	–
7	0.101 g Fe(NO$_3$)$_3$·9H$_2$O+0.135 g Na$_2$HPO$_4$+15 mL H$_2$O+5 mL [BMIM]BF$_4$	30	–	Solid microspheres	1–1.5

The second stage occurs between 443 and 513 K and is attributed to the departure of the remaining H_2O. The third process reflects the departure of NH_4^+ and OH^- (NH_3 and H_2O).

Morphology and structure of the synthesized nanostructures were observed by SEM and TEM and are shown in Fig. 2. When 0.202 g $Fe(NO_3)_3 \cdot 9H_2O$ and 0.100 g $(NH_4)_2HPO_4$ were used in the mixed solvents of deionized water and ionic liquid, solid microspheres with sizes ranging from 2 to 2.5 μm were obtained after microwave heating at 433 K for 5 min (sample 1, Fig. 2a and b). As the microwave heating time was increased to 30 min while the other conditions were kept unchanged, microspheres with the core in the hollow shell were obtained (sample 2, Fig. 2c and d). The average size of the microspheres is similar to that of sample 1. It was found that a reduction of
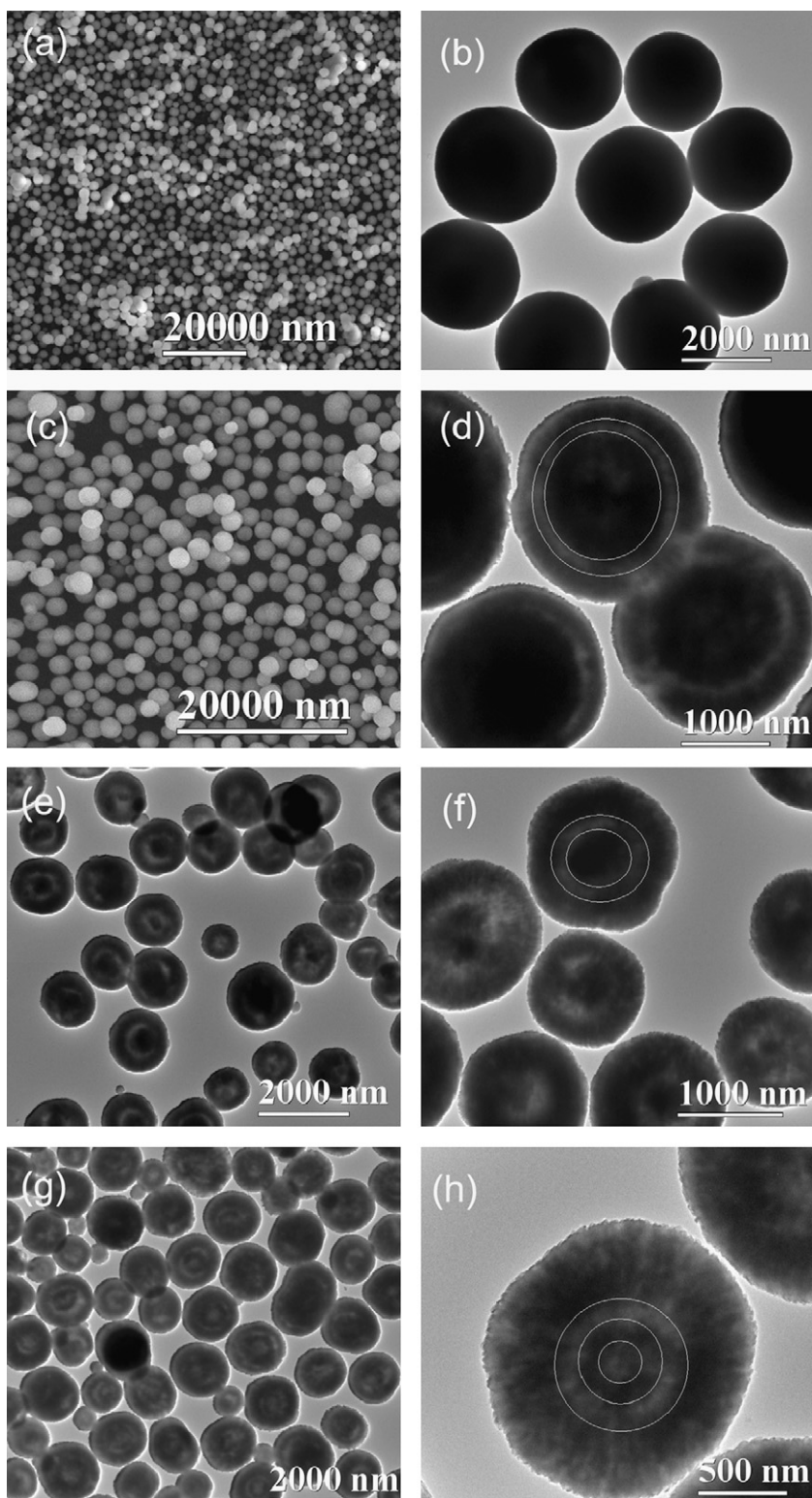

Fig. 2. SEM (a) and TEM (b) micrographs of sample 1; SEM (c) and TEM (d) micrographs of sample 2; TEM micrographs of sample 3 (e, f), and sample 4 (g, h).

reagent concentration resulted in a decrease of the microsphere size. When 0.101 g $Fe(NO_3)_3 \cdot 9H_2O$ and 0.050 g $(NH_4)_2HPO_4$ were used, 1–1.5 μm microspheres with the core in the hollow shell were obtained after microwave heating for 5 min (sample 3, Fig. 2e and f). Interestingly, prolonged microwave heating up to 60 min resulted in the growth of double-shelled hollow microspheres with sizes of 1–1.5 μm while the other conditions were kept the same as sample 3 (sample 4, Fig. 2g and h).

The formation mechanism of double-shelled hollow microspheres of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ is likely similar to that of ZnS double-shelled hollow spheres, which is caused by the associated Ostwald ripening processes composed of "outward ripening" (i.e. outward hollowing) and "inward ripening" (i.e. inward hollowing) [24,27]. The formation mechanism of the double-shelled hollow microspheres is schematically illustrated in Scheme 1. Specifically, the "inward ripening" refers to the mass relocation starting from the surface region, leading to the formation of the core in hollow shell spheres [28]. In the "outward ripening" process, the mass transport starts from the center of a crystallite aggregate. A typical example was demonstrated in TiO_2 hollow spheres [29]. The Ostwald ripenings are slow processes which often take days to form double-shelled spheres. For example, the preparation of ZnS double-shelled hollow spheres needs several days to complete the mass relocation. In contrast, our double-shelled hollow microspheres of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ were obtained in one hour. As such, the mechanism reported here is referred to as "fast associated Ostwald ripenings".

Scheme 1. Schematic illustration of the formation mechanism of double-shelled hollow microspheres.

In order to investigate the effect of [BMIM][BF_4] on the formation of microspheres, a control experiment was performed without using [BMIM][BF_4] while the other conditions were kept unchanged. A different product was obtained (sample 5) and its XRD pattern is shown in Fig. 3a. The diffraction peaks can be indexed to a single phase of well-crystallized $Fe_5(PO_4)_4(OH)_3 \cdot 2H_2O$ with an orthorhombic structure (JCPDS no. 45-1436). This result indicates that the ionic liquid [BMIM][BF_4] plays an important role in the formation of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$. Fig. 3b and c shows the SEM micrographs of sample 5, from which one can see that star-like structures were obtained. The TEM image of Fig. 3d suggests that the intergrowth of spindles may cause the formation of the star-like structures. These results indicate that the ionic liquid [BMIM][BF_4] influences not only the crystal phase but also its morphology. In fact, the ionic liquid [BMIM][BF_4] is an effective additive for the control of crystal phase and morphology by changing the pH value, complexation of ions in the solution, etc [12,13].

The ratio of $Fe(NO_3)_3 \cdot 9H_2O$ to $(NH_4)_2HPO_4$ in the source solution also significantly influences the morphology of the resultant materials. When 0.101 g $Fe(NO_3)_3 \cdot 9H_2O$ and 0.100 g $(NH_4)_2HPO_4$ were used, flower-like structures instead of microspheres were obtained (sample 6, Fig. 4a). In addition, we have investigated the morphology change of the final product by replacing $(NH_4)_2HPO_4$ with Na_2HPO_4. It was found that solid microspheres with sizes of 1–1.5 μm were obtained (Fig. 4b) when 0.101 g $Fe(NO_3)_3 \cdot 9H_2O$ and 0.135 g Na_2HPO_4 were used and microwave heated for 30 min (sample 7). These results indicate that the dosage of $(NH_4)_2HPO_4$ is critical for the formation of hollow spheres.

Fig. 5 shows photoluminescence spectra of as-prepared samples with different morphologies. A broad emission band around 445 nm was observed from the double-shelled hollow microspheres of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ (sample 4, Fig. 5d), which is believed to result from their unique structures. Note that the
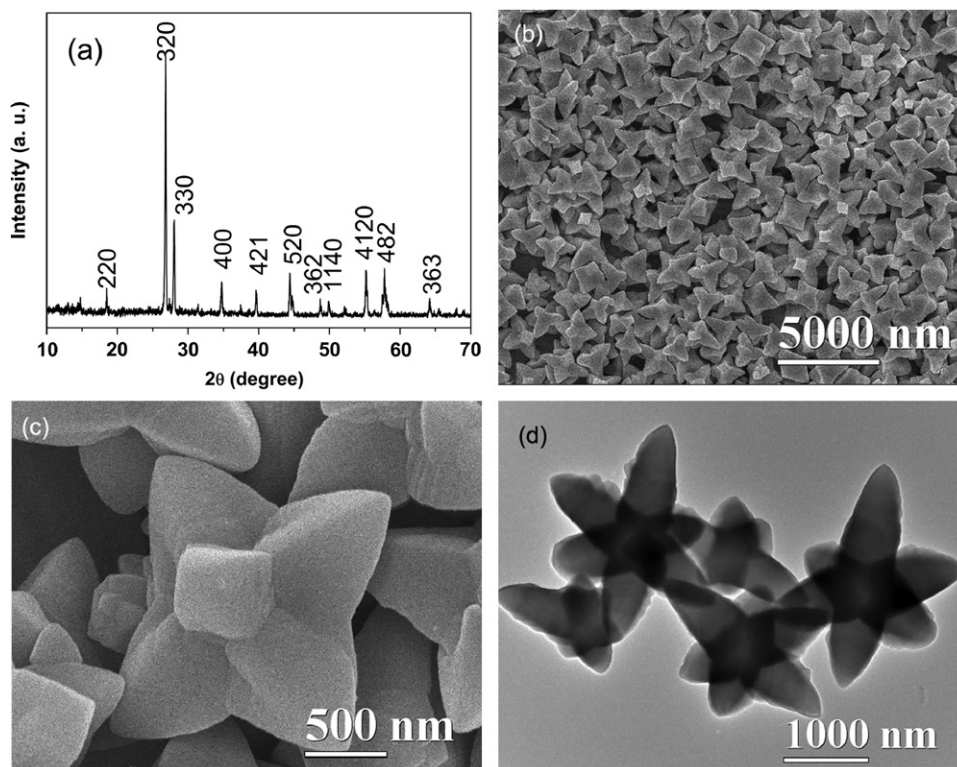

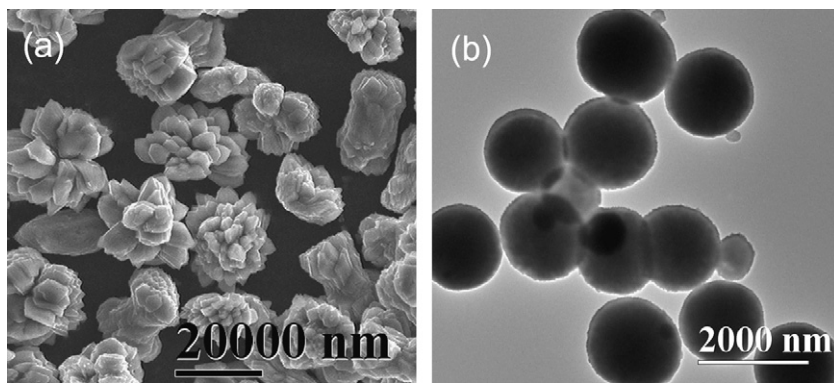**Fig. 3.** XRD pattern (a), SEM (b, c), and TEM (d) micrographs of sample 5.

Fig. 4. (a) SEM micrograph of sample 6 and (b) TEM micrograph of sample 7.
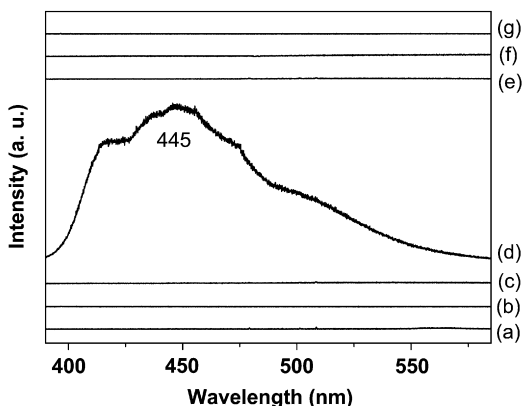

Fig. 5. Room-temperature photoluminescence spectra of the as-prepared samples excited at 325 nm: (a–g) samples 1–7, respectively: (a) solid microspheres (sample 1); (b) microspheres with the core in hollow shell (sample 2); (c) microspheres with the core in hollow shell (sample 3); (d) NH_4Fe_2 $(PO_4)_2OH \cdot 2H_2O$ double-shelled hollow microspheres (sample 4); (e) Fe_5 $(PO_4)_4(OH)_3 \cdot 2H_2O$ star-like structures (sample 5); (f) flower-like structures (sample 6); and (g) solid microspheres (sample 7).

samples with other morphologies such as solid microspheres, microspheres with the core in the hollow shell, star-like structures, and flower-like structures, did not show PL emission, as shown in Fig. 5. These results indicate that the unique structures of the double-shelled hollow microspheres resulted in the photoluminescent properties of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$. Photoluminescence from iron hydroxyl phosphates of double-shelled hollow spheres likely results from the thermal and magnetic relaxations in the magnetic materials [30].

The photoluminescence of the $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ double-shelled hollow microspheres may be explained as follows. Nanoclusters could be formed on the inner surfaces of the double-shelled hollow microspheres due to the prolonged heating and the fast ripening processes. The small size and large surface area of the nanoclusters cause the formation of surface trapped states and the reduction of the magnetic interaction, i.e. formation of nonmagnetic covalent bonds which could contribute to photoluminescence. In addition, quantum confinement effects may also induce delocalized states within the nanoclusters and enhance the electron–phonon interaction, leading to optical transitions in the nanoclusters which are not present in bulk materials [30–32]. $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ was described as a transparent material in thin sections [5], which allows the PL from the inner surface of the microspheres to be observed.

The size effect induced PL in other magnetic materials such as Fe_2O_3 was previously demonstrated [33–35]. Bulk Fe_2O_3 does not show PL while the nanometer-sized Fe_2O_3 exhibits PL in the visible wavelengths. Such a PL property was attributed to the aforementioned mechanisms in terms of size effects.

4. Conclusion

In summary, we have successfully synthesized a variety of nanostructures of iron hydroxyl phosphates such as solid microspheres, microspheres with the core in the hollow shell, and double-shelled hollow microspheres of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ by adjusting the concentration of reagents or microwave heating time in a simple, one-step, microwave-solvothermal ionic liquid method. Simple reagents of $Fe(NO_3)_3$ and $(NH_4)_2HPO_4$ in the mixed solvents of deionized water and ionic liquid [BMIM][BF$_4$] were used. The ionic liquid [BMIM][BF$_4$] significantly influences the morphology of the products as well as their crystal phase. Star-like structures of $Fe_5(PO_4)_4(OH)_3 \cdot 2H_2O$ were obtained without [BMIM][BF$_4$]. Among the various morphologies, only double-shelled hollow microspheres of $NH_4Fe_2(PO_4)_2OH \cdot 2H_2O$ exhibited photoluminescence in the visible range, which likely results from the size effect of the nanoparticles formed on the inner surface of the microspheres. The photoluminescent properties of the double-shelled hollow microspheres may extend the potential applications of iron hydroxyl phosphates.

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