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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.

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

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ionic liquid 1-*n*-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]) under microwave-solvothermal conditions. The rich morphologies of $NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$ 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 $NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$ 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 $NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$

In a typical synthetic procedure, 0.101 g $Fe(NO_3)_3\cdot 9H_2O$ and 0.050 g $(NH_4)_2HPO_4$ 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 Cu*K*α 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 $NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$ 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_2O.

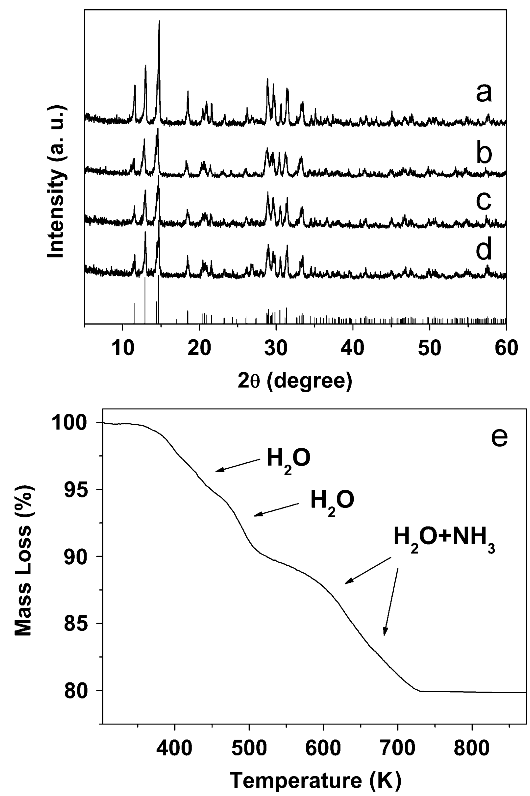

Fig. 1. XRD patterns: (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4, and (e) TG curve of sample 4.

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 $Fe(NO_3)_3\cdot 9H_2O$+0.100 g $(NH_4)_2HPO_4$ +15 mL H_2O+5 mL [BMIM]BF_4	5	$NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$	Solid microspheres	2–2.5
2	Same as sample 1	30	$NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$	Microspheres with the core in hollow shell	2–2.5
3	0.101 g $Fe(NO_3)_3\cdot 9H_2O$+0.050 g $(NH_4)_2HPO_4$ +15 mL H_2O+5 mL [BMIM]BF_4	5	$NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$	Microspheres with the core in hollow shell	1–1.5
4	Same as sample 3	60	$NH_4Fe_2(PO_4)_2OH\cdot 2H_2O$	Double-shelled hollow microspheres	1–1.5
5	0.101 g $Fe(NO_3)_3\cdot 9H_2O$+0.050 g $(NH_4)_2HPO_4$+20 mL H_2O	30	$Fe_5(PO_4)_4(OH)_3\cdot 2H_2O$	Star-like structures	–
6	0.101 g $Fe(NO_3)_3\cdot 9H_2O$+0.100 g $(NH_4)_2HPO_4$+15 mL H_2O+5 ml [BMIM]BF_4	30	–	Flower-like structures	–
7	0.101 g $Fe(NO_3)_3\cdot 9H_2O$+0.135 g Na_2HPO_4+15 mL H_2O+5 mL [BMIM]BF_4	30	–	Solid microspheres	1–1.5