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Controllable synthesis of $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ using two-step route: Ultrasonic-intensified impinging stream pre-treatment followed by hydrothermal treatment

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ABSTRACT

$(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ samples with different morphology are successfully synthesized via two-step synthesis route – ultrasonic-intensified impinging stream pre-treatment followed by hydrothermal treatment (UIHT) method. The effects of the adoption of ultrasonic-intensified impinging stream pre-treatment, reagent concentration (*C*), pH value of solution and hydrothermal reaction time (*T*) on the physical and chemical properties of the synthesised $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ composites and $FePO_4$ particles were systematically investigated. Nano-seeds were firstly synthesized using the ultrasonic-intensified T-mixer and these nano-seeds were then transferred into a hydrothermal reactor, heated at 170 °C for 4 h. The obtained samples were characterized by utilising XRD, BET, TG-DTA, SEM, TEM, Mastersizer 3000 and FTIR, respectively. The experimental results have indicated that the particle size and morphology of the obtained samples are remarkably affected by the use of ultrasonic-intensified impinging stream pre-treatment, hydrothermal reaction time, reagent concentration, and pH value of solution. When such $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ precursor samples were transformed to $FePO_4$ products after sintering at 650 °C for 10 h, the SEM images have clearly shown that both the precursor and the final product still retain their monodispersed spherical microstructures with similar particle size of about 3 μm when the samples are synthesised at the optimised condition.

1. Introduction

$(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ is an isopytic mineral of $KFe_2(PO_4)_2OH\cdot 2H_2O$ (leucophosphite) and has received increasing attentions due to its magnetic properties and rich crystal chemistry [1]. The synthetic $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ has been considered as a promising material and applied in the fields of catalysts [2], magnetics [3,4], optics [5], and lithium ion battery as positive electrode material [6–8]. As a functional material, the physical and chemical properties of $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ are significantly affected by its morphology and particle size. Many methods have been developed to prepare $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ particles, and various efforts are endeavoured to conduct the synthesis for different morphologies and particle sizes.

Shaowen Cao et al. (2010) proposed a simple one-step microwave-solvothermal ionic liquid method using [BMIM][BF_4] to prepare $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ composites that contained various nanostructures, such as solid micro-spheres, microspheres with the core in the hollow shell, and double-shelled hollow microspheres while the synthesis was conducted by adjusting reagent concentration and microwave heating time [5]. Pure and well-crystallized spheniscidite $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ was obtained by Delacourt et al. when NH_3 was added as an agent to raise pH value [8]. Shuyang Ju et al. (2013) reported a low temperature (at 80 °C) hydrothermal method to synthesize peanut-like microscale $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ particles that were used as the precursor of $LiFePO_4$ positive electrode material [6]. The as-synthesized $LiFePO_4$ composites presented desirable electrochemical performance and high tap density. Li et al. (2014) synthesized ellipsoid-shaped $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ composites that have micro-nano structures for being used as the precursor of $LiFePO_4$ positive electrode material, adopting a facile chemical precipitation route [7]. The obtained $LiFePO_4$ products exhibited excellent rate capability and good cyclic performance. Camino Trobajo et al. (2000) applied the hydrothermal method for preparation of $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ at relatively high pH values of 9–11 and used excess amount of urea [1]. Kaipeng Wu et al. (2018) adopted sonochemical method to synthesise $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ particles that possess red-blood-cell-like

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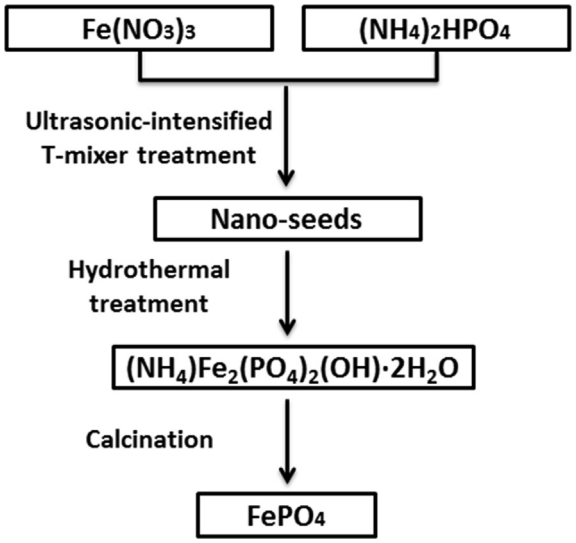

Fig. 1. Schematic illustration of main procedures in two-step hydrothermal synthesis of $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ and $FePO_4$ samples.

shape [9]. In addition, Hong Zhou et al. (2010) also used hydrothermal method to synthesise $(NH_4)Fe_2(PO_4)_2(OH)\cdot 1.5H_2O$ which exhibited the behaviour of spontaneous magnetization below 25 K [4]. It can be claimed that as a self-assembly synthesis approach, hydrothermal method has been widely used to design and fabricate $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ particles due to its mild operation temperature, simple process, homogeneous particle size distribution, improved cycle life and has the potential for large-scale production [10,11]. However, most of the synthesis route still needs long reaction time (up to 3 days) and additional additives (such as glycol and $C_2H_4O_4\cdot 2H_2O$).

It has been recognised that the application of high intensity ultrasonic-irradiation has a remarkable function which can significantly intensify the processes. It has been applied in industrial manufacturing process and also the material synthesis process with the features of cost-effective and environmental-friendly. It has been revealed that the particles synthesized using ultrasonic treatment usually present porous structures [12,13]. Since ultrasonic wave can acoustically create the tiny cavitation, such instantaneous collapse of the created micro bubbles due to cavitation can provide the extreme conditions in a very small volume, characterised by occurrence of extremely high temperature up to 5000 K, pressures up to 1000 atm, and the heating and cooling rate greater than 10^{10} Ks^{-1} inside the cavitation zone [14]. Thus, ultrasonic-assisted hydrothermal synthesis method has been applied to the synthesis of catalysts [15–18], zeolite [19–22], hydrogen storage material [23], and MOFs [24].

Adoption of confined impinging T-jet mixer (CITJ) for synthesis of micro particles was also reported in the open literatures [25,26]. A CITJ reactor which has T-shaped branches is the simplest component that contains two inlet tubes, allowing two streams to flow in, and one outlet tube, allowing the mixture to be collected. Local intensive micro-mixing in a CITJ takes place through the collision between two impinging streams, usually resulting in a fast homogenization of reactants so that both mass transfer rate and chemical reaction rate can be effectively enhanced. The kinetic energy and mass transfer rate in the mixing zone (reactor chamber) are influenced by the pressure fluctuation [27] while the intensive mixing occurring in a small confined volume of reaction chamber enhances the crystallisation and promote the growth of particle size [28].

A novel two-step preparation route that combines ultrasound-assisted CITJ and hydrothermal treatment (UIHT) to synthesize $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ is developed in the present study. To the best of our knowledge, the application of UIHT method to synthesis of $(NH_4)Fe_2(PO_4)_2(OH)\cdot 2H_2O$ has not been reported in the literature. The effects of the use of ultrasonic-intensified impinging streams, reagent concentration, pH value of solution, and hydrothermal reaction time on the chemical and physical properties of the synthesized particles are

Table 1
Dimensions of experiments for the systhesis of samples.

Experiments	Samples	Method	Reaction time (h)	pH value	Reagent concentration (*C*, mol L^{-1})
S1	Seed-UIHT	UIHT	0	0.8	1.0
S2	Prod-UIHT	UIHT	4	0.8	1.0
S3	Seed-HT	HT	0	0.8	1.0
S4	Prod-HT	HT	4	0.8	1.0
S5	UIHT-1h	UIHT	1	0.8	1.0
S6	UIHT-2h	UIHT	2	0.8	1.0
S7	UIHT-3h	UIHT	3	0.8	1.0
S8	UIHT-0.5	UIHT	4	0.8	0.5
S9	UIHT-1.5	UIHT	4	0.8	1.5
S10	UIHT-pH1.2	UIHT	4	1.2	1.0
S11	UIHT-pH1.5	UIHT	4	1.5	1.0
S12	UIHT-pH1.8	UIHT	4	1.8	1.0

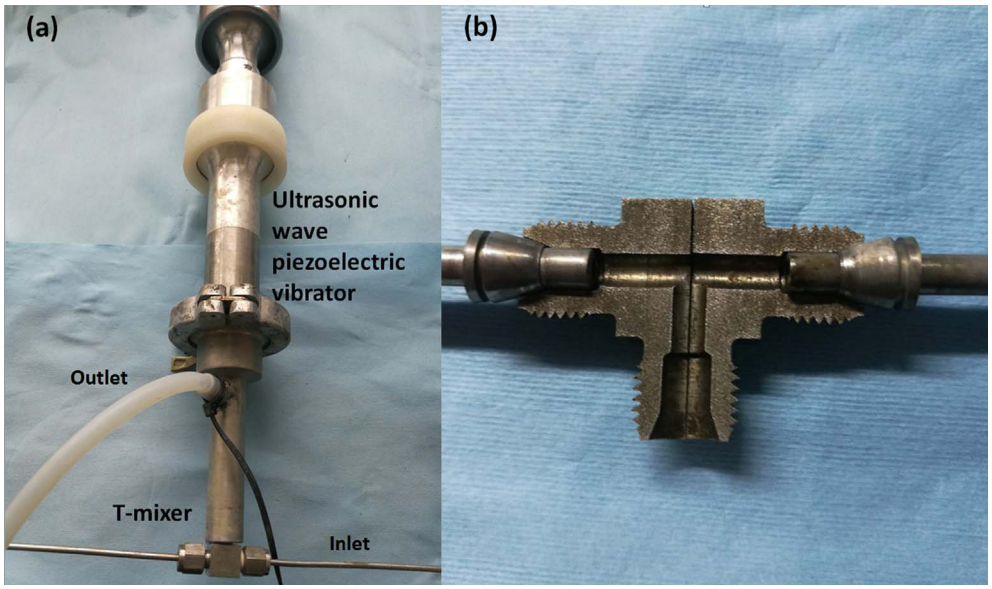

Fig. 2. (a) Experimental set-up of ultrasonic-intensified T-mixer and (b) internal structure of T-mixer.