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Microwave-assisted rapid synthesis of hexagonal α -zirconium phosphate nanodisks as a Pickering emulsion stabilizer



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ABSTRACT

It is the first time that a rapid microwave-assisted method was developed to synthesize alpha phase of zirconium phosphate (α -ZrP). The dimension and thickness of α -ZrP nanodisks were varied by altering the concentration of added phosphoric acid. In addition, laminar structure of α -ZrP can be exfoliated into monolayers to provide with more surface area by intercalating tetrabutylammonium hydroxide. The results revealed that uniform and highly-crystallized α -ZrP nanodisks were obtained in an efficient manner and could be utilized as a Pickering emulsion stabilizer after exfoliation.

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1. Introduction

Alpha phase of zirconium phosphate (α -ZrP) has been well studied as an acidic layered metal salt whose lattice structure is depicted in Fig. 1(a), where each layer of α -ZrP is composed of a ZrO_6 sheet coordinated with HPO_4^{2-} tetrahedrons forming a covalent network and the layers are packed by Ver der Waals forces [1,2]. By intercalating guest species into the interlayer spacing (shown in Fig. 1(b)), the α -ZrP could serve as a host structure [3] or be exfoliated by the guest species. The modified α -ZrP has connected to new applications such as drug delivery [4], foams [5,6], and Pickering emulsions [7]. In general, α -ZrP could be obtained from hydrothermal, reflux, or hydrofluoric acid assisted methods [8,9]. However, growth of α -ZrP through a facile and rapid microwave-assisted synthesis with good control over size and uniformity is scarcely reported in literatures.

Microwave heating has been used in organic chemistry for decades, but not been used for growth of nanomaterials until recent years [10]. The merits of microwave techniques are with efficient heating and instantaneous controllable parameters in real time. When reaction solution is irradiated by microwave power, dipoles existing in molecules are trying to align themselves

accordingly to the applied electromagnetic fields. As a result, heat is generated from frictions and that is more efficient in terms of heat transfer compared to traditional convection heating used in hydrothermal and reflux methods. Hence, the growth of crystals could be significantly accelerated and well-controlled.

Pickering emulsion was named after Pickering and coworkers' pioneering work over a century ago using solid particles as emulsion stabilizers [11] whose function is similar to molecular surfactants. Nanomaterials act as barriers for emulsion destabilization because the energy required for removing nanomaterials from the surface of emulsion droplets is several orders higher than that of stabilized by molecular surfactant [12]. In addition, two dimensional nanomaterials show better stability of formed emulsion droplets by reducing transport of molecules from interior phase [13]. Recently, Pickering emulsion also has been used for polymerization [14], polycondensation [15,16], encapsulation [17,18], and pharmaceutical applications [19].

In this research, to the best of our knowledge, it is the first time that α -ZrP with high uniformity and crystallinity was prepared from microwave-assisted method and the application of α -ZrP nanodisks as Pickering emulsion stabilizer was also demonstrated.

2. Experimental

2.1. Preparation of α -ZrP nanodisks

All chemicals were of analytical grade and used as received

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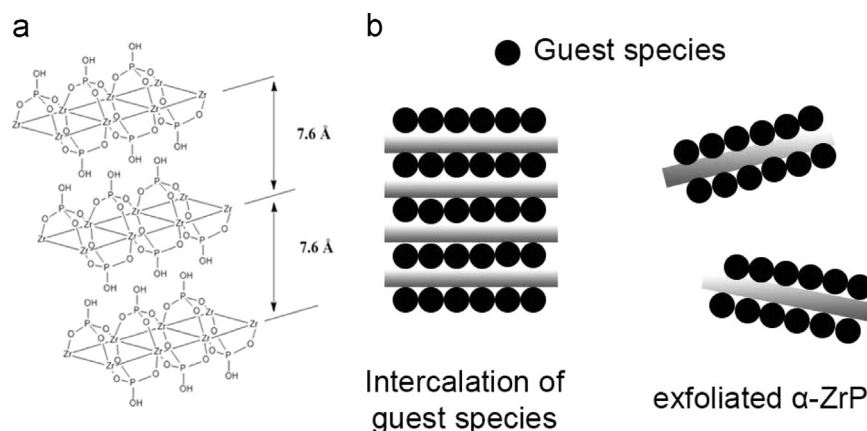


Fig. 1. (a) Lattice structure of α -ZrP crystal. (b) Schematic illustrations of the guest species intercalated into α -ZrP interlayers and exfoliated laminar α -ZrP layer-by-layer.

without any further purification. 1 g of zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was mixed with 10 mL of 6.0/9.0/12.0 M phosphoric acid (H_3PO_4) under vigorous stirring (hereafter marked as ZrP-6 M, ZrP-9 M, and ZrP-12 M, respectively). The resulting solutions were introduced into a 20 mL glass vessel specified for microwave oven (Discover SP, CEM) and then irradiated by 2.45 GHz microwave at 180 °C for 1 h. After the microwave-assisted hydrothermal synthesis, the as-synthesized ZrP was washed for three times with deionized water and collected by using a centrifuge. The obtained products were dried in an oven at 65 °C overnight and ground into fine powders by a mortar and pestle.

2.2. Exfoliation of α -ZrP nanodisks and preparation of emulsion droplets

Tetrabutylammonium hydroxide (TBAOH) was used as exfoliation agent. In a typical procedure, molar ratio of ZrP:TBAOH (1:1) was selected to ensure completely exfoliation. 1 g of obtained ZrP was mixed with 2.213 mL of TBA and 25.967 mL of DI water under vigorous stirring for 24 h. For preparation of Pickering emulsion, 2 mL of dodecane was added to 2 mL of 1 wt% exfoliated ZrP nanodisk suspensions, and then emulsified with a sonication probe (Sonifier 250, Branson) for 10 s at 10% of power.

2.3. Characterizations

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were analyzed on a Bruker-AXS D8 Advanced Bragg-Brentano X-ray powder diffractometer. The morphologies were observed by field emission scanning electron microscopy (FE-SEM, Quanta 600) and transmission electron microscopy (TEM, 2010, JEOL) operated at an accelerating voltage of 200 kV. The size distribution of ZrP nanodisks was analyzed by a dynamic light scattering analysis (DLS, Zetasizer Nano ZS90, Malvern). Optical microscopy was performed with scanning laser confocal microscopy (ECLIPSE Ti, Nikon).

3. Results and discussion

After microwave-assisted hydrothermal process in different concentration of phosphoric acid at 180 for 1 h, the crystal phases of ZrP nanodisks were first identified by XRD (Fig. 2). The XRD patterns of as-synthesized ZrP showed sharp characteristic peaks corresponding to alpha phase of ZrP based on JCPDS card no. 34-0127, suggesting good crystallinity of obtained ZrP after 1 h of microwave heating. It is also noticeable that relative peak intensity of (110) to (112) increased with concentration of phosphoric acid.

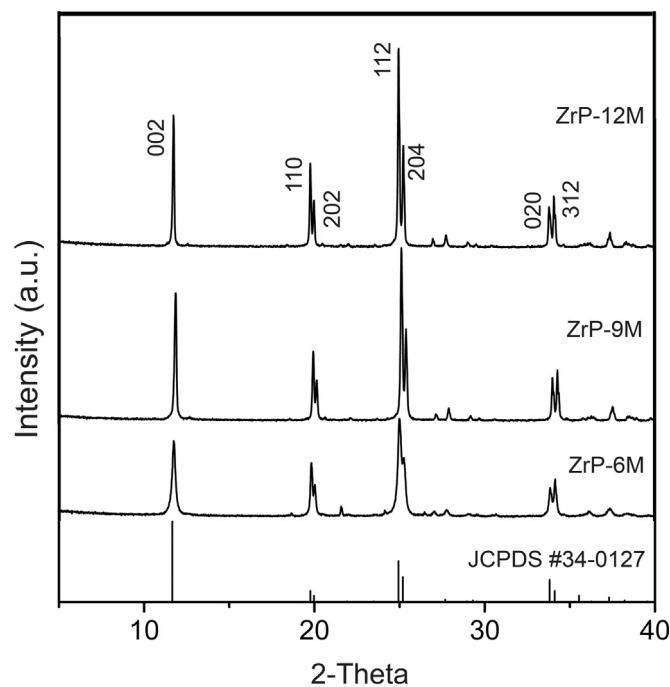


Fig. 2. X-ray diffraction spectra of α -ZrP treated with H_3PO_4 of various concentrations.

This growth mechanism of α -ZrP could be described that the growth rate along (001) plane is getting faster in the phosphoric acid of a higher concentration, and also would restrain the growths along other crystalline planes, which is in a good agreement with the result reported by our group previously [1].

Fig. 3(a)–(c) shows SEM and TEM (insert) images of α -ZrP prepared from phosphoric acid of different concentrations. It was observed that α -ZrP nanodisks were hexagonal in shape and their thickness increased as concentration of phosphoric acid increased. The insert SEM image in Fig. 3(c) reveals a zoomed-in image showing layered structure of α -ZrP on the bottom left. It presents an important property that the number of interlayer spacing and overall surface area provided by individual α -ZrP nanodisks could be tailored through controlling the concentration of phosphoric acid. Fig. 3(d) shows that the average size of α -ZrP obtained from 6.0 M/9.0 M/12.0 M phosphoric acid are 196.3 ± 55 , 307.8 ± 83 , and 324.8 ± 95 nm with polydispersity index of 0.17, 0.074, and 0.129, respectively. The high uniformity of each obtained α -ZrP nanodisks are indicated; in addition, the result is very promising because synthesizing anisotropic nanomaterial has always been a

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