

Interface mechanism of a rapid and mild aqueous–organic method to prepare CePO₄ nanostructures



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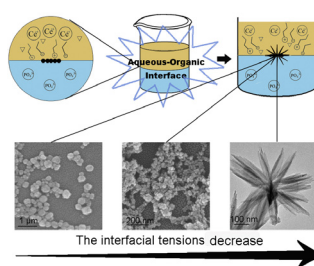
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HIGHLIGHTS

- For the first time, 3D-hierarchical nanostructures are self-assembled at the aqueous–organic interfaces.
- The strategy was energy-saving and time-efficient as it was conducted at room temperature within 30 min.
- A relationship between the products and the aqueous–organic interfaces was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

This is the first time that uniform self-assembled 3D-hierarchical nanostructures were prepared at an aqueous–organic interface. Besides, the strategy is time and energy efficient, as it could be conducted at room temperature within 30 min. In order to investigate the influence of the nature of the interface to the nanostructure, a relationship between the morphologies and crystallinities of the products and the interfacial tensions of different aqueous–organic interfaces was investigated, and it was found that the flower-like crystalline nanostructures preferred generating at the interface with lower tension, and the spherical amorphous products were likely to form at higher-tension interface area, and fractal networks tended to occur at the interface with its tension between the above two.

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1. Introduction

It is well-known that the size and morphology are crucial in determining the properties of nanomaterials [1]. 1D rare earth orthophosphates (REPO₄) play important roles in the fields of phosphors, bio-sensors, and lasers [2–5]. 3D hierarchical rare earth nanostructures self-assembled by fundamental building blocks are

Abbreviations: IL, ionic liquid; ILE, ionic liquid extractant; RE, rare earth; NP, nanoparticles.

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attracting more and more interest because of the novel properties arising from their size and morphology [6,7]. Lots of efforts have been paid to fabricate 3D hierarchical nanostructures. Among these methods, hydrothermal synthesis is the mostly used one [8–10]. But this methodology has some disadvantages like long reaction time, high energy consuming, and low yields.

Ionic liquids (ILs) are liquid salts in low temperature (usually below 100 °C), which are also named as low temperature molten salt [11,12]. ILs are considered as “green” solvents compared with traditional organic solvents or electrolytes because of their high thermal stability and negligible vapour pressures [13–16]. Applying ILs in the liquid–liquid extraction could introduce the advantages of ILs like desingability and high thermal stability [17]. A series of bifunctional ionic liquid extractants (Bif-ILEs) based on methyl tri-octyl ammonium chloride (Aliquat 336) have been prepared in this

lab [18]. The Bif-ILEs show more extraction capacities and higher selectivity than the widely used extractants, and more friendly to the environment for the avoidance of saponification wastewater, which is inevitable in the acidic extractants systems. The extractant used here was [A336][Cyanex272] ([methyl trioctyl ammonium] [bis(2,4,4-trimethylpentyl)phosphinate]).

As a novel system for preparing materials, the extraction system shows some interesting advantages like high efficiency, low economical cost, and friendly to the environment. For the widely used extractants, like TBP (tributyl phosphate) and TOPO (trioctylphosphine oxide), the formation of reverse micelles or microemulsions in the organic loaded phase is proved [19], and various materials have been prepared in the microemulsion system. Such as Shi et al. synthesized nanocrystals of TiO_2 [20] in TOPO extraction systems and Guo et al. prepared CaF_2 hollow spheres by mixing the D2EHPA and N1923 organic phases loaded with Ca^{2+} and F^- respectively [21]. The third phase formed in liquid–liquid extraction is a well known phenomenon [22–24]. Methods have been taken to avoid the third phase because of its negative impact on the transfer process of interphase in the liquid–liquid extraction system. An earlier research in this lab has discussed the third phase formed in Bif-ILEs ([A336][P204] and [A336][P507]) extraction system [25]. It indicated that the third phase was formed probably because the extracted complex could not be dissolved in the diluent (n-heptane), but further examines need to be taken to prove this conjecture. For the nanomaterials prepared from the third phase, Yang et al. synthesized mesoporous ZrO_2 [26] and Hu et al. prepared ultrafine powders of TiO_2 with the third phase generating from TBP systems [27]. But the literatures on self-assembled 3D-hierarchical nanostructures synthesized from extraction systems still cannot be found. For the best of our known, this is the first time the self-assembled 3D-hierarchical nanostructures are prepared from an extraction system.

As an important approach to offer effect on the self-assembling process by nanoparticles (NPs), the liquid–liquid interfaces are attracting more and more interests [28–31]. The highly dynamic of the NPs offered by aqueous–organic interfaces allows reversible assembly of them and the emulsions or microemulsions stabilized by NPs make the modification of the particles by functional molecules accessible [32]. Although the assembly of NPs at the liquid–liquid interface are well explored, researches on the preparing of NPs and their assemblies at the liquid–liquid interface is still rare. Rao et al. proved that the liquid–liquid interfaces could generate ultrathin films of crystalline Au and CdS [33]. And the organic phases used in this work was prepared by dissolving liposoluble precursors in organic solvents. But the liposoluble precursors are often expensive, compared with the above organic phase, the loaded phases of the extraction process are more abundant and unexpensive. Therefore the organic loaded phases are well suitable as the organic phases to form aqueous–organic interfaces for producing nanomaterials. In this work, self-assembled 3D-hierarchical flower-like CePO_4 nanostructures were prepared at the aqueous–organic interface formed by the third phase from an ionic liquid extraction process and the aqueous solution of K_3PO_4 . Different interfaces formed by the same aqueous and other two loaded phases were also examined in this work, their interfacial tensions were measured and a relationship between the morphologies and crystallinities of the products and the interfacial tensions was found.

2. Materials and methods

2.1. Materials

All of the starting materials were of analytical grade. The cerium (III) nitrate and potassium phosphate was purchased from

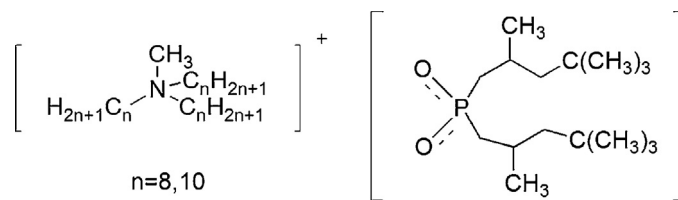


Fig. 1. The structure of [A336][Cyanex272].

Sinopharm Chemical Reagent Co. Ltd. A336 was purchased from ACROS. Bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) was kindly supplied by the CYTEC Inc.

2.2. Preparation of [A336][Cyanex272] ([methyl trioctyl ammonium] [bis(2,4,4-trimethylpentyl) phosphinate])

[A336][Cyanex272] were prepared by the reference method [17]. The products were examined by NMR and the results were:

^1H NMR: 0.86 (t, $J = 1.2$ Hz, 9H), 1.18 (s, 3H), 1.26 (s, 30H), 1.33 (s, 16H), 1.61 (s, 6H), 3.26 (s, 3H), 3.378–3.419 (t, $J = 8.0$ Hz, 6H), 4.44 (s, 2H), 6.892 (d, $J = 7.2$ Hz, 2H), 7.125 (m, 2H).

^{13}C NMR: 13.81, 22.35, 26.11, 26.78, 27.46, 28.81, 29.03, 29.38, 31.62, 35.34, 41.31, 43.18, 48.47, 51.73, 54.03, 61.05, 62.04, 68.09, 113.84, 126.81, 139.06, 156.64, 173.12.

The results indicated that the as-prepared [A336][C272] was a pure substance. Its structure was shown in Fig. 1.

2.3. Extraction process

[A336][Cyanex272] was dissolved in n-heptane. The solution of CeNO_3 was dissolved in HNO_3 with its concentration varying from 0.1 mol/l to 10 mol/l. In a classical synthesis, 4 ml 0.5 mol/l HNO_3 solution containing 0.4 mmol Ce^{3+} was mixed with 4 ml n-heptane solution containing 0.4 mmol [A336][Cyanex272] in 10 ml centrifuge tubes, then the centrifuge tubes were vibrated in a constant temperature vibrator at 25 °C for 30 min, which was sufficient for the reaction equilibrium. Centrifuging at 5000 rpm for 3 min to enhance phase separation afterwards. After that, the as-prepared third phase was separated and washed by water to eliminate free rare earth ions, and then, it was collected for the subsequent experiments.

2.4. Nanostructures preparation process

In a typical synthesis, 4 ml third phase was added dropwise to 4 ml aqueous solution containing 0.4 mmol K_3PO_4 in a beaker at 25 °C. After several minutes, white precipitate was found at the interface area. Several hours later, the precipitates were selected by centrifugation and washed by alcohol and water respectively for several times, then dried at 60 °C in vacuum for 24 h.

2.5. Characterization methods

^1H and ^{13}C NMR experiments were carried out on a Bruker Advance DRX400 and a Varian INOVA-500 spectrometer. The structure and phase purity of the as prepared samples were determined by X-ray diffraction (XRD) analysis on a Bruker AXS D8 Advance Powder X-ray diffractometer (using $\text{Cu K}\alpha$ radiation: $\lambda = 1.5418 \text{ \AA}$). The morphology and size of the as-prepared products were observed under a scanning electron microscope (Hitachi S-4800) and a transmission electron microscope (JEM-3010). The interfacial tension experiment was conducted on a Spinning Drop Video Tensiometer (Dataphysics SVT 15N).

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