Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

A simple preparation method for rare-earth phosphate nano materials using an ionic liquid-driven supported liquid membrane system

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ARTICLE INFO

Article history:
Received 22 January 2017
Received in revised form 2 May 2017
Accepted 11 June 2017
Available online xxx

Keyword:
Rare earth nano-material
Ionic liquid
Supported liquid membrane
Membrane nano-reaction
Hydrophobic HVHP

ABSTRACT

For the first time, our group has developed a novel, high-flux strategy for shape-controlled synthesis of rare earth nano-materials ($CePO_4$) using ionic liquid(IL)-driven supported liquid membrane (HVHP, DUPAPORE®) system. The system contains three phases including a supply phase of rare earth ions, a feed phase of phosphates, and ionic liquid-driven supporting liquid membrane phase. The imidazolium IL-driven supported liquid membrane is promising for nano-synthetic reaction of $CePO_4$. The anion types of immersed imidazolium IL have a critical role in the formation rate of $CePO_4$ nano-materials. Moreover, the adding SO_4^{2-} anion or adjustment of pH in supply phase containing Ce(III) ions could control effectively the morphology of the $CePO_4$ nano-materials. The result can be regarded as a good example, the IL:$[C_4mim][Tf_2N]$ –driven support liquid membrane systems can be used to prepare nano-wire and nano-sphere structures of $CePO_4$ with high efficiency and flux. Besides, the IL-driven supported liquid membrane can be cycled many times by using the back flush activation method.

Introduction

Rare earth phosphate nano-materials have stable physical and chemical properties and are used in high-performance optical devices, catalysis, biological fluorescence tracer tagging, photon conversion, lasers, etc [1–3]. Rare earth phosphate nano-crystals with special morphology also have potential applications in magnetic, electronic and optical materials [4,5]. Most of these applications require particles with a uniform shape and narrow particle size distribution. Different preparation methods and reaction conditions can influence the microstructure, particle size and luminescence properties of luminescent materials, and this influences their applications [6–9]. There have been numerous reports on the controlled synthesis and applications of one-dimensional rare earth phosphate nano-materials. The three-dimensional materials developed in these reports are also widely developed [10–13].

There are currently many synthetic methods to prepare rare earth phosphates including sol–gel method, co-precipitation method, micro-emulsion method, polymer complexometry method, ultrasonic method, hydrothermal method and spray pyrolysis method [14–18]. Of these, the hydrothermal method is one of the common. Crystals prepared via the hydrothermal method have good crystallinity and small particle size with a monodisperse size distribution. However, the hydrothermal method is also limited by a long reaction time, high energy consumption and low production rate. It is still challenging to prepare large batches of nanocrystals with good particle distribution and uniform appearance via this simple method [19–21].

Supported liquid membrane (SLM) systems have been widely applied in liquid–liquid extraction in recent decades [22–25], but these are rarely applied to industrial production because of stability and chronic accumulation [26,27]. However, the solvent used in the liquid membrane phase restricts these factors. In recent years, researchers have found an ideal solvent—the "ionic liquid"—to replace traditional organic solvents. Room

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http://dx.doi.org/10.1016/j.jiec.2017.06.017
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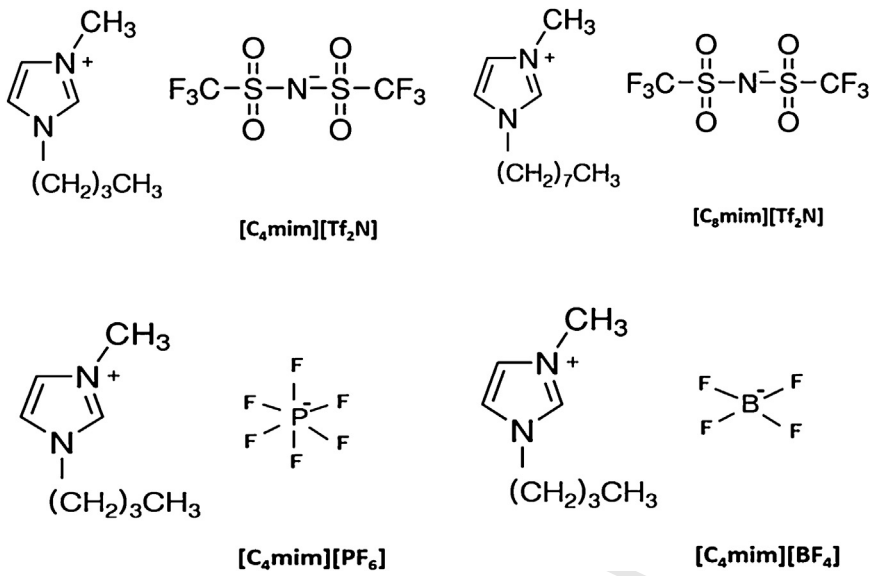

Fig 1. Molecular structures of ILs.

temperature ionic liquids (RTILs) are prepared from an organic cation and either an organic or an inorganic anion. They are considered "green" solvents relative to traditional organic solvents or electrolytes because of their high thermal stability and negligible vapor pressures. Numerous studies have demonstrated that they offer long-term stable operation [28–33].

As innovative works, we developed a strong controllable and a good reproducible ionic liquid-driven supported liquid membrane system to obtain nano-sized $CePO_4$ at room temperature and constant pressure in high flux. As a novel system for preparing $CePO_4$ nano-materials, the ionic liquid-driven supported liquid membrane system show some interesting advantages like high efficiency, low cost, and environmental-friendly characteristics, etc. We can easily control the morphology of the rare earth phosphate nanostructures by controlling the pH and the concentration of SO_4^{2-} in the supply phase of the rare earth ions. To the best of our knowledge, this is the first report that nano-wire and nano-sphere structures of $CePO_4$ can be prepared simultaneously from an ionic liquid-driven supported liquid membrane system.

Experimental

Materials

One of the hydrophobic porous polyvinylidene fluoride film: HVHP-04700 (pore size 0.45 μm and thickness 125 μm, ø:5.5 cm, DUPAPORE®), was obtained from Millipore Corp. The ionic liquids (ILs) were purchased from the Center for Green Chemistry and Catalysis (99% purity by NMR), Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The ILs were $[C_4mim][PF_6]$, $[C_4mim][BF_4]$ and $[C_4mim][Tf_2N]$, $[C_8mim][Tf_2N]$, and molecular structures of the ILs are shown in Fig. 1. The cerium (III) nitrate, phosphoric acid solution, ammonium sulfate were all purchased from Aladdin (Shanghai, China), and all starting materials were analytical grade.

Preparation of solutions of Ce(III) supply phase and PO_4^{3-} supply phase

The Ce(III) supply phase: cerium nitrate aqueous solutions with different concentrations (100 ppm–2000 ppm) were prepared in a

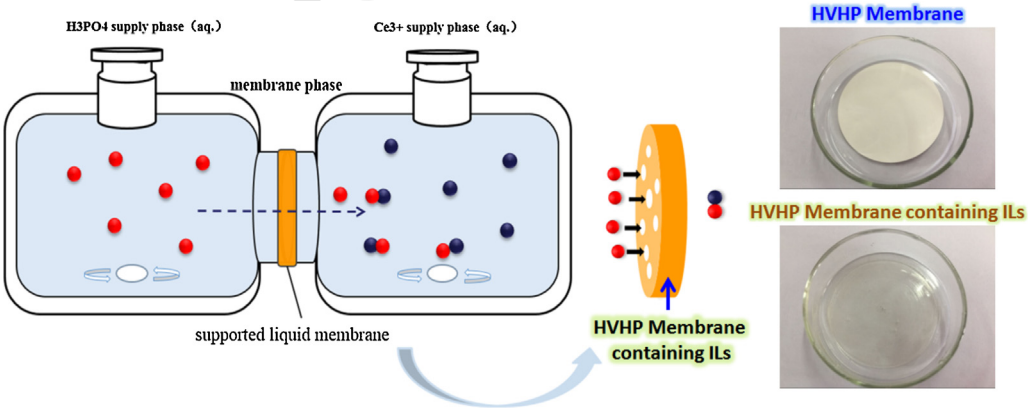

Fig. 2. Schematic overview of the experiment.

Please cite this article in press as: P. Zhao, et al., A simple preparation method for rare-earth phosphate nano materials using an ionic liquid-driven supported liquid membrane system, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.06.017