

# (Sub)Micron $\text{CaF}_2$ Cubes and Hollow Rods From Ionic Liquid Emulsions

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## Abstract

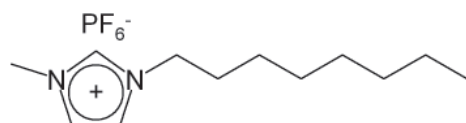
Uniform  $\text{CaF}_2$  cubes and rods with a well-defined crystal habit have been grown from emulsions of an ionic liquid (IL) in aqueous  $\text{CaCl}_2$  solutions via the hydrolysis of the  $\text{PF}_6^-$  counterion of the IL. Intriguingly, at high IL contents, hollow  $\text{CaF}_2$  rods form, which has not been observed before. The rods can reach lengths up to over ten micrometers and widths of up to ca. 2.5  $\mu\text{m}$ . Furthermore, the surface of the IL droplet has a strong influence on the nucleation efficiency of the precipitating mineral.

**Key words:** ionic liquids, emulsions, calcium fluoride, hollow rods

## Introduction

Ionic liquids (ILs) have attracted interest as reaction media for organic reactions, for extraction, and for electrochemistry.<sup>1</sup> Recently, the self-assembly of ILs and the self-assembly of organic molecules in ILs,<sup>2,3</sup> inorganic synthesis in ILs,<sup>3–10</sup> and emulsions with ILs<sup>11</sup> have also been studied. It has been demonstrated that ILs can act as solvents for reactants and as precipitation templates for inorganic matter at the same time.<sup>3,4</sup> If the IL is not consumed during the reaction, it can be retrieved after synthesis and thus provides an economical and potentially ecological approach to inorganic materials. However, in some cases the IL does react with the environment: for example,  $\text{PF}_6^-$  and  $\text{BF}_4^-$  hydrolyse in water over time and release fluoride  $\text{F}^-$ .<sup>12</sup>

Fluorides are widely used as a matrix material for rare earth ions and the controlled synthesis of  $\text{CaF}_2$  nanoparticles has recently attracted some interest.<sup>13</sup> This communication introduces a new pathway towards  $\text{CaF}_2$  crystals from emulsions of the IL 1-methyl-3-octyl imidazolium hexafluorophosphate **1** (Scheme 1) in aqueous  $\text{CaCl}_2$  solutions. The system takes advantage of the slow hydrolysis of the  $\text{PF}_6^-$  anion and the subsequent release of  $\text{F}^-$ . Interestingly, high concentrations of the IL lead to hollow  $\text{CaF}_2$  rods with a square or rectangular cross-section, which has not been described before.

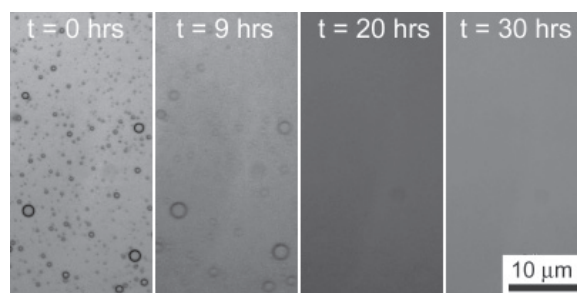


1-Methyl-3-octyl imidazolium hexafluorophosphate **1**

Scheme 1

## Results and discussion

IL/water emulsions are stable for about two hours at room temperature and the droplet diameters range from ca. 0.3 to ca. 4  $\mu\text{m}$ . Figure 1 shows that replacing water with an aqueous 1 M  $\text{CaCl}_2$  solution increases the emulsion stability to ca. 9 hours, after which the smaller droplets start to disappear. Larger droplets have been observed up to ca. 22 hours.

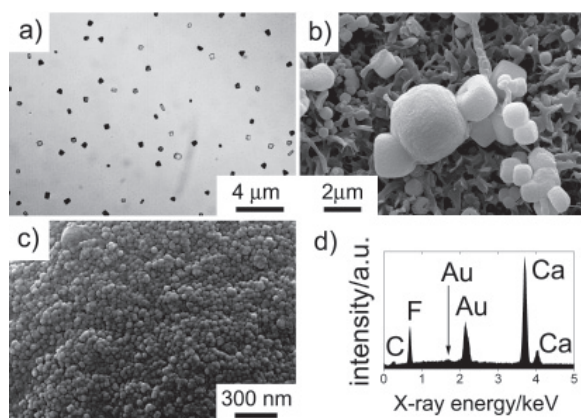


**Figure 1.** Optical micrographs showing the transformation of a 10% (v/v) emulsion of **1** in 1 M  $\text{CaCl}_2$ . The small droplets disappear after ca. 8 to 10 hours; larger droplets persist up to 20 to 22 hours.

The disappearance of the droplets is not only associated with a demixing of the emulsion (though this is also observed), but can also be explained as follows:  $\text{PF}_6^-$  hydrolyses and releases  $\text{F}^-$ .<sup>12</sup> At some point the solution becomes supersaturated and  $\text{CaF}_2$  precipitates. The  $\text{Cl}^-$  introduced via the  $\text{CaCl}_2$  replaces  $\text{PF}_6^-$  as the counterion for the imidazolium cation, leading to a more water-soluble compound. The slight size increase of the IL droplets with increasing time suggests that with increasing  $\text{PF}_6^-$  hydrolysis level, water penetrates into the IL droplets, further hydrolyzes  $\text{PF}_6^-$ , and ultimately dissolves the IL into the aqueous phase. In this context it would also be interesting to

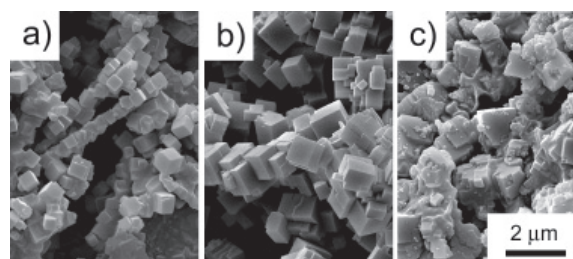
monitor the stability of the emulsions obtained by Binks et al.<sup>11</sup> Some of them are possibly also not stable over a longer period of time due to counterion hydrolysis.

CaF<sub>2</sub> crystals precipitated from a 1 M CaCl<sub>2</sub> solution (Figure 2) have a relatively uniform shape but a size distribution that is broader than that of CaF<sub>2</sub> nanoparticles obtained via hydrothermal synthesis.<sup>13</sup> SEM images show particle sizes from ca. 300 nm to over 4 μm; typical sizes are ca. 1 μm. High magnification SEM images show that the surface of the particles is relatively rough. It appears as if the particles were composed of even smaller nanoparticles that aggregate during the reaction similar to earlier findings on CaCO<sub>3</sub>,<sup>14</sup> TiO<sub>2</sub>,<sup>15</sup> ZnO,<sup>16</sup> and iron oxides.<sup>17</sup> Figure 2d shows that only a negligible fraction of organic material is adsorbed on or incorporated into the crystal because intense Ca and F signals but only a weak C line are observed in the energy dispersive X-ray spectra of the particles.



**Figure 2.** a) Optical micrograph of CaF<sub>2</sub> crystals precipitated from a 10% (v/v) emulsion of **1** in 1 M CaCl<sub>2</sub>. b) SEM image of typical CaF<sub>2</sub> crystals on a 0.22 μm filter. c) High magnification SEM image of a CaF<sub>2</sub> crystal surface showing the nm-sized subunits. d) X-ray spectrum of a CaF<sub>2</sub> crystal showing that the crystals only contain Ca and F and little impurities. The Au lines are from sample sputtering for SEM.

To explore the tunability of the system with respect to control of particle shape, size, and size distribution, the reaction conditions were modified: rather than standing at room temperature, the reaction mixture was vigorously stirred for 48 hours and the concentration of the CaCl<sub>2</sub> solutions was varied from 0.01 to 10 M. At 0.01 M no precipitation was observed but Figure 3 shows that the CaCl<sub>2</sub> concentration and the stirring both influence CaF<sub>2</sub> precipitation: at all concentrations above 0.01 M, cubic crystals form but stirring leads to a more uniform crystal habit with well-defined crystal faces. Between CaCl<sub>2</sub> concentrations of 0.1 and 10 M the crystal size slightly increases from ca. 220–450 nm at 0.1 M CaCl<sub>2</sub> to over 1 μm at 10 M CaCl<sub>2</sub>. The particles are not isolated like similar particles obtained via hydrothermal synthesis,<sup>13</sup> but form larger entities.



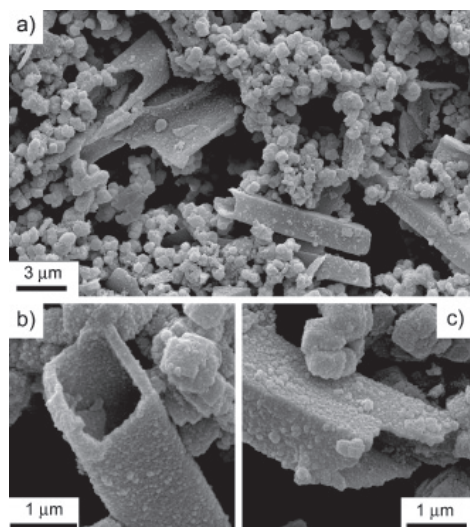
**Figure 3.** The effect of CaCl<sub>2</sub> concentration on CaF<sub>2</sub> crystallization: a) 0.1 M CaCl<sub>2</sub>, b) 1 M CaCl<sub>2</sub>, c) 10 M CaCl<sub>2</sub>. Compare Figure 3b to 2b for the effect of stirring.

As the hydrolysis of the PF<sub>6</sub><sup>-</sup> counterion causes the precipitation, control experiments were made with NH<sub>4</sub>PF<sub>6</sub> to elucidate whether the imidazolium ion had an effect on the crystallization or not. SEM shows no effect on the morphology, as also without the IL cubes are observed (data not shown).

While no effect on the morphology is observed on replacing the imidazolium by NH<sub>4</sub><sup>+</sup>, it is interesting to note that the IL **1** appears to promote CaF<sub>2</sub> nucleation: in the control experiment with NH<sub>4</sub>PF<sub>6</sub> (i.e. no IL) only ca. 1 mg of CaF<sub>2</sub> was obtained, but all precipitations with the IL yield ca. 10 to 15 mg of precipitate, which indicates a strong influence of the IL/water interface on nucleation. The author suspects that the ionic nature of the IL droplet (or droplet surface) is a key parameter to control nucleation and crystallization; this phenomenon is interesting and should be investigated further because it is possible that the use of another IL generates different precipitation conditions favoring other crystal morphologies or sizes.

To further investigate the effect of the IL **1** on CaF<sub>2</sub> precipitation, the ratio of IL to a 1 M CaCl<sub>2</sub> solution was varied. Neither a 30%, 50%, nor a 70% (v/v) mixture changed the appearance or size of the crystals significantly except for some roughening of the cube surfaces. However, a 90% (v/v) mixture leads to a mixture of rods and cubes, Figure 4. The rods are considerably larger than the previously described particles and reach lengths up to over ten microns and a width of up to ca. 2.5 μm. Moreover, SEM images show that the rods are actually hollow structures with a square or rectangular cross section and a wall thickness of ca. 200 nm. The walls resemble the rough surfaces shown above.

The formation of hollow CaF<sub>2</sub> rods is intriguing and to the best knowledge of the author, they have not been described before. The reason for nanorod formation is not clear yet, but as the author has not observed liquid crystalline behavior of the 90% IL/10% CaCl<sub>2</sub> reaction mixture, liquid crystal (LC) templating is rather unlikely. This is even more so because the mixture was stirred during the whole reaction time, which would greatly disturb the order in any presumed LC template.



**Figure 4.** SEM image of  $\text{CaF}_2$  nanocrystals obtained from a 90% (v/v) emulsion with a 1 M  $\text{CaCl}_2$  solution: a) overview showing a typical mixture of cubes and rods; b) and c) are typical rods that have broken up during SEM sample preparation.

## Experimental

In a typical precipitation, 2 mL of a 1 M aqueous  $\text{CaCl}_2$  solution were thoroughly mixed with 200  $\mu\text{L}$  of **1** (Solvent Innovation, Germany) by shaking and stirring the mixture for ca. 20 minutes. The resulting liquid is slightly opaque and exhibits droplets of **1** surrounded by the aqueous phase under the optical microscope (Leica DM-RP), Figure 1. This mixture was allowed to stand at room temperature for 48 hours, during which time the  $\text{CaF}_2$  crystals form. The crystals were isolated by filtration through an 0.22  $\mu\text{m}$  Millipore filter and washed with 10 mL of water. SEM images and X-ray spectra were obtained with a Philips XL-30 ESEM/Noran X-ray detector operated at 20 kV and a working distance of 10 mm. Samples were sputtered with gold prior to imaging.

## Conclusions

This paper demonstrates that ILs provide a flexible means for the controlled growth of  $\text{CaF}_2$  cubes and rods. It also shows that the IL does affect nucleation efficiency. While the rods are rather poorly defined and accompanied by regular (solid and cubic) particles, the approach presented here opens a new pathway towards  $\text{CaF}_2$  particles with unexpected shapes. Potentially, other fluorides can be grown using

the approach presented here or doped structures can be generated; it is thus interesting to pursue further research into these processes and materials. Of particular interest is the investigation of the effect of the IL droplet surface on the nucleation efficiency and particle shape selection; furthermore, the use of microwaves, which heat up ILs quickly, could further enable the synthesis of novel compounds from IL emulsions.

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## Povzetek

Iz emulzije ionskega topila in vodne raztopine  $\text{CaCl}_2$  smo s hidrolizo  $\text{PF}_6^-$  aniona ionskega topila. dobili pravilne kristale  $\text{CaF}_2$  v obliki kock in valjev. Pri visoki vsebnosti ionskega topila v suspenziji smo kot prvi opazili votle valje  $\text{CaF}_2$ . Valji imajo dolžino tudi več kot deset mikrometrov in premer do 2.5  $\mu\text{m}$ . Površina kapljic ionskega topila vpliva na učinkovitost nukleacije kalcijevega fluorida.