Exfoliation of Layered Phenylphosphonates of Alkaline-Earth Metals

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INTRODUCTION

Phenylphosphonates of alkaline-earth metals

Layered phenylphosphonates of calcium $CaC_6H_5PO_3 \cdot 2H_2O$ (CaPhP), barium $BaC_6H_5PO_3 \cdot 2H_2O$ (BaPhP) and strontium $SrC_6H_5PO_3 \cdot 2H_2O$ (SrPhP) belong to a group of hybrid organic-inorganic materials.

Their particles consist of layers which are stacked together by van der Waals forces so it should be possible to exfoliate them into single sheets having thickness of several nanometers.

For illustration we provide model of chemical structure of CaPhP (Figure 1) and real shape of particles obtained by scanning electron microscopy (Figure 2).

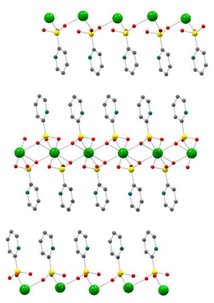

Figure 1

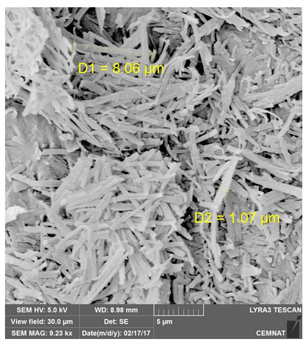

Figure 2

Exfoliation

Procedure for peeling apart the layers of material to obtain thinner sheets. This phenomenon occurs when the van der Waals interactions are overcome by action of mechanical forces.

EXPERIMENT

Synthesis of phenylphosponates[1,2,3]

First, the phenylphosphonic acid is dissolved in water and pH of obtained solution is adjusted to 8-9 by adding concentrated ammonia solution, then the source of metal dissolved in water (e.g., $CaCl_2$ in the case of CaPhP) in a molar ratio 1:1 with phosphonic acid is added. After 30 minutes of stirring the white precipitate is collected by filtration and washed with water and ethanol.

Exfoliation

- 50 mg of particles is placed into a round bottom flask with 50 mL of solvent: propan-2-ol, acetonitrile, dimethylformamide or toluene
- Samples are sonicated in an ultrasound-bath with frequency 37 kHz, in an ice-bath (Figure 3)
- The ability to form stable opalescent dispersion is evaluated (Figure 4)

Figure 3

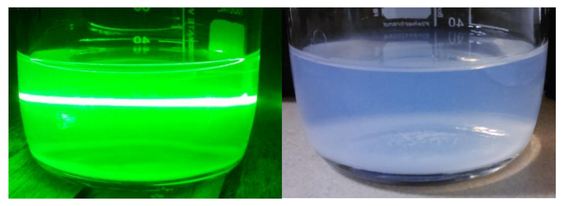

Figure 4

RESULTS

The most promising system seems to be CaPhP in propan-2-ol which formed a dispersion stable for more than two weeks. The size distribution of the particles was measured by dynamic light scattering (DLS) and the thickness of lamellas was obtained from atom force microscopy.

Atom force microscopy

Atom force microscopy measurement confirmed the presence of layered particles with thickness of tens of nanometers, which corresponds to several layers as well as the presence of single lamellas with height only in units of nanometres (Figure 5). Lateral dimensions are in a good agreement with the DLS measurements.

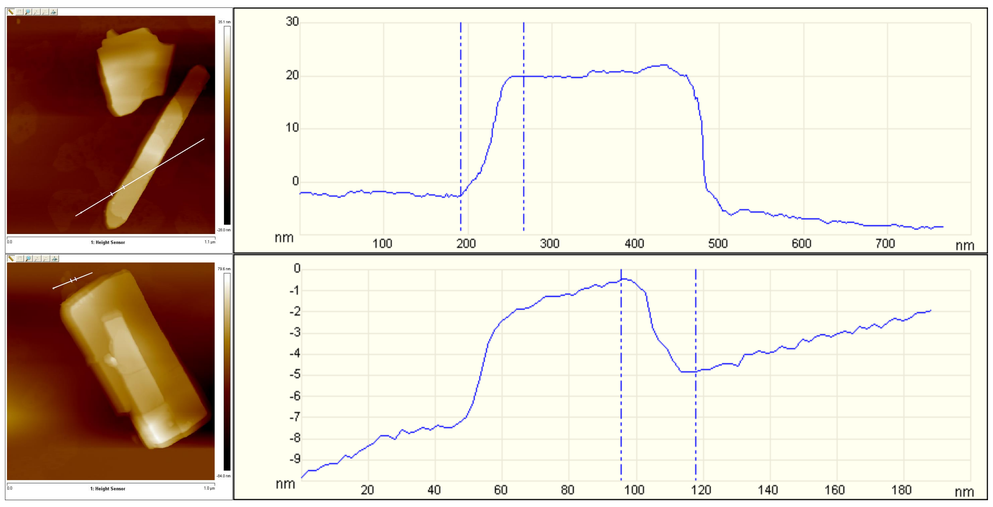

Figure 5

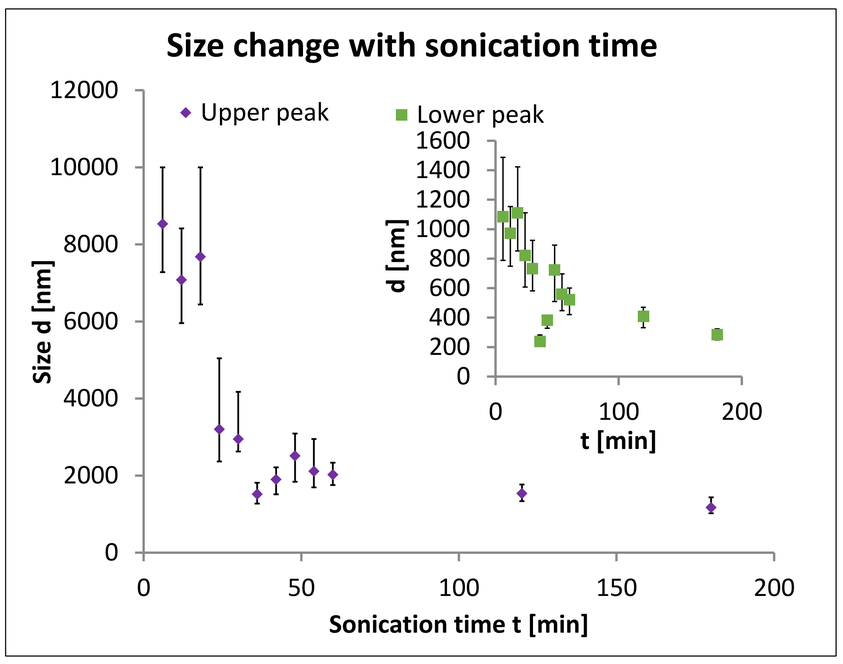

Figure 6

Dynamic light scattering

Size distribution of the CaPhP sample sonicated in propan-2-ol is bimodal in all cases which corresponds to a rod shape of the particles. The color symbols (Figure 6) belong to a size with the highest measured intensity, the dark lines determine the range of the sizes being detected. The size decreases with sonication time from 10 µm to approximately 1,5 µm for the upper peak and from 1,5 µm to about 250 nm for the lower peak.

CONCLUSION

- We were able to exfoliate CaPhP via sonication in a suitable solvent
- The most stable dispersion was formed in propan-2-ol
- This procedure leads not only to exfoliation but also to fragmentation of the particles

LITERATURE

1. Svoboda, J., V. Zima, et al. (2005). Inorganic Chemistry **44**: 9968-9976. 2. Svoboda, J., V. Zima, et al. (2008). Journal of Physics and Chemistry of Solids **69**(5-6): 1439-1443. 3. Zima, V., J. Svoboda, et al. (2006). Solid State Sciences **8**(11): 1380-1385.

ACKNOWLEDGEMENT

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