Layered Organophosphonates as Suitable Starting Materials for Production of Nanosheets via Top-down Approach

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INTRODUCTION

Layered metal organophosphonates belong to a large group of hybrid organic-inorganic materials. They benefit from a well-defined structure of their inorganic part in combination with organic moieties, which can be modified to obtain desired properties.

Thanks to their structure, with strong covalent bonds between the atoms in the layers but with rather weak interactions between the layers, these compounds can be used as host materials in intercalation reactions or as starting materials for production of 2D nanosheets by exfoliation.

In this work we studied exfoliation of layered phenylphosphonates of alkaline-earth metals with general formula $MeC_6H_5PO_3 \cdot 2H_2O$ (Me = Ca, Sr, Ba). Production of nanosheets was performed by a so-called liquid-based exfoliation[1]. This technique is based on dispersing layered solids in a suitable solvent followed by application of normal and shear forces, which cause separation of individual layers from the bulk.

EXPERIMENTAL

Synthesis of layered phenylphosphonates

The starting layered materials were prepared by a procedure described before.[2, 3, 4]

Exfoliation

In the first step, preliminary tests were performed to find a solvent suitable for the exfoliation. Typically, 10 mg of sample was put into a glass vial and 5 ml of a solvent was added. Then the sample was sonicated for one hour in an ultrasound bath (f = 37 kHz). The suitability of the selected solvent for the exfoliation was evaluated on the basis of stability of the dispersion prepared and on the presence of Tyndall scattering.

For the following exfoliation experiments 50 mg of sample was put into a round bottomed flask and 50 ml of the suitable solvent was added. The mixture was sonicated for 1 h in an ultrasound bath and then the sample was divided into three fractions by centrifugation (5 min at 3000, 6000 and 9000 rpm). The fractions were characterized by dynamic light scattering and the thickness of the obtained lamellas was evaluated by an atom force microscopy (AFM).

RESULTS AND DISCUSSION

We succeeded in preparation of nanosheets from bulk layered phenylphosphonates of alkaline-earth metals via liquid-based exfoliation. We also developed methodology for evaluation of exfoliation in different solvents, which can be applied also to other types of layered materials.

The most promising system so far is calcium phenylphosphonate exfoliated in propan-2-ol. The Tyndall scattering which was used to evaluate the presence of small particles in the dispersions is shown in Figure 1 A. We obtained monolamelar particles with the thickness of 1,2 – 1,6 nm, as determined by AFM (Figure 1 B), which is in a good agreement with their basal spacing obtained from powder X-ray diffraction (XRD) measurements. However, it is worth to note that the exfoliation does not proceed completely and it is necessary to use centrifugation to separate monolamelar sheets from the remaining bigger particles.

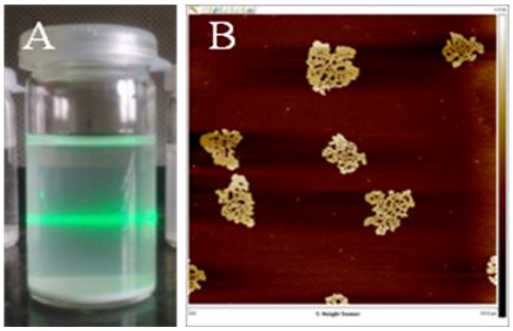

Fig. 1. Tyndall scattering of calcium phenylphosphonate exfoliated in propan-2-ol (A); lamellas detected by AFM in the same sample centrifuged at speed 9000 rpm (B). These lamellas are only 1,6 nm thick but their lateral dimensions are still around 1 μm.

CONCLUSION

It was proved that it is possible to prepare nanosheets of phenylphosphonates of alkaline-earth metals from bulk material via liquid-based exfoliation approach. These particles have a platelet shape and a high aspect ratio. Their hybrid character, especially the presence of hydrophobic phenyl groups on their surface, makes them promising fillers for polymer nanocomposites.

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