

Production of organic nanomaterials by liquid phase exfoliation

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Liquid phase exfoliation (LPE) has become an important production technique giving access to single and few-layered nanosheets in colloidal dispersion. It has been shown to be applicable to a whole host of inorganic crystals with the nanosheet morphology being defined by the in plane and out of plane binding strength in the parent crystal.[1] In addition to layered inorganic crystals, organic sheet stacks such as 2D polymers or covalent and metal organic frameworks have received increasing attention in recent years. Such organic sheet stacks can be made by a number of techniques, e.g. using reversible solution phase chemistry, polymerisation after assembly on the liquid-air or liquid-liquid interface or polymerisation after precisely aligning monomers in single crystals.

With the single crystal to single crystal transformation, perfectly single crystalline 2D polymer sheet stacks can be synthesised and are an ideal starting point for LPE. We found that crystalline nanosheets are produced after LPE of charge-neutral polymers.[2] By optimising the size selection, mg fractions with up to 29% of monolayers of a model 2D polymer with an average length of ~130 nm were obtained. This is the first time that the amount of monolayers of an exfoliated organic 2D material has been quantified. Overall, LPE of this derivative is equally efficient as graphite exfoliation producing nanosheets with average length/thickness aspect ratios of ~60.[2]

In contrast, LPE of metal organic frameworks (MOFs) yields relatively small and thick sheets. Using a Zr-MOF as model system an average length/thickness aspect ratio of ~6 was determined [3] which is significantly lower than for many layered inorganic materials (e.g. transition metal dichalcogenides). In a comparative study using a range of Ga, Sc and Zr-based MOFs,[4] as well as Cu(HHTP)₂ we find that the aspect ratio varies between 4-10 when performing LPE in aqueous surfactant. We attribute this to the typically polycrystalline nature of the starting materials.

Finally, we were intrigued by the question whether materials with only noncovalent bonds could be exfoliated using LPE. With the realisation that the binding strength anisotropy governs the (average) shape of the LPE nanomaterials, it should be possible to obtain nanomaterials with distinct shape from exfoliation of organic molecular crystals. To test this, orthorhombic and triclinic single crystals of the organic semiconductor rubrene with only non-covalent π - π interactions between the molecules were used in LPE.[5] Distinct nanorods and nanobelts of rubrene with only a few molecular layers are formed, stabilized against aggregation in aqueous sodium cholate solution and isolated by liquid cascade centrifugation.

References

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