OSMOTIC SWELLING AS A KEY FOR PERFECT NANOSHEETS DISPERSION: FROM WATER TO ORGANIC SOLVENTS

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MOTIVATION

Layered silicates have a wide range of applications due to their unique platelet like structure, high aspect ratio, and natural abundance. Particularly in nanocomposites, which require the perfect delamination of nanosheets.

The conventional method of liquid-phase exfoliation are not suitable for the fabrication of high aspect ratio filler due to high shear force exceeded on the clay particles, which leads to the diminishing of the aspect ratio. Osmotic swelling is an alternative method, which allows a gentle delamination with the preservation of aspect ratio of pristine mineral. So far the osmotic swelling were limited to the water systems and the range of applications would be further expanded if clay delamination could be achieved in non-aqueous solvents. For this purpose, so-called "organophilic" clays have previously been developed but, quite often, the materials thus prepared show poor delamination.

OSMOTIC SWELLING

1

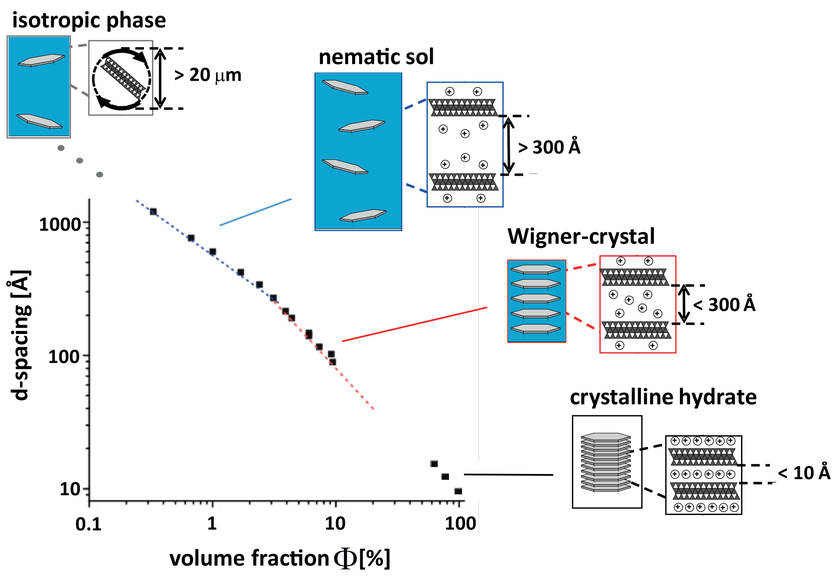
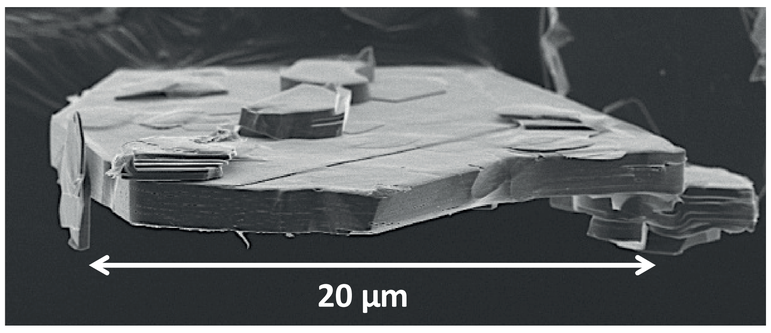


Fig 1. Different swelling regimes. Wigner-crystal, nematic sol and isotropic phase are referred to as being delaminated by osmotic swelling.

2.A



2.B

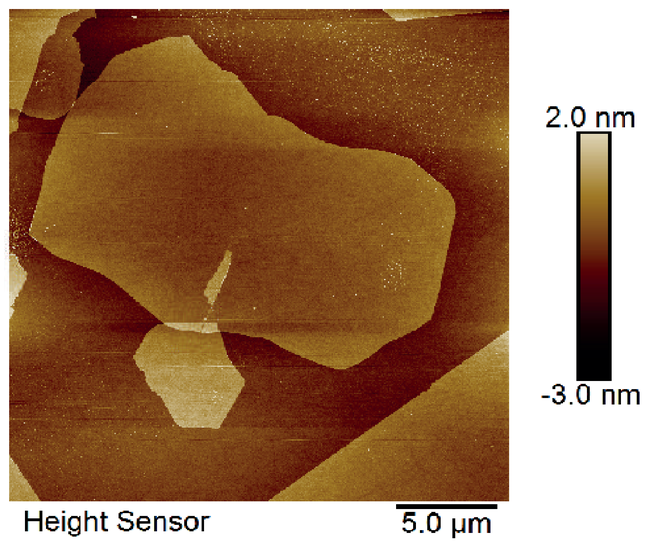
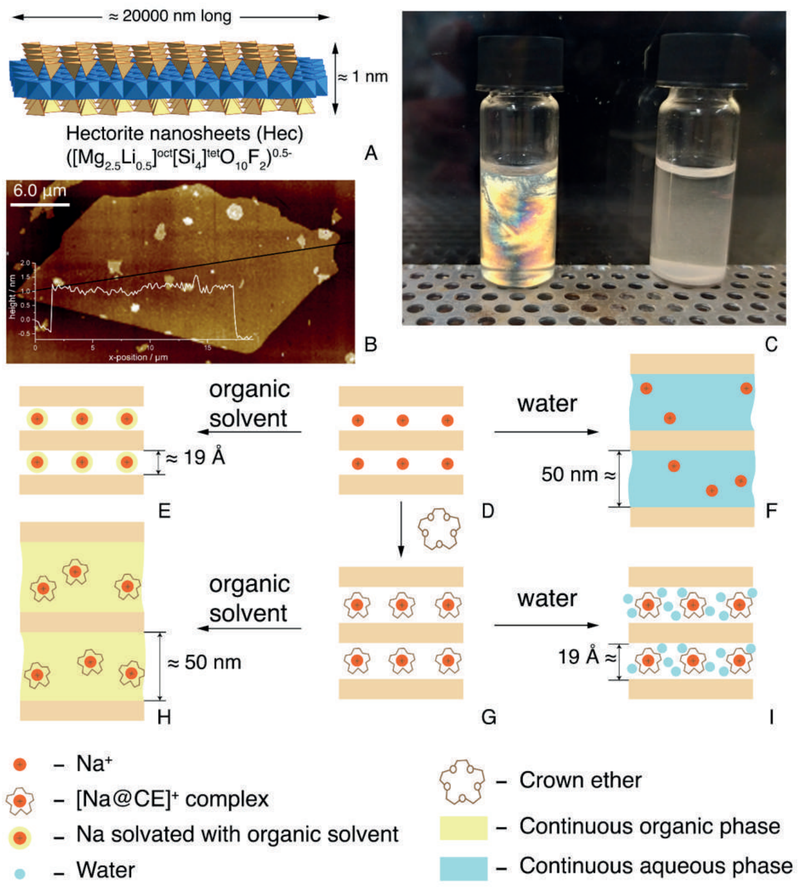


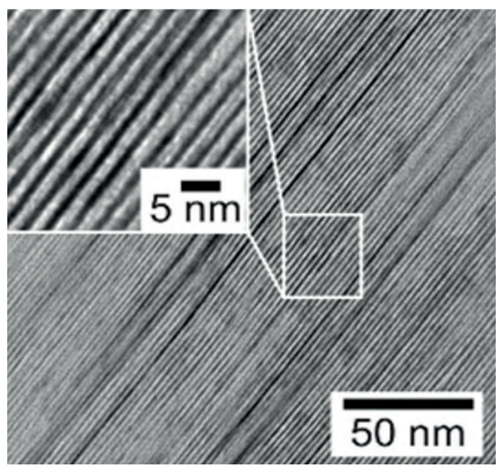
Fig 2. A Sodium Hectorite crystal before the swelling, B AFM picture of the delaminated singlelayer nanosheet

ORGANIC SOLVENTS

3



4.A



4.B

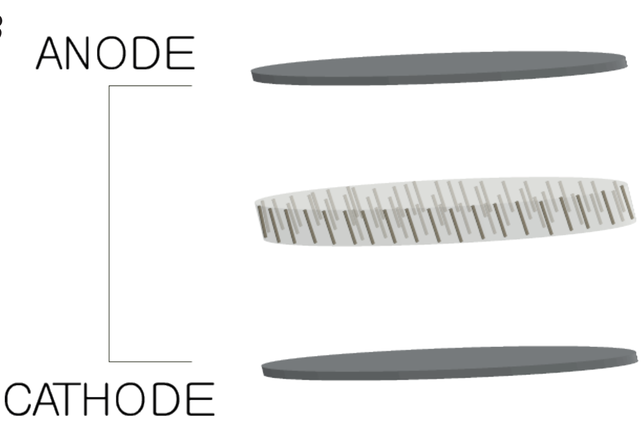
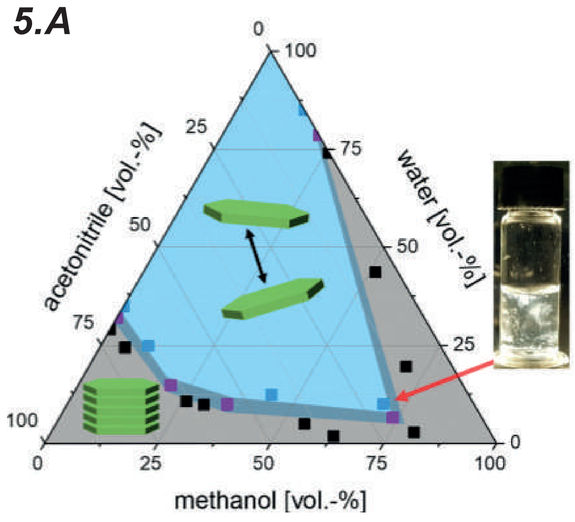


Fig 3. A Schematic illustration of the structure of a negatively charged unilamellar hectorite nanosheets. B Topographic AFM image of unilamellar Na-Hec nanosheet C (left) Birefringent suspension of osmotically swollen CE modified Na-Hec in NMF and (right) crystalline swollen CE modified Na-Hec in water. D Pristine Na-Hec with the negatively charged layers held together by cations. E Crystalline swelling of Na-Hec in organic solvents. F Spontaneous delamination by osmotic swelling of pristine Na-Hec in water. G Na-Hec intercalated with the crown-ethers (CE) forming [Na@CE]+ complex. H CE modified Na-Hec spontaneously delaminates by osmotic swelling in organic solvents. I CE modified Na-Hec no longer osmotically delaminates in water.

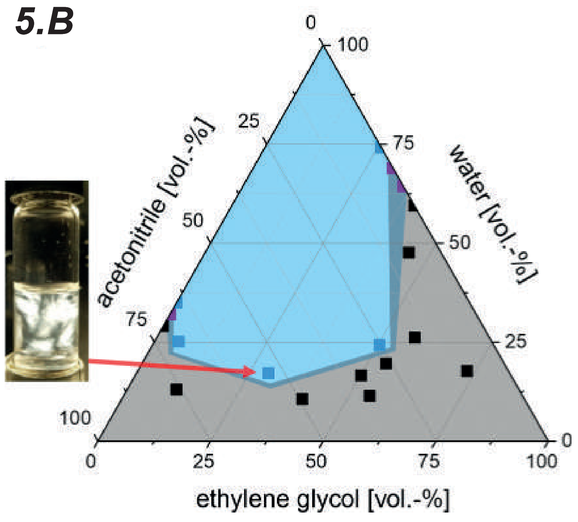
Fig. 4 Potential application of the Hectorite nanosheets osmotically swollen in the organic phase A. Homogenious periodic nanocomposite. B Gel-inorganic electrolyte for battery systems

SOLVENTS BLENDS

5.A



5.B



5.C

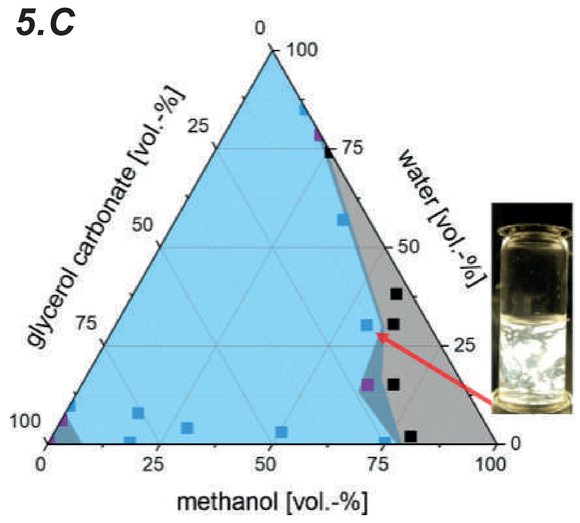


Fig. 5 A Ternary phase diagram of NaHec swollen in methanol-water-acetonitrile mixtures (blue squares: osmotically swollen, purple squares: biphasic system, black squares: crystalline swollen)
B Ternary phase diagram of NaHec swollen in ethylene glycol-water-acetonitrile
C Ternary phase diagram of NaHec swollen in methanol-water-glycerol carbonate

CONCLUSIONS

Gentle and utter delamination down to monolayers by thermodynamically allowed osmotic swelling clearly is not restricted to aqueous media but can be extended to water-free and aprotic solvents. The nematic suspensions in water-free organic solvents will allow for an extended range of polymer matrices possible for fabricating ordered nanocomposites via solution blending. This will give access to composites of uniformly dispersed nanosheets within hydrophobic polymer systems, including isocyanate-based polyurethanes.

REFERENCES:

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[2] L. Mayr et al.: Langmuir 36, 3814 (2020).

[3] V Dudko, submitted to Langmuir.