Experimental report

10/06/2016

Proposal: **9-10-1417** **Council:** 10/2014

Title: Contrast study of Janus-typed layered clays with huge aspect ratio

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Matthias STOETER**

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Local contacts: Peter LINDNER

Samples: hybrid layered clay (hectorite modification)

Instrument	Requested days	Allocated days	From	To
D11	3	1	15/07/2015	16/07/2015
D22	3	0		

Abstract:

Surface compartmentalize layered clays with a huge aspect ratio have a high potential for applications as they combine different chemical and physical properties. Designing the texture and confinement of one compound between single clay platelets opens the way to new artificial materials in optoelectronics and gas barrier applications. We developed a way to obtain layered hybrid clay material with a huge aspect ratio up to 20000, including Janus-type modifications. Proving the hybrid morphology of (exfoliated) clay platelets is extremely difficult. Within the proposed experiment we want to study the morphology of layered hybrid clays with contrast variation to proof the compartmentalized Janus-type nature.

EXPERIMENTAL REPORT

EXPERIMENT: N° 9-11-1417 INSTRUMENT: D11

DATES OF EXPERIMENT: 15.7.-17.7.2015

TITEL: Contrast Study of Janus-typed layered clays with huge aspect ratio

EXPERIMENTAL TEAM (names and affiliation):

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LOCAL CONTACT: Dr. Peter Lindner

REPORT:

A synthetic sodium fluorohectorite ($Na_{0.5}^{inter}[Mg_{2.5}Li_{0.5}]^{oct}<Si_4>^{tet}O_{10}F_2$) with typical lateral dimensions in the range of several microns (median ≈ 18 μm) is partially ion exchanged with ammonium cations (NH_4^+) to yield a crystalline layered heterostructure. When NH_4^+ and Na^+ are chosen as the segregated interlayer cation pair, alternating NH_4^+ interlayers are formed, which do not hydrate, while adjacent Na^+ interlayers readily hydrate (Figure 1a).

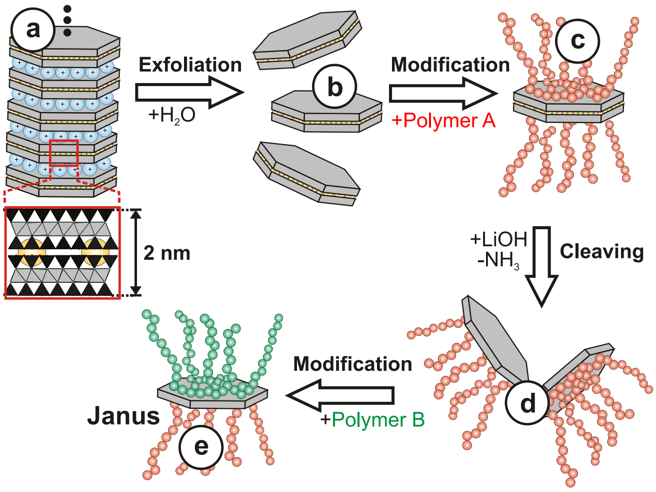

Figure 1. Selective swelling of a crystalline heterostructure (a) with NH_4^+ interlayers (yellow) and hydrated Na^+ interlayers (blue) induces highly selective exfoliation into bilayers (b). After external modification with a polycation A (red) (c), modified bilayers can be cleaved under basic conditions using, e.g., LiOH (d) while the symmetry is simultaneously broken at this stage. The platelets can be further modified (green) to form Janus-type platelets (e) with differently functionalized surfaces.

Selective swelling of the sodium interlayers was used to produce bilayers of huge aspect ratio (Figure 1b). When starting with the bilayers, breaking symmetry is beautifully simple (Figure 1d). Janus platelets should be obtained by first coating both surfaces of the bilayer by a cationic polymer, followed by cleaving of the NH_4^+-interlayer of the Bilayer (Figure 1c-Figure 1d). Commercial polyethyleneimine-ethyleneoxide (PEI-EO) was used as a cationic polymer. The main goal of the contrast study of Janus-typed layered clays with huge aspect ratio was to investigate the transition from Figure 1c to Figure 1d.

Results:

As a first test, the bilayer structure (Figure 1b) measured in advance by small angle x-ray scattering measurements was confirmed by small angle neutron scattering (SANS) [1]. Next, cleaving of PEI-EO modified bilayers (Figure 1c-d) was followed by SAXS and SANS in D_2O (Figure 2).

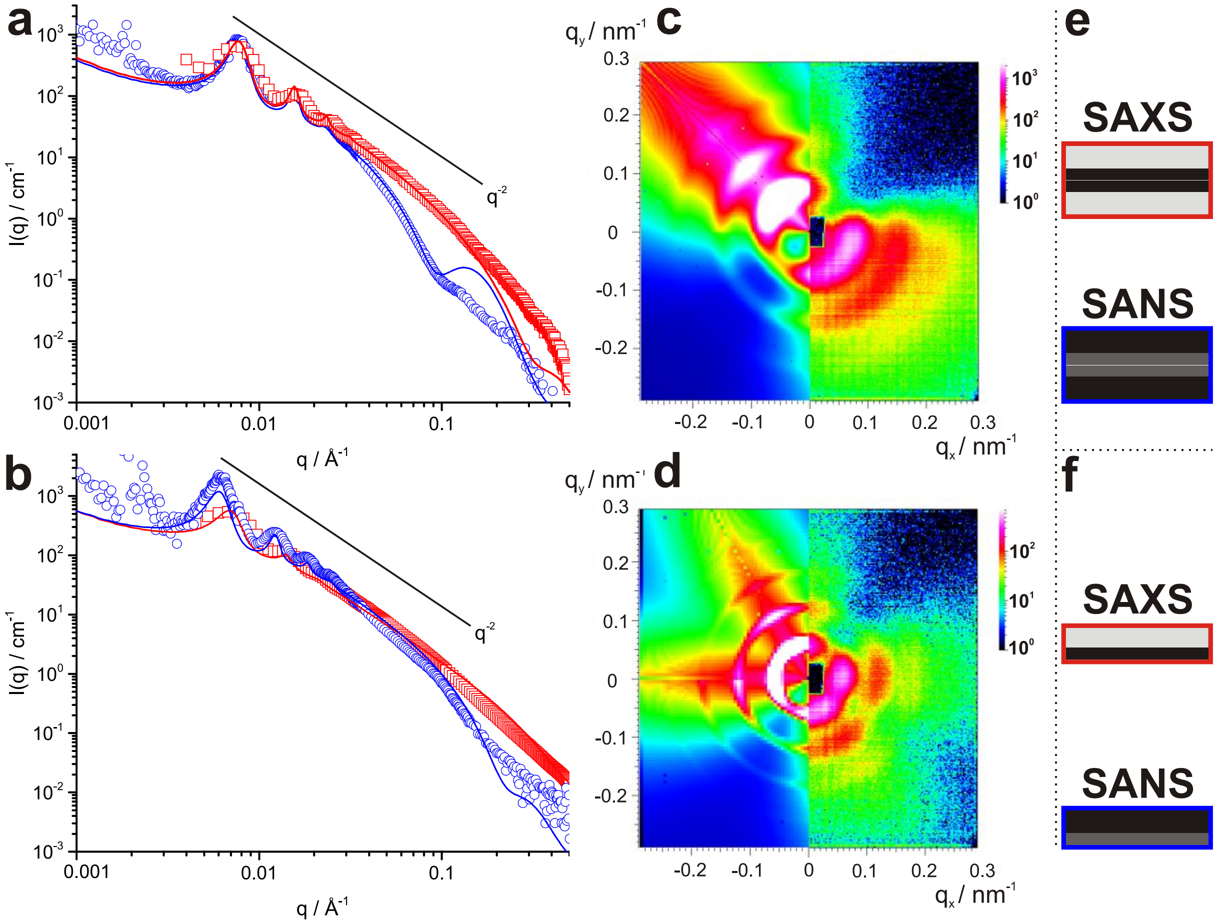

Figure 2 SAXS- and SANS-pattern of PEI-EO modified bilayers in D_2O before (a, c) and after cleaving (b, d). To assist comparison, 1D SANS data are normalized to the SAXS data. On the left radial averaged data (a, b) of SAXS (red squares), SANS (blue circles) and theoretical intensities (bold lines) are shown. The thin lines indicate a q^{-2} scaling behavior. The schemes on the right (e, f) depict corresponding SAXS- (red border) and SANS (blue border) contrasts. In the middle 2D SANS raw data (c right side, d right side) are shown, taken at a sample to detector distance of 8 m. Modeling for PEI-EO modified bilayers (c, left side) (3.3 wt%; description by hamburger model: D = 2000 nm, h = 2.1 nm, h + 2 l = 5.8 nm, *d* = 80 nm; contrast ratio of l / h was set to 0.064 for SAXS and 2.88 for SANS). Modeling for cleaved Janus platelets (d, left side) (description by disc model with D = 2000 nm; SANS 2.9 wt%, thickness h = 3.0 nm, *d* = 102 nm; SAXS: 3 wt%, h = 1.05 nm, d = 88 nm).

Even though both methods are sensitive to the scattering of the PEI-EO modification, the SAXS intensity is more dominated by the strong electron contrast of the layered silicate (Figure 2, red line). Due to the better scattering contrast of the PEI-EO modification and the solvent (D_2O) SANS is more sensitive to the modification. Clear differences between SAXS and SANS become evident in the high q-range. A sharp first form factor minimum as observed for unmodified bilayers is not detected in SAXS. This effect is most probably due to variations in the density or thickness of the PEI-EO coating (statistical copolymer). The complete individualization of platelets by osmotic swelling is proven by the observed large separation distances. The PEI-EO modified bilayers and the cleaved Janus platelet both exhibit a preferred orientation in the 1 mm pathway cuvette as indicated by the anisotropic 2D SANS scattering patterns (Figure 2c and d). The scattering intensities of the PEI-EO modified bilayers (Figure 2, a and c) can be described using the simple model of separated hamburgers. The averaged overall thickness of the PEI-EO modified bilayer was found to be 5.8 nm from the fit of the SANS data. As expected, cleaving bilayers into Janus-platelets results in a significant change of the form factor and the minimum in the SANS pattern shifts to higher q-values (Figure 2, b and d), indicating a reduced platelet thickness. The modeling of a Janus particle is, however, very challenging. We used a very simplified approach based on the different SAXS and SANS contrasts and the description of the particles as homogeneous discs. The SAXS patterns can be approximated by a disc with a thickness $h = 1.05$ nm and the SANS intensity with $h = 3.0$ nm which corresponds to a 1-nm-thick silicate layer coated on one side with an approximately 2 nm-thick monolayer of PEI-PEO (Figure 2b).

As a conclusion, the contrast study of Janus typed layered clays with huge aspect ratio provided a good indication for the successful cleavage of the bilayers and have therefore significantly contributed to an in-depth understanding of controlled exfoliation of 2D materials into bilayer and their conversion to giant Janus platelets. The results of this study are already published in 2016 in Angewandte Chemie International Edition. [1]

References

[1] M. Stöter, S. Gödrich, P. Feicht, S. Rosenfeldt, H. Thurn, J. W. Neubauer, M. Seuss, P. Lindner, H. Kalo, M. W. Möller, A. Fery, S. Förster, G. Papastavrou, J. Breu, *Angew. Chem. Int. Ed.* **2016,** http://dx.doi.org/10.1002/anie.201601611.