Characterisation of solution-processed 2D nanosheets by MIR and FIR vibrational spectroscopy

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Characterisation of the exact chemical composition of solution-processed and functionalised 2D materials is still a challenging task. Typically, a combination of Raman spectroscopy, XPS, TGA-MS and electron-microscopy based EDX is used. Some reports also complement this portfolio with IR vibrational spectrocopy in the MIR range which is suitable to detect organic functionalities which are physisorbed or chemisorbed on the surface. However, any quantitative information is lacking and a destinction between physisorption (of e.g. solvent) and covalently-grafted moieties is hardly possible.
In this talk, we address this by systematic studies of solution-processed and/or functionalised MoS_2 nanosheets as model substance, where we extend the spectroscopic range to the FIR, where Mo-S vibrations can be discerned. This is possible through diffuse-reflectance Fourier transform IR spectroscopy (DRIFT) in CsI matrix. Through normalisation to the Mo-S vibrations, it is possible to obtain semi-quantitative information on the amount of organic molecules associated with the MoS_2 surface.
By using this technique, we first investigate the purity of the starting materials and develop washing procedures to remove as much physisorbed solvent and surfactant after exfoliation and size selection as possible as a starting point for further derivatisation. We find that small molecule surfactants such as sodium cholate can be removed to below the detection limit after three centrifugation-based washing steps with water and isopropanol, while the solvent NMP cannot be removed this way. Polymeric adsorbates such as PVP commonly used as stabiliser in electrochemical exfoliation is also more challenging to remove.
The purified nanosheets are then subjected to functionalisation with diazonium salt to investigate the reactivity of nanosheets produced by different exfoliation strategies in the liquid phase. Different IR-active vibrations can be discerned which evidence a difference in the chemical binding motif.