

Assessing Degradation of Liquid-Exfoliated Nanosheets

Claudia Backes

Physical Chemistry of Nanomaterials, Kassel University, Heinrich-Plett Str. 40, 34132 Kassel, Germany

backes@uni-kassel.de

An established, widely applied technique to produce 2D materials is liquid phase exfoliation (LPE) which relies on breaking down layered crystals through mechanical forces, e.g. sonication, and subsequent stabilization in liquid media to form colloidal nanoplatelets. To date, this process has been applied to ~60 layered van der Waals crystals. However, for some materials, the 2D nanosheets are considerably more reactive than the parent crystals so that oxidative degradation can occur. While this can also be the case for micromechanically-exfoliated nanosheets, it will be more crucial for LPE materials, as the harsh exfoliation conditions not only result in delamination, but also in-plane tearing [1] creating more reactive edge sites. It is thus crucial to investigate potential degradation under external stimuli which will define the framework for further processing.

In this talk, I will review our work on assessing the degradation of LPE nanosheets. This is achieved by measuring extinction, absorbance or emission as function of time under external stimuli (e.g. temperature, addition of water) using ensembles of size-selected nanosheets in liquid media. Typically, we find first order decay kinetics which allow us to extract half lives and portion of reacted material after infinite time. This is extremely powerful, as it allows for a comparison across materials (NiPS₃, [2] FePS₃, [3] MnPS₃, [3] RuCl₃, [4] CrTe₃, [5] TiS₂, InSe) with black phosphorus [6] being the original benchmark. Through the variation of the nanosheet size or changes in the spectroscopic profile, it is possible to infer whether degradation preferably occurs on edge or basal plane. Addition of water to nanosheets exfoliated under inert gas conditions can also be useful to investigate the degradation mechanism. [5,6]

Through the measurement of the spectroscopic signature as function of time and temperature, it is possible to extract macroscopic, average activation energies of the degradation as shown for transition metal phosphorus trisulfides [3], RuCl₃ [4] and monolayered WS₂ [7]. Here, one can find peculiarities, such as a combination of slow decay kinetics and low activation energies in the case of RuCl₃ [4]. This is an indication of relatively complex nanoscale kinetics in solution that can be dominated by the solvent environment.

In a first comprehensive study to demonstrate this, we focused on WS₂ monolayers measured through luminescence in aqueous surfactant solution [7] and were able to show a significant effect of the surfactant on the degradation. For example, in sodium cholate we observe a protection of the basal plane and an edge-centered photo-induced degradation, whereas an additional thermal basal plane degradation is observed with sodium dodecyl sulfate.

References

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