The role of defects in liquid-exfoliated nanosheets: from degradation to functionalisation

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Liquid phase exfoliation has become an important top down production technique giving access to large quantities of nanosheets in colloidal dispersion. Importantly, this is a highly versatile technique that can be applied to numerous layered materials which can be exfoliated in a similar way using aqueous surfactant or suitable solvents as stabilisers. Nanosheets in dispersion are extremely polydisperse with broad lateral size and thickness distributions. To narrow size and thickness distributions, liquid cascade centrifugation has proven to be a powerful tool for efficient size selection yielding nanosheet dispersions with well-defined dimensions facilitating the characterisation. This has been the foundation to reach a better understanding of the exfoliation process which can be understood in terms of an equipartition of energy between exfoliation and tearing.[1] However, the role of defects present in the starting material or introduced during exfoliation has not been previously addressed. This is addressed here using graphite as model substance.

Furthermore, the size-selected nanosheet dispersions can be used to track degradation of the nanosheets by exposure to light or elevated temperature in different liquid environments.[2] The current status on degradation of various materials (different TMDCs, BP, MPS_3, $RuCl_3$, CrTe3, InSe) is summarised as function of nanosheet dimension and external stimulus.

In particular, degradation kinetics of WS_2 nanosheet ensembles in the liquid phase are investigated through photoluminescence measurements which selectively probe the monolayers.[3] Since it was observed that the reactivity towards oxidation of LPE WS_2 is strongly dependent on the surfactant,[4] data from sodium cholate (SC) and sodium dodecyl sulfate (SDS) is compared. Well-defined degradation kinetics are observed which enabled the determination of activation energies of the degradation and to decouple photo-induced and thermal degradation. The thermal degradation is slower than the photo-induced degradation, requires higher activation energies and is suggested to occur predominantly on the basal plane. Using SC as surfactant, it is sufficiently suppressed. The photo-induced degradation can be widely prevented through chemical passivation achieved through the addition of cysteine which, on the one hand, coordinates to defects on the nanosheets and, on the other hand, stabilises oxides on the surface which shield the nanosheets from further degradation.

References

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