Covalent functionalization of photoluminescent liquid-exfoliated WS_2 nanosheets

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Transition metal dichalcogenides (TMDs), such as WS_2, turn from indirect into direct semiconductors when exfoliated to monolayer thickness. For applications in (opto) electronics, enhancement of the intrinsically low photoluminescence quantum yield of TMD nanosheets would be required. One potential approach to tackle this task, is the introduction of new types of defects to the nanosheet surface, which might allow for localized emission. In this project the covalent aryl functionalization of liquid-phase exfoliated WS_2 nanosheets (f-WS_2) and effects upon optical properties – both in dispersion and thin films – were investigated. Since first results pointed towards an improved nanosheet-nanosheet separation in thin films from functionalized monolayer-enriched dispersions, the material was embedded in cavities and reflectivity experiments were performed, to learn whether strong-coupling can be achieved from our largely liquid-based processing protocols.
Liquid-phase exfoliated WS_2 nanosheets in water/surfactant dispersions were size selected, according to literature known centrifugation protocols.[1] Dispersions with high monolayer content were treated with aryl diazonium salts in different concentrations to achieve functionalization. By performing solvent transfer to IPA, colloidal stable dispersions of WS_2 nanosheets were obtained, which were used for further film fabrication. Extinction, Raman and photoluminescence (PL) spectroscopy suggest reduced nanosheet aggregation due to functionalization. In thin films spectral features typical of individual TMD monolayers, such as A exciton PL, are largely maintained. A potential correlation between the observed Raman modes and surface coverage with aryl moieties is discussed. Characterization of films, assembled at liquid-liquid interfaces and deposited via a Langmuir based method, suggests that functionalization leads to improved high film homogeneities and increased hydrophobicity of surfaces. Such films of f-WS_2 embedded in cavities allow for the detection of exciton-polaritons, which might represent a further step towards polaritonic devices from liquid-phase processed TMDs.

References

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