

Wet chemical functionalisation of transition metal dichalcogenides

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Over the last few years the study of 2-dimensional (2D) nanomaterials has become one of the most important areas of both materials science and nanotechnology. While this work originally focused on graphene, the palette of 2D materials currently under study includes transition metal dichalcogenides (TMDs) such as MoS₂ and WSe₂, layered transition metal oxides and a host of other interesting structures. Particularly useful is the diversity of 2D materials: depending on the combination of elements and their arrangement, they can be metals, semi-conductors, insulators or superconductors. They display a range of interesting properties from thickness-dependent bandgaps to catalytic activity to the ability to act as drug delivery vehicles. These properties make them useful for both fundamental studies and applications in areas as diverse as optoelectronics, electrochemistry and medicine.

However, to tap their full potential and to combine their diverse and unique properties with those of other substance classes, methods to functionalise layered materials are sought for. Here we present three methods to chemically functionalise the MoS₂ basal planes by i) noncovalent functionalisation, ii) coordination chemistry and iii) reductive covalent functionalisation.

Noncovalent functionalisation is probably the easiest way to modify surface properties of nanomaterials in liquids. As we showed using liquid exfoliated WS₂ in poly vinyl alcohol as model system,[1] noncovalent functionalisation also offers exciting possibilities to change the doping level in the TMD. In addition, the bulky stabiliser shields the exfoliated nanosheets from restacking in thin films so that monolayer properties are widely maintained. These composites offer exciting perspectives both for fundamental studies and applications.

The coordination chemistry approach [2] relies on anchoring transition metal cations such as Cu²⁺ or Ni²⁺ to the sulphur atoms of the dichalcogenide surface after liquid-phase exfoliation of the nanomaterial by established techniques. Ligands in the periphery of the transition metal cations can be replaced potentially providing a diversity of functional entities. Critically, X-ray photoelectron spectroscopy reveals that up to 50% of the S atoms can be functionalised (maximum loading).

In addition, we show the covalent reductive functionalization of MoS₂. [3] The MoS₂ basal planes can be functionalised in analogy to graphene. The reaction sequence is based on intercalation of the material by *n*-butyl lithium to yield negatively charged MoS₂ nanosheets that are exfoliated down to monolayers in water. The negative charges can subsequently be quenched by the addition of a diazonium salt to obtain covalently functionalised MoS₂. In contrast to graphene, the reaction can be carried out in water under ambient conditions after the initial intercalation step.

We expect these approaches to be applicable to other transition metal dichalcogenides giving access to a broad palette of new functional materials with modified surface properties, improved processability and yet unknown properties. Most importantly, we believe that these materials can be used as building blocks in composites and hybrid structures by further derivatisation.

References

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