Materials Science & Engineering Doctoral Defense

Materials Chemistry of Two-Dimensional Nanosheets: Surface Functionalization and Liquid Phase Exfoliation

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Abstract

Two-dimensional (2D) materials have nanometer-scale thickness in one dimension but macroscopic sizes in the other two dimensions and have unique physical and chemical properties that arise from this dimensionality. For example, atomically thin forms of semiconducting materials like transition metal dichalconides (TMDs) have attracted significant attention for electric and optical device applications due to their tunable bandgaps. Most 2D materials are derived from layered materials with weak van der Waals (vdW) bonds between layers, but more recently, non-vdW materials with stronger bonds and non-layered structures have also been formed into nanosheets. Because of their aspect ratios, surface chemistry plays a substantial role in both vdW- and non-vdW-derived 2D materials, and involves intercalation and exfoliation, surface modification and functionalization, which contribute to their use in diverse applications. In this thesis, the materials chemistry of nanosheets from both vdW and non-vdW materials has been studied.

First, we demonstrate the covalent functionalization of a new rising 2D material in the TMDs family, palladium diselenide (PdSe2), which has a layer-dependent bandgap and is much more stable in air than many other 2D materials. Aryl diazonium salts were used to functionalize monolayer PdSe2 nanosheets, and the reaction kinetics were studied as a function of reaction time and concentrations. Raman spectroscopy suggests the structure of PdSe2 is undisturbed after functionalization, which will expand its future applications in areas like electronics, sensors, and energy storage.

Next, liquid-phase exfoliation (LPE), an economical, scalable, and efficient method, was used to produce nanosheets of two types of non-vdW materials: metal diborides (MB2) which are a family of ceramic materials with a layered structure, and boron carbide (B4C), a non-layered material with covalent bonding. Quasi-2D nanosheets were formed from eight different metal diborides, with sizes and thicknesses that were found to correlate with the hardness of the bulk compounds. CrB2 nanosheets incorporated into polyvinyl alcohol (PVA) thin films showed enhanced mechanical properties that exceed the specific performance of additives from other 2D materials. Boron carbide, the third hardest known material, has also been successfully exfoliated into ultrathin by LPE. Combined theory and experiment show the rich surface structures of B4C nanosheets.

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