Molecular self-assembly on 2D materials

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Abstract:

Two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides (TMDs), have been the subject of intense research due to their potential applications as various electronic devices, such as field-effect transistors and photodetectors. A fundamental issue of graphene is the lack of a band gap, which can potentially be opened by chemical functionalization, stress, or electric field, yet remains small and makes graphene unsuitable as a semiconductor[1]. MoS_2 and other TMDs show potential for semiconductor applications but possess significant drawbacks, such as chalcogen vacancies, instability in ambient conditions, and difficulty in doping the material, which can significantly affect TMD band structures and therefore electronic and optical properties[2,3]. One of the methods to mitigate these drawbacks is modification of the TMDs with organic molecules, which can assemble into nanoscale structures on the TMD surface[4] and/or form a protective layer. Therefore, it is important to study the self-assembly of such molecular nanostructures in order to achieve a degree of control over 2D material modification.

Molecular self-assembly dynamics are governed by the interplay of intermolecular, molecule-2D material, and molecule-substrate interactions[5]. Intermolecular interactions can be tuned by molecule design (*e.g*. substitution of hydrogen atoms with fluorine) which affects a number of properties (*e.g*. solid-liquid phase transition of $C_{60}F_{48}$ based on coverage)[5]. The molecule-2D material interactions are dependent on the specific choice of molecules and 2D material and can range from van der Waals interactions to covalent bonding. The effect of the substrate on molecular self-assembly is always mediated by the 2D material, which partially screens the substrate, but can also enable site-specific adsorption of molecules due to the *moiré* pattern caused by the lattice mismatch between the substrate and the 2D material (*e.g.* 1-3-5-Benzenetribenzoic acid (BTB) on Cu(111) and Graphene/Cu(111))[6]. The dimensionality of self-assembled molecular structures can range from 0D to 3D and includes nanowires, porous network structures, 2D layers, and layered bulk structures[5].

The size of molecular self-assemblies is usually 10 – 100 nm and therefore the primary characterization technique is scanning-tunneling microscopy (STM)[3,4,5]. Diffraction methods, such as low-energy electron diffraction (LEED) and X-ray diffraction (XRD) are also useful in studying 2D and layered 3D structures and can give precise crystal lattice constants[5,6]. X-ray photoelectron spectroscopy (XPS) can be used to obtain information about molecule-2D material covalent bonding, while electrostatic force microscopy (EFM) can give information about self-assembly charge distribution[3,7].

Keywords: 2D materials, organic molecules, molecular self-assembly, heterostructures, scanning-tunneling microscopy

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