

The Interface between Polyaromatic Hydrocarbons (PAH's) and Graphene: Insight from Molecular Simulations.

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Among other graphene production methods, liquid phase exfoliation of graphene, in particular, is pointed out interesting [1,2], due to its ease, scalability and versatility for a wide range of applications, such as inkjet printing [3,4], aerogels [5,6], conductive thin films [7,8], and solar cells [9,10]. This method involves the chemical wet dispersion of graphite followed by ultrasonication in water [11,12] or organic solvents [12,13]. Solvents which minimize the interfacial tension with graphene flakes are the most suitable ones for high yield and stability of the graphene suspension [11]. For water, the “natural solvent”, with too high surface tension ($\gamma \sim 72$ mN/m [14]), surfactants [1,2,11] can be used to stabilize the suspension. Some study [2], for example, showed the aqueous exfoliation of graphene, using amphiphilic molecules, with concentrations up to 1.5 mg/mL. The usual amphiphils used consist of Polyaromatic hydrocarbon (PAH) cores with functionalized hydrophilic side chains such as alkyl carboxylates [1] or oligoethers [2]. It is believed that the hydrophobic aromatic cores interact with both sides of the graphene surface via non-covalent interaction, while the hydrophilic side chains interact with the solvent medium [1], hence, leading to the stable dispersion of the graphene sheets in the aqueous solution. Understanding the PAH-graphene interface and the exact mechanism of the exfoliation process is very helpful for designing surfactants with enhanced effects.

In this work, the interface between graphene and pyrene compounds with systematic pattern of functionalization was studied, theoretically, using force field methods. We have compared the relative conformation, in ethanol and vacuo, of pyrene compounds with long-chain polar side-groups on graphene surface. We show that in vacuo, the functional side groups interact with the surface to form a mixture of conformations, while in ethanol they are fully desorbed from the surface and hang in the solvent medium. We have also studied the adsorption mechanism of pyrene-based pH-indicator dyes (pyrene sulfonates), on the surface of graphene, in aqueous medium. When the pyrene core is highly functionalized with sulfonate, local minima were observed on the adsorption free energy profiles, which correspond to a metastable conformation in which the molecules are in an edge-on interaction with the surface. In addition, the more the number of functional groups, the more the pyrene core is engulfed and becomes less accessible. This reduces the attractive dispersive interaction of the core with the surface and the hydrophobicity of the molecule, resulting in lower adsorption free energy. But we show that this situation is also dependent on the pattern of functionalization; in the case when two corners of the core bear sulfonates, higher dipole moment and adsorption free energy were found than for the case only one corner is functionalized. Our results demonstrate the role of polar groups vs. aromatic cores in suspension stabilization and how the extent and pattern of functionalization affects the affinity of polyaromatic hydrocarbons (PAH's) towards graphene.

References

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Figures

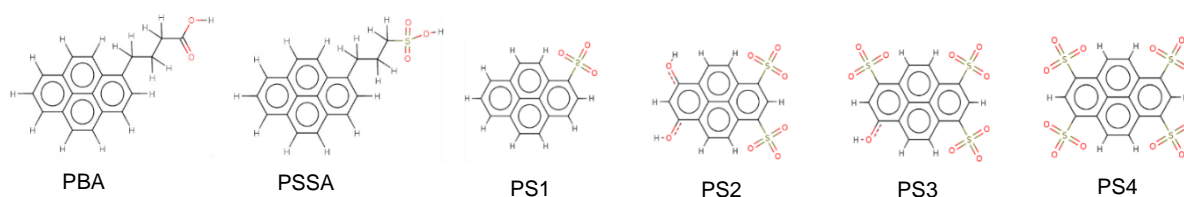


Figure 1: Structures of studied molecules: Pyrene-1-butrylic acid (PBA), Pyrene-1-propylsulfonic acid (PSSA), 1-pyrenesulfonate (PS1), 6,8-dihydroxy-1,3-pyrenedisulfonate (PS2), 8-hydroxypyrene-1,3,6-trisulfonate (PS3) and pyrene-1,3,6,8-tetrasulfonate (PS4).

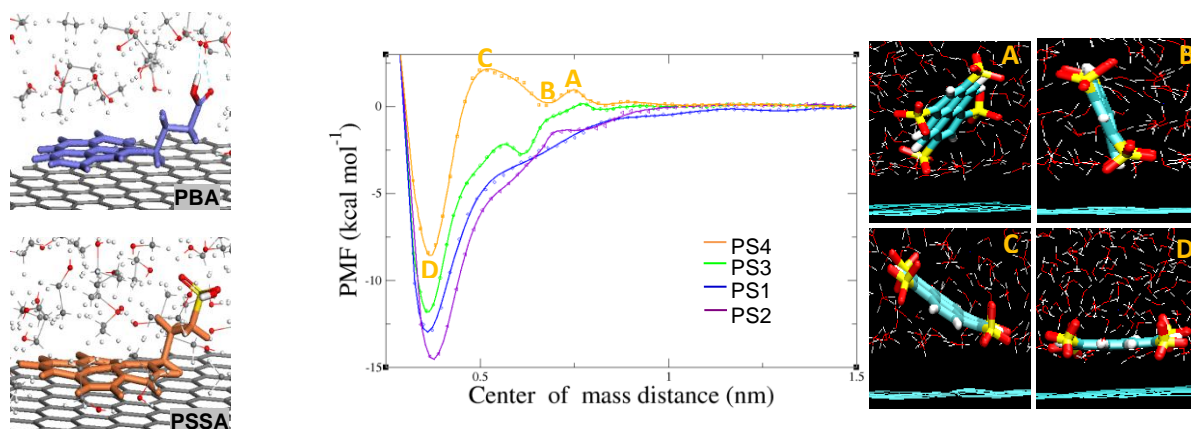


Figure 2: Snapshots of simulated structures of PSA and PSSA on graphene surface in ethanol.

Figure 3: Simulated potential of mean force (PMF) curves of the adsorption process of PS_x ions on graphene and snapshots of typical conformations of PS4 as it approaches to the surface of graphene, corresponding to points on the PMF curve-as indicated by letters.