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Molecular dynamics simulation of adsorption of pyrene–polyethylene glycol onto graphene

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ABSTRACT

The nonvalent interaction between amphiphilic polymers and graphenes is important to provide the surface functionalization of graphene. Herein, molecular dynamics simulations were carried out to investigate the interaction of pyrene–polyethylene glycol (Py–PEG) with graphene. The dynamic adsorption process and self-assembly morphology of Py–PEG onto nanoscale graphene surface have been demonstrated. The effects of the graphene size and the length of polymer chain were explored. It was shown that Py–PEG could spontaneously adsorb onto graphene surface. The Py–PEG polymer generally exhibits a coil structure with the hydrophobic pyrene surrounded by the PEG chain. However, once the Py–PEG molecule approaches the graphene surface, the PEG chain can unfold its structure on the graphene surface and the pyrene group can display a flat binding mode with the surface. Comparatively, the water solvent has an obvious impeding effect on the surface adsorption due to the hydrogen bonding interaction between PEG chain and water molecules. The thermodynamic free energy shows that the interaction between pyrene and carbon surface provides the main interaction contribution to the adsorption performance.

1. Introduction

Graphene has attracted enormous interest due to its unique properties [1–6]. However, graphene is hydrophobic with low solubility in aqueous solution [7]. The surface functionalization of graphene [8,9] can enhance its dispersion in solvents and broaden its application scopes. For instance, polymer–graphene composites through the noncovalent functionalization can improve its processability [8,10,11]. In addition, experiments have shown that graphene can be decorated with various conjugated compounds, such as polyethylene glycol (PEG) [12], aromatic compounds [13,14], and polyacetylenes [15].

The pyrene–polyethylene glycol (Py–PEG) polymer has been reported as a water-soluble associative thickener [16] and an amphiphilic fluorescent surfactant [17]. In the Py–PEG molecular structure, the aromatic pyrene not only provides strong π-interaction with carbon surfaces [18–20], but also acts as a fluorescence probe [16,17,21–23]. In addition, the hydrophilic PEG chain has been widely used to create hydrophilic surfaces [18,24]. Recently, the presence of PEG group in the pyrene–PEG is useful in improving the solubility of pyrene-labeled polymer [16,25]. PEG can also cause the exfoliation of graphite oxide to yield graphene sheets [26].

Research efforts have been devoted to study the surface noncovalent functionalization of graphene using the amphiphilic pyrene derivant. The strong interaction between SWNT and pyrene–PEG along with the butyramide linker is able to prevent the non-specific adsorption of the well-known adhesive protein streptavidin in aqueous solution, in which SWNTs were well dispersed with high fluorescence intensity [18]. In particular, by using an aromatic amphiphile consisting of four pyrene units and a PEG Dendron, Lee et al. [27] readily exfoliates graphite flakes into graphene sheets in aqueous solution [28,29]. Recently, the functionalization of SWNTs with pyrenyl-PEG proposed by Jang et al. [30] paves the way for the future biomedical imaging and cancer therapy in both photothermal therapy and fluorescent imaging.

The interaction between the amphiphilic molecule (Py–PEG) and graphene plays a critical role in the surface functionalization of the graphene surface [8,10,11]. Although the interaction between aromatic systems and graphite surface has been investigated [14,31], the adsorption behavior of the Py–PEG molecules on graphene nanosheets, in particular, the interaction mechanism between Py–PEG and graphene, has not been studied so far. Understanding the adsorption interaction and self-assembly process will guide an improvement in the graphene dispersion and exfoliation. Furthermore, it will facilitate the design of novel graphene-based nanomaterials via supramolecular noncovalent interaction.

In this work, molecular dynamics (MD) simulation has been performed to study the interaction between graphene and

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Py–PEG. The adsorption packing behavior of Py–PEG onto the graphene surface has been demonstrated both in aqueous solvent and vacuum condition. Various lengths of the hydrophilic PEG chain will be considered [32]. This simulation will provide an insight into the self-assembly structure of a Py–PEG/graphene hybrid and the molecular origin of the adsorption interaction.

2. Methodology

For graphene, each carbon atom was modeled as an uncharged Lennard–Jones (L–J) particle following the previous works [33,34]. Monolayer graphene was selected as an infinite rigid sheet in the *x*–*y* plane and kept fixed at the bottom of the simulation cell. For the Py–PEG molecules (Fig. 1), the fully atomistic OPLS-AA force field [35–37] was used, which has been successfully used to simulate the rupture mechanism of pyrene–PEG from graphite [20]. In this work, the simple SPC/E model [38] was used, which is justified by the fact that our main goal is to study the adsorption self-assembly of Py–PEG onto graphene, and the SPC/E model is able to provide rational description of solvent medium. For example, SPC/E model has been extensively used in the simulation of the solvation behavior around pyrene derivative [39] and graphene [40] in aqueous environment. The van der Waals (vdW) interaction between different atoms was calculated by employing the geometric averaging rule [36]: $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$, $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$.

The self-assembly simulations of Py–PEG on graphene in aqueous solution were performed in the canonical ensemble (NVT) using the Lammps MD package [41]. Periodic boundary conditions in three directions were used. The Nose–Hoover thermostat [42] was chosen to maintain the constant temperature condition at 298.15 K. The electrostatic interactions were calculated using the Particle Mesh Ewald (PME) method with a real-space cutoff of 10.0 Å and a tolerance of 10^{-5}. The cutoff distance for the L–J interactions was 11.0 Å. A time step for integrating Newton's equation in the MD simulation is 1 fs.

For the MD simulation in aqueous conditions, sufficient water molecules were inserted into the simulation cell in order to reach the desired bulk phase density ($\sim$1.0 g/cm^3). For the adsorption simulation process, the graphene surface and Py–PEG were well separated and the final equilibrium configuration of Py–PEG in the bulk phase was used as the initial structure for the adsorption process. All the simulation systems are listed in Table S1 in the Supporting information. In this work, four specified groups within the Py–PEG molecule structure have been designed, as shown in Fig. 1, where the aromatic pyrene segments were denoted as the other groups (I) and the groups (II, III, and IV) are used to represent three designed PEG segments.

3. Results and discussion

3.1. Adsorption process of Py–PEG in aqueous phase

In this work, we simulated the adsorption self-assembly of single chain polymer from aqueous phase to graphene sheet, for three types of Py–PEG molecules with different PEG segment lengths (Py–PEG$_9$, Py–PEG$_{45}$, Py–PEG$_{113}$). Fig. 2 shows the dynamic snapshots of Py–PEG$_{45}$ adsorbed on the graphene surface at several specific time steps. It reflects the time evolution of the Py–PEG$_{45}$ motion toward the graphene.

Initially, the Py–PEG$_{45}$ was well solvated in the aqueous phase. With the adsorption simulation starting, the Py–PEG "finds" the graphene and the Py–PEG$_{45}$ chain begins to approach the graphene surface. After 4 ns, most of Py–PEG$_{45}$ structure has been adsorbed onto the surface except for the terminal part (IV) of the PEG chain. From the simulation, pyrene seems like an "anchor", which is "thrown" by Py–PEG$_{45}$ to lock itself onto the graphene surface. This dynamic process suggests that the interaction between Py–PEG$_{45}$ and graphene is strong enough to produce the spontaneous adsorption. The simulation result is similar with the experimental observation [18] that the pyrene–PEG is easily adsorbed onto the carbon nanotube surface.

The separation (d), defined as the distance between the mass center of each part of Py–PEG$_{45}$ and the graphene surface, is plotted as a function of simulation time in Fig. 2b. It shows that the separation distances for the groups (I, II, and III) decrease rapidly at the first 4 ns, suggesting that these groups display a fast adsorption toward the surface. However, the separation for the group (IV) presents a fluctuating behavior, representing a relatively slow adsorption process.

It is noted that the pyrene unit forms a flat binding mode with the graphene, which is possibly a good indication that aromatic hydrocarbon compounds [19,22] have a strong interaction with carbon surface due to the π–π stacking interaction [18–20,43–45]. Further energy calculation also shows that the interaction strength of the pyrene group with the graphene surface is the largest among the four groups (I–IV) in the Py–PEG molecule. This may suggest that the π–π interaction [27,28] between the pyrene group and graphene is the critical force determining the adsorption of the Py–PEG molecule.

As shown in Fig. 2(a), at the final adsorption equilibrium, the PEG chain prefers to remain as a somewhat flat conformation with a stable separation of $\sim$3.5 Å (Fig. 2b). This is in line with the experimentally measured distance [20] between pyrene and the surface. This adsorption mode is due to the interaction between PEG chain and the surface. Our result provides a direct molecular-level

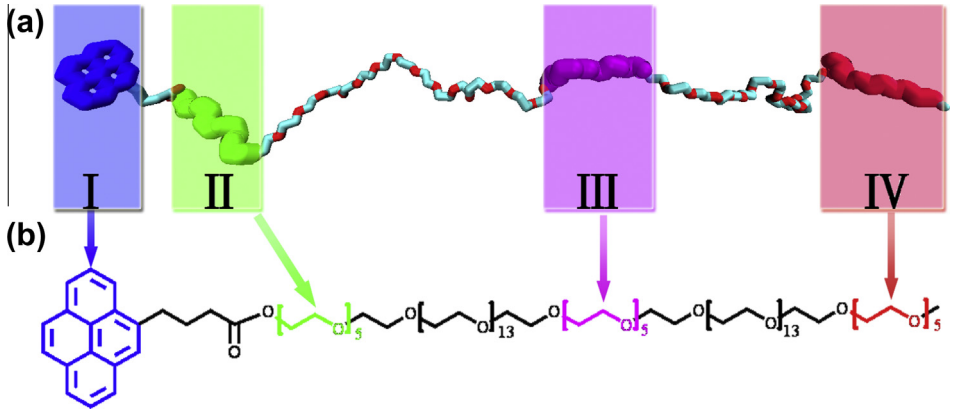

Fig. 1. (a) Molecular CPK structure of pyrene–polyethylene glycol (Py–PEG$_{45}$). It is shown by CPK with blue: the pyrene group (I); green, purple, and red represent the group (II), the group (III), and the group (IV), respectively, in the PEG chain. The hydrogen atoms of the polymer are not shown. (b) Chemical structure of Py–PEG$_{45}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)