Simulating Aqueous Adsorption of Polycyclic Aromatic Hydrocarbons on Graphene and Graphene Oxide Quantum Dots

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Abstract. Interactions of polycyclic aromatic hydrocarbons (PAHs) with graphene quantum dot (GQD) and graphene oxide quantum dot (GOQD) were probed by local density approximation of density functional theory with empirical dispersion correction. Simulation reveals that van der Waals force is the main mechanism for the GQD-PAH and GOQD-PAH interactions and the van der Waals interaction is mainly dispersion interaction. The computed adsorption energies of the GQD-PAH systems in the aqueous phase exhibited a positive linear correlation with the hydrophobicity of PAH molecules, while the GOQD-PAH systems showed a relatively weak correlation. This implies that hydrophobic interactions play an important role in the interactions between PAHs and GQD. Furthermore, the hydrophobic effect contributes more to the adsorption mechanism through increasing the number of the PAH rings.

Introduction

Graphene is a typical carbonaceous nanomaterial consisting of one monolayer of carbon atoms arranged in a two-dimensional honeycomb lattice [1]. Graphene exhibits many outstanding physical and chemical properties because of sp2-hybridized carbon atoms [2]. The unique properties of graphene (such as huge surface area, high stability, and strong adsorption ability) have paved the way to its potential capacity for environmental applications [3]. Graphene oxide, which is oxidized graphite with enhanced aqueous solubility, has also been applied in various fields, such as graphene manufacture, coating, flexible rechargeable battery electrode, and water purification [4].

It was previously revealed that Graphene and graphene oxide show excellent performance in adsorption with many organic pollutants [5], in particular for polycyclic aromatic hydrocarbons (PAHs) [6]. However, molecular mechanism for the adsorption of PAHs by graphene materials was still being debated. For instance, graphene displayed high affinity to PAHs by $\pi-\pi$ interactions to the flat surface, whereas graphene oxide adsorption was significantly reduced after oxygen-containing groups were attached to graphene surfaces [6]. In addition, the dispersive interaction is the most important contribution to the binding of PAH molecules onto graphene [7]. Therefore, more studies are needed to probe the potential adsorption behaviors of graphene materials at a molecular level.

The aim of the present study was to elucidate adsorption mechanism of PAHs by graphene materials. Local density approximation (LDA) with dispersion correction was carried out to estimate the equilibrium geometry, adsorption energy (E_a), and charge transfer.

Computational Methods

The studied system. Eight PAHs, i.e., naphthalene (NAP), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), pyrene (PYR), fluoranthene (FLT), benzo[a]anthracene (BaA), and benzo[b]fluoranthene (BbF), were selected for this study as adsorbates. The constructed adsorbents included coronene, a monolayer graphene quantum dot (GQD), and a monolayer graphene oxide

quantum dot (GOQD). The GQD is composed of 70 carbon atoms and 22 saturated hydrogen atoms. The GOQD consists of 50 carbon atoms, 11 oxygen atoms, and 24 saturated hydrogen atoms.

Theoretical computation. Forcite Plus code was used to obtain the initial optimized structures of the studied systems at a molecular mechanics (MM) level. The atomic configuration with the lowest total energy for each system was built as a set of inputs for geometry optimization and properties calculation at a quantum mechanics (QM) level. In this study, the local density approximation (LDA) and the LDA with the DFT-correction (DFT-D method of OBS) methods were employed to calculate the isolated molecules and compounds. The conductor like screening model (COSMO) was employed to simulate the solvent (water) environment [8]. The dielectric constant for water was chosen to be 78.54. The obtained structures were optimized with the COSMO model using the LDA+DFT-D functional. The charge transfer between the adsorbate and adsorbent molecules was estimated by the Mulliken population analysis.

Results and Discussion

The computed E_a values derived from van der Waals energies (E_{v-a}) between the PAHs and GQD/GOQD by the MM method are shown in Fig. 1, which are approximate to the E_a values derived from the potential energies (E_{p-a}). This indicates that van der Waals interaction mainly contributes to the interaction mechanisms for the GQD-PAHs and GOQD-PAHs interactions. Furthermore, the main bodies of both GQD and GOQD are composed of sp2 hybridized carbon atoms, implying that van der Waals interaction may contribute equally to the GQD-PAH and GOQD-PAH systems.
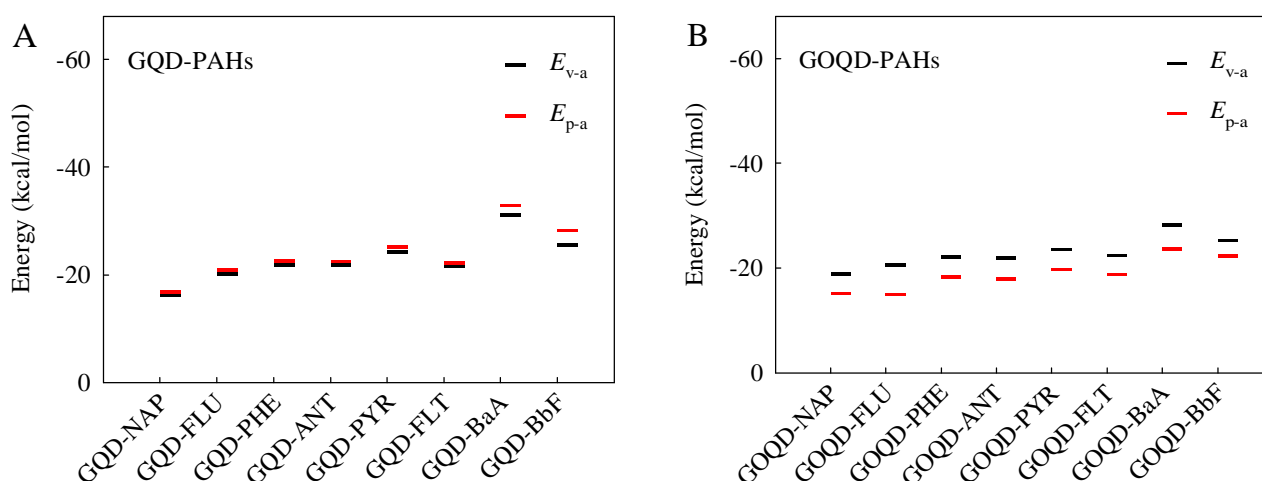

Fig. 1. Calculated potential energy adsorption energies (E_{p-a}) and van der Waals adsorption energies (E_{v-a}) for the PAHs molecules adsorbed upon the GQD (A) and GOQD (B) surfaces using the MM method

To precisely elucidate the interaction mechanisms, we have used the quantum-chemical parameters including the E_a values derived from the total energies (E_{t-a}), molecule-adsorbent distances, and charge transfer (Table 1). The E_{t-a} obtained at the LDA+DFT-D level are significantly higher than the adsorption energies from the LDA level. This suggests that the dispersion interactions were found to play the main role in the adsorption of PAHs on the graphene material surfaces. For the GQD-PAH systems, the absolute E_{t-a} values obtained at the LDA+DFT-D level increase with the increase of the PAH ring numbers. However, for the GOQD-PAH systems, the PAH ring numbers have no impacts on the GOQD-PAH interactions. Generally, the absolute E_{t-a} values of the PAHs on the GQD are higher than those of the PAHs on the GOQD, implying that the GQD exhibited higher adsorption capacity for the PAHs than the GOQD. An experimental study by Wang et al. [6] also implies that GQD displayed high affinity to PAHs, whereas GOQD adsorption was significantly reduced after oxygen-containing groups were attached to GQD surfaces.

Table 1. Calculated parameters of the PAH adsorption systems including the adsorption distances (d), the adsorption energy derived from total energies (E_{t-a}), the charge transfer (q) as well as the logarithm of the n-octanol/water partition coefficient ($\log K_{OW}$) values of the PAH congeners

PAHs	$\log K_{OW}$	d (Å)[c]		E_{t-a} (kcal/mol)				Δq (e)[d]	
		GQD	GOQD	GQD		GOQD		GQD	GOQD
				LDA+DFT-D	LDA	LDA+DFT-D	LDA		
NAP	3.36[a]	2.54	3.03	-52.55	-11.75	-58.41	-15.18	-0.006	0.003
FLU	4.18[b]	2.68	3.10	-66.06	-15.28	-64.83	-14.38	-0.002	0.031
PHE	4.57[b]	2.60	4.00	-70.15	-15.87	-61.22	-10.59	-0.026	0.008
ANT	4.54[a]	2.65	3.24	-67.24	-14.58	-62.97	-14.87	-0.026	0.101
PYR	5.18[b]	2.57	3.47	-77.31	-17.87	-67.88	-16.08	-0.032	0.018
FLT	5.22[b]	2.64	3.27	-75.26	-16.65	-55.55	-8.91	-0.046	0.007
BaA	5.91[b]	2.76	3.20	-99.76	-22.45	-73.64	-12.10	-0.063	0.065
BbF	5.80[b]	2.74	3.87	-94.86	-20.50	-65.84	-14.75	-0.057	0.027

[a] $\log K_{OW}$ values are from ref 9.
[b] $\log K_{OW}$ values are from ref 10.
[c] d is a distance (Å) from the center mass of each PAH molecule to the surface of GQD or GOQD and was determined from the results of the LDA+DFT-D calculations.
[d] Δq (e) is the charge transfer between the PAH molecules and the adsorbents (the negative values indicate that the GQD is a charge donor; the positive values indicate that the GOQD is a charge acceptor) and was estimated by the LDA+DFT-D method.

As shown in Table 1, the molecule-adsorbent distances are mostly shorter in the case of GQD-PAHs when compared with those of GOQD-PAHs obtained at the level of theory LDA+DFT-D. This confirms that the PAH compounds bind more strongly with the GQD surface than the GOQD surface. Additionally, Mulliken analysis results showed that only a little charge transfer (< 0.08 e) occurs between each PAH and the GQD/GOQD (Table 1). This also means that there exist weak donor-acceptor interactions between the PAHs and the GQD/GOQD.
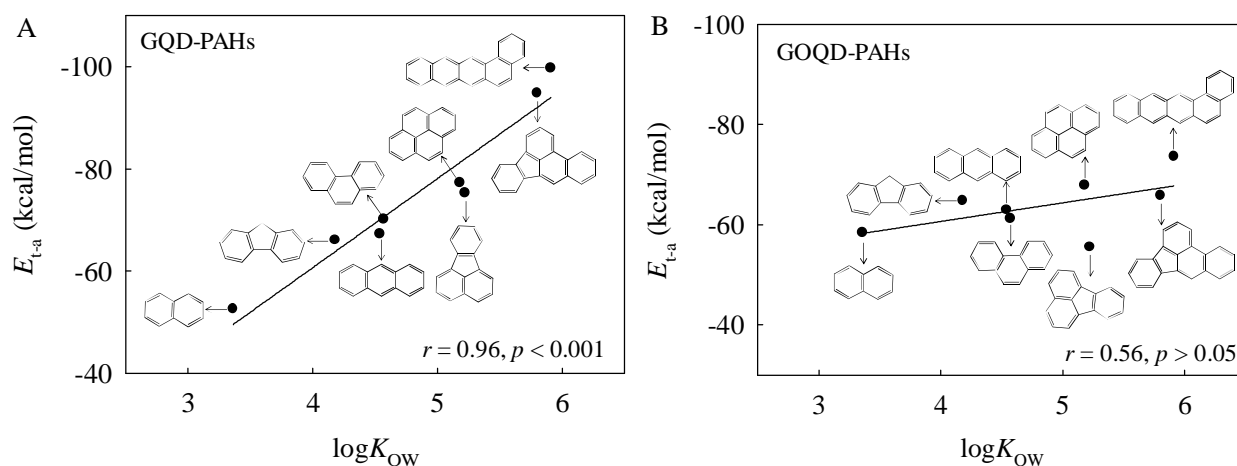

Fig. 2. Correlation between the $\log K_{OW}$ values of PAHs and the adsorption energy values derived from the total energies (E_{t-a}) of the GQD-PAH complexes (A) and the GOQD-PAH complexes (B)

The polar functional groups on the edge of GOQD make it hydrophilic, while the hydrogen attached to the edge of GQD has no polarity, making the hydrophobic effect of the GQD-PAH system significant. Herein, to confirm the effect of hydrophobicity of PAHs on the adsorption strength, the relationship between the E_{t-a} of the PAHs and the logarithm of the octanol-water partition coefficient ($\log K_{OW}$) of the PAHs was obtained (Fig. 2). For the GQD-PAH systems, the E_{t-a} values correlate with $\log K_{OW}$ significantly ($r = 0.96$, $p < 0.001$) and increase with increasing $\log K_{OW}$ (Fig. 2A). Thus,

the stronger the hydrophobicity of the PAHs, the stronger their interactions with each GQD. As aforementioned, the absolute E_{t-a} values for the GQD-PAH systems increase with the increase of the PAH ring numbers, implying that the hydrophobic effect contributes more to the adsorption mechanism through increasing the number of the PAH rings. However, for the GOQD-PAH systems, the E_{t-a} values correlate with $\log K_{OW}$ insignificantly ($r = 0.56$, $p > 0.05$) (Fig. 2B). This may be due to the strong hydrophilicity and high polarity of GOQD. We can thus conclude that the interactions between GOQD and nonpolar PAH molecules are very weak compared with that of GQD.

Summary

We have found that the van der Waals force is the main mechanism for the GQD-PAH and GOQD-PAH interactions and the van der Waals interaction is mainly dispersion interaction. The computed E_a of the GQD-PAH systems in water exhibited a positive linear correlation with the hydrophobicity of the PAH molecules, while the GOQD-PAH systems showed a relatively weak correlation. The hydrophobic effect contributes more to the adsorption mechanism through increasing the number of the PAH rings.

Acknowledgments

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