



Full length article

Adsorption of ion pairs onto graphene flakes and impacts of counterions during the adsorption processes



Chang Zhu, Jiena Yun, Qian Wang, Gang Yang*

College of Resources and Environment & Chongqing Key Laboratory of Soil Multi-scale Interfacial Process, Southwest University, Chongqing 400715, China

ARTICLE INFO

Article history:

Received 17 August 2017

Received in revised form 31 October 2017

Accepted 13 November 2017

Available online 16 November 2017

Keywords:

Adsorption configuration

Counterion effects

Electron transfer

Density functional theory calculations

Edge-functionalization

ABSTRACT

Although cations and anions are two integral constituents for all electrolytes, adsorption of ion pairs onto carbonaceous materials gains obviously less attention than adsorption of only cations or anions. Here DFT calculations are employed finding that four adsorption configurations emerge for KI onto graphene flakes (GF) instead of three for the other ion pairs. Reservation of ionic bonds is critical to their stabilities, and the bilateral configurations, where GFs couple with both cations and anions, are disfavored due to rupture of ionic bonds. Relative stabilities of two vertical configurations can be regulated and even reversed through edge-functionalization. Surprisingly, the horizontal adsorption configurations, which are global energy minima as long as present, are non-existent for a majority of ion pairs, and their existence or not is determined by the adsorption differences between halide ions and alkali ions (ΔE_{ad}). Counterion effects for both cations and anions increase with the atomic electronegativities and cations correspond to stronger counterion effects; e.g., Li^+ added on the other side of GFs promotes the adsorption of F^- more pronouncedly than edge-functionalization. Mechanisms of electron transfers are also discussed, and three alteration patterns by counterions are observed for each type of adsorption configurations. Furthermore, addition of counterions causes band gaps to vary within a wider range that may be useful to design electronic devices.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Graphene, carbon nanotube and fullerene are carbonaceous materials that exhibit unique electric, thermal and mechanical properties and find applications in a wide spectrum of fields, such as sensing devices, solar cells, adsorption and catalysis [1–4]. With adsorption of metal cations or anions, the electronic properties of carbonaceous materials are significantly altered [5–7]; e.g., the semiconducting single walled carbon nanotubes have been tuned to metallic when metal cations are placed close to the tube axis. Meanwhile, a great deal of attention has been given to decipher the cation- π and anion- π interactions that are ubiquitous in chemical and biological systems, and considerably more efforts are necessitated to unveil such interactions, with respect to their nature, type and extent [8–11].

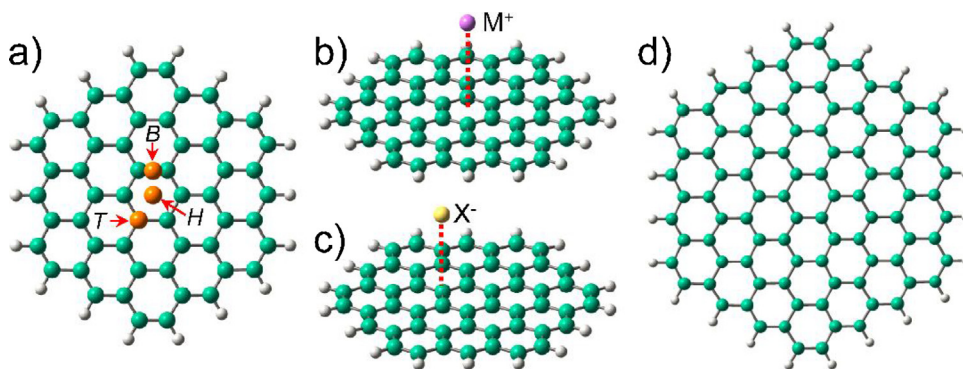
Both metal cations and anions are capable of regulating the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of carbonaceous materials, which further produce significant effects to band gaps and other

electric properties [11–16]. Regarding to metal cations of the same valence, interaction strengths with graphene reduce gradually with increase of ionic radii [12], and the resembling trends were observed for the adsorption of halide ions [13,14], although their interacting mechanisms are distinct from each other: Graphene serves as electron donors during the adsorption of metal cations while electron acceptors during the adsorption of halide ions. In addition, their preferential interaction sites with graphene surfaces were reported to be different from each other: Adsorption of metal cations onto graphene is driven by electrostatic force and cation-induced polarization [17] and hence occupies favorably the *H*-site (the center of a hexagon) [6,8,16], whereas the priority is given to the *T*-site (i.e., directly above a C atom) when halide ions are adsorbed onto graphene, see Scheme 1 [13].

As compared to metal ions and anions [10–16], relatively less attention has been given to the adsorption of ion pairs onto carbonaceous materials. It is known that cations and anions are two integral constituents for all electrolytes and should be concomitant with each other. Colherinhas et al. [18] investigated the adsorption of inorganic salts onto graphene surfaces and indicated that ion pairs are able to significantly polarize the electron energy levels of graphene. Shi and et al. [19] used classical molecular dynamics simulations and found that Cl^- ions can be enriched on graphene

* Corresponding author.

E-mail address: theobiochem@gmail.com (G. Yang).



Scheme 1. a) Three potential sites for the adsorption of ions onto graphene flakes: *H*-site (hollow site, at the center of a hexagon), *B*-site (bridge site, at the midpoint of a C-C bond) and *T*-site (top site, directly above a C atom) as well as the most favorable adsorption sites for b) alkali ions (*H*-site) and c) halide ions (*T*-site). A larger model ($C_{96}H_{24}$) for graphene flakes than the default (a: $C_{96}H_{24}$) is shown in d).

surfaces as Na^+ ions although to a less extent. Despite the great importance, a number of critical issues regarding to the adsorption of ion pairs remain enigmatic, such as the adsorption behaviors (e.g., how many adsorption configurations and their relative stabilities) and the counterion effects during the adsorption processes (metal cations and anions refer to each other as counterions).

To address the issues including those posed above, density functional theory (DFT) calculations were conducted to investigate the adsorption of ion pairs composed by the various alkali ions (M^+) and halide ions (X^-) onto graphene flakes (GFs), which were outlined as: 1) Adsorption behaviors of different ion pairs onto pristine GFs. Three adsorption configurations were found for all ion pairs and the adsorption configurations with GFs showing direct interactions with alkali ions (M^+) are the most favorable; 2) Counterion effects during the adsorption of ion pairs. Stronger counterion effects were observed for alkali ions (M^+) than halide ions (X^-), and regulation of band gaps by counterions may be useful for designing electronic devices; 3) Mechanisms of electron transfers during the adsorption of ion pairs onto GFs, which are distinct for different adsorption configurations. For each type of adsorption configurations, there emerge three different alteration patterns of electron transfers by counterions; 4) Regulating the relative stabilities of different adsorption configurations through edge-functionalization. Edge-functionalization has been regarded as a facile and efficient method to regulate the electronic properties of graphene, through the alteration of π -conjugation and electron distribution [20–25]. It was found that relative stabilities of two vertical adsorption configurations can be reversed through edge-functionalization; 5) A fourth adsorption configuration (*vide post*) emerges for KF adsorption onto pristine GFs and it possesses superior stability than the other adsorption configurations. To our surprise, such stable adsorption configurations are non-existent for other ion pairs. The seeming dilemma was then deciphered by presenting a number of such adsorption configurations through edge-functionalization as described in 4), and it clearly indicated that their existence or not is decided by the adsorption differences of anions vs. metal cations. The present results are general and beneficial to understand the adsorption processes onto carbonaceous materials.

2. Calculation details

2.1. Models

In line with literature reports [6,13,17,18,26], model of pristine graphene flakes (GFs) consists of 19 aromatic rings and has chemical formula of $C_{54}H_{18}$, see Scheme 1a. Li^+ , Na^+ , K^+ and F^- , I^- were respectively the choices of alkali ions (M^+) and halide ions (X^-), and

their combinations result in a total of six ion pairs, as $MX = LiF, LiI, NaF, NaI, KF$ and KI . The results of $C_{54}H_{18}$ were further validated by using a larger model ($C_{96}H_{24}$, see d), and related discussions were given in Sections 3.1 and 3.5.

Edge-functionalization was constructed by replacing the terminal H atoms of GFs with functional groups ($-CHO$, $-COCl$, $-CN$) to regulate the electronic properties, and three different edge-functionalization degrees ($\Theta = 16.7\%$, 33.3% and 50.0%) were taken into account [13].

2.2. Methods

First-principles density functional theory (DFT) calculations were conducted with Gaussian 09 software of packages [27]. Structural optimizations were performed using B3LYP density functional, and all elements were handled by the 6–31+G(d,p) basis set, except iodine (I), whose valence and inner electrons were respectively described by the LanL2DZ basis set and LanL2DZ effective core potential (ECP) [28]. All adsorption configurations were verified by frequency analyses to be the local energy minima. After structural optimizations, natural population analyses using the natural bond orbital program [29] were carried out to investigate the mechanisms of electron transfers between ion pairs and GFs. On basis of B3LYP optimized structures, single-point energy calculations were performed using M06-2X meta hybrid exchange-correlation functional [30] in combination with the mixed 6–311++G(d,p)+LanL08d basis sets (6–311++G(d,p) for all elements except I, and LanL08d especially for I) [31]. Unless otherwise specified, all electronic energies were reported at this level.

3. Results and discussion

3.1. Adsorption of Ion Pairs onto GFs

For all ion pairs (MX) composed by alkali ions (M^+) and halide ions (X^-), three stable configurations (Ver^M , Ver^X and Bil , see Fig. 1) have been determined during the adsorption onto GFs, as a combined effect of cation- π and anion- π interactions. In Ver^M and Ver^X , M^+ and X^- are situated on the same side with respect to GFs and ion pairs (MX) are held vertically to the GF surfaces: M^+ and X^- couple directly with GFs in Ver^M and Ver^X , respectively. Distinct from the condition of Ver^M and Ver^X , the ionic bonds of ion pairs are broken in Bil and M^+ and X^- therein are distributed bilaterally at the GF surfaces. With regard to Ver^M and Bil , the constituent alkali ions (M^+) and halide ions (X^-) remain at their preferred sites; i.e., respectively at the *H*- and *T*-sites [6,9,13,16,18,21], while halide ions (X^-) in Ver^X shift to the *H*-site.

Download English Version:

<https://daneshyari.com/en/article/7835952>

Download Persian Version:

<https://daneshyari.com/article/7835952>

[Daneshyari.com](https://daneshyari.com)