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Original Article

A computational study of adsorption of divalent metal ions on graphene oxide

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Abstract

Adsorption of divalent metal ions (Pb^{2+},Cd^{2+}, Zn^{2+},Cu^{2+}) on graphene oxide (GO) was studied using density functional theory (DFT). Adsorption geometries and energies, as well as the nature of the binding energy, were calculated for the interaction of divalent metal ions with oxygen-containing groups on the surface of GO. The configurations of the complexes were modeled by placing the divalent metal ions above the center and perpendicular to the surface. Binding of Cu^{2+} to the GO sheet was predicted to be much stronger than that for other divalent metal ions. Calculated results show good agreement with experimental observations and provide useful information for environmental pollution cleanup.

Keywords: graphene oxide, divalent metal, binding energy

1. Introduction

Graphene is a two-dimensional material consisting of a single layer of carbon atoms arranged in a honeycomb nanostructure (Novoselov *et al.*, 2004). Functionalization of the graphene sheet by strong acid/base treatment permits synthesis of graphene oxide (GO) (Yang, Zhou, Zhang, & Zhang, 2012), which has a potential application in removal of heavy metals from water solution and is more hydrophilic than graphene. The surface of GO has π electrons delocalized on oxygen atoms in epoxy, hydroxyl, carboxyl groups. These electron pairs can bind a metal ion to form a metal complex (He, Zhang, & Wang, 2011), as also found for other materials and adsorbents (Chen, Liu, Chen, & Chen, 2008). This property makes GO of interest for the clean-up of an environment polluted by metal ions.

The GO structure based on the Lerf-Klinowski model (He, Klinowski, Forster, & Lerf, 1998) contains oxygen atoms on the graphene surface (54 carbon atoms) in epoxy, hydroxyl and carboxyl groups. In a comparison of the experimental spectrum with simulated spectra based on various models, Casabianca *et al.* (2010) found that the Lerf-Klinowski model best matched the experimental spectrum.

In a study of the size effect of a graphene sheet on nucleobase binding, Rungnim *et al.* (2012) found that coronene (C24) was too small and that the edge effect may perturb the binding of nucleobases. Therefore, the size of graphene sheet suitable for adsorption of nucleobases should be larger than C24, and at least about 54 carbon atoms (Antony & Grimme, 2008). We used CP BSSE calculations with the standard LANL2DZ (Los Alamos National Laboratory 2 Double-Zeta) pseudopotential and also a modified ECP aimed at improving the divalent metal atom basis set (Yang, Weaver, & Merz, 2009). More sophisticated basis sets have been developed for use in highly accurate calculations with correlated methods (Martin & Sundermann, 2001). Based on

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this background, adsorption of divalent metal ions on the GO surface made from a C54 sheet was examined for four transition metals: lead, cadmium, zinc and copper. The results show the details of the interaction between these metal ions and oxygen-containing groups on the GO surface.

2. Materials and Methods

2.1 Model of graphene oxide with metal ions

To model the GO structure, epoxy (C-O-C) and hydroxyl (-OH) groups were built on the graphene (C54) surface. Epoxy groups were located in two positions relative to a central ring of the graphene sheet (Figure 1). Three epoxy models were used containing one epoxide or two epoxides in 1,2- (ortho-epoxide) and 1,3- (meta-epoxide) positions on the ring. These functional groups are located at the center of the graphene oxide. The GO model in this work has 2 epoxy and 1 hydroxyl groups on one side, 1 epoxy and 1 hydroxyl groups on another side, and 5 carboxylic acid, 2 hydroxyl and 1 carbonyl groups at the edge of GO.

The configurations of the complexes were modeled by placing M^{2+} perpendicular to the benzene ring (Figure 1). In this GO system, the positions of the functional groups were three points above the surface and one point below the surface (Figure 1). To study cation adsorption on GO surface, binding energy of metal cation on the GO was determined at four different positions. Positions 1-3 were at the top of GO sheet, while Position 4 was at the bottom of GO sheet. Position 1 was placed at the GO center without any functional group. Position 2 was between the epoxide and hydroxyl groups. Position 3 was located between the two epoxide groups. Lastly, Position 4 was opposite to Position 1 at the bottom of GO sheet close to the epoxide and hydroxyl groups.

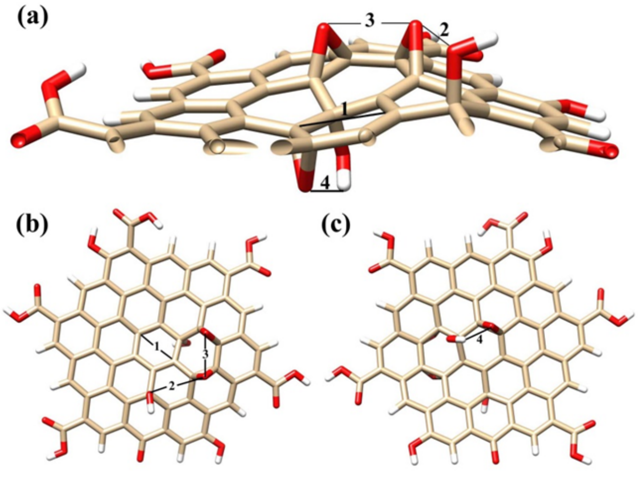

Figure 1: (a) Four adsorption sites, 1-4, of the GO surface for each ion. (b) View of the top of the GO surface showing ion position 1 at the center of GO, position 2 between the epoxide and hydroxyl group, and position 3 between two epoxide groups. (c) Bottom-up view of the GO surface, showing ion position 4 between the epoxide and hydroxyl groups. Note that the metal ion is placed above the surface by 5 Å on each side.

2.2 Validation of calculation method for energies and geometries of GO-M^{2+} complexes

Binding energies (ΔE_{bind}) and binding distances (R) computed with various basis sets for the cation-benzene complexes are summarized in Table 1. Calculated results in previous studies of the same system (Ho, Yang, Klippenstein, & Dunbar, 1997; Steckel, 2005) and experimental “H values (Chen & Armentrout, 1993; Ho *et al.*, 1997; Meyer, Khan, & Armentrout, 1995; Steckel, 2005) are also shown. In each case, R was measured from the center of mass of the benzene ring to the metal cation. In Table 1, the binding energies and distances obtained from the B3LYP/6-31g(d) with LANL2DZ level of accuracy are in good agreement with experimental values (Chen & Armentrout, 1993; Ho *et al.*, 1997; Meyer *et al.*, 1995; Steckel, 2005), and the binding distances are in agreement with previous calculations (Ho *et al.*, 1997; Steckel, 2005). Therefore, B3LYP/6-31g(d) with LANL2DZ was used in this study.

2.3 Binding energy calculations of GO complexes

The graphene oxide was fully optimized by B3LYP and M06 at the 6-31g(d) level of theory. The adsorption energies of the divalent metal ions-GO systems were calculated using B3LYP and M06 methods with 6-31g(d) level of theory for oxygen, carbon, and hydrogen atoms and an effective core potential (ECP) basis set, LANL2DZ, was used for M^{2+}. The interaction energy was then corrected by basis set superposition error (BSSE) using the counterpoise correction (CP) (Boys & Bernardi, 1970). The M^{2+} ion (Cd^{2+}, Cu^{2+}, $Hg^{2+}$and Zn^{2+}) was located above the center and perpendicular to functional groups on the GO sheet (Figure. 1) and then the complex geometries were fully optimized using the B3LYP and M06 at the 6-31g(d) level of theory. All calculations were performed with the GAUSSIAN 09 quantum chemistry software package (Frisch *et al.*, 2009), which has been expanded to include a number of DFT methods. The binding energy of complexes is defined by

$$\Delta E_{bind} = E_{cpx} - E_{GO} - E_{M^{2+}} \qquad (1)$$

where E_{cpx}, E_{GO} and $E_M{}^{2+}$ the energies of the optimized complex, GO and M^{2+}, respectively. The interaction energies of each metal cation were obtained at four different positions on the GO surface.

3. Results

3.1 Binding energies of GO-M^{2+} complexes

The complex geometries were fully optimized using the B3LYP/6-31g(d)/LANL2DZ basis set. An improved effective

Table 1. Binding energies (ΔE_{bind}), derived according to Equation 1, for the benzene–cation (Cd^+, Cu^+, Hg^+, Zn^+ and Ag^+) obtained in this work and in previous studies. The distance (R) was measured from the center of mass of the benzene ring to the cation.

Methods	Basis set	ΔE_{bind} (kcal.mol^{-1})					R(Å)				
		Cd^+	Cu^+	Hg^+	Zn^+	Ag^+	Cd^+	Cu^+	Hg^+	Zn^+	Ag^+
B3LYP	LANL2DZ	-34.94	-51.41	-38.45	-30.48	-41.96	2.44	1.93	2.77	2.29	2.30
	aug-cc-pVQZ-PP	-36.90	-61.83	-55.95	-41.31	-41.31	2.56	1.79	2.78	2.34	2.39
	aug-cc-pVTZ-PP	-40.16	-57.97	-55.62	-35.65	-47.26	2.54	1.80	2.79	2.34	2.34
M06	LANL2DZ	-40.13	-58.28	-40.61	-39.36	-43.30	2.54	1.88	2.76	2.24	2.32
	aug-cc-pVQZ-PP	-40.57	-64.15	-56.99	-48.10	-48.10	2.51	1.70	2.79	2.33	2.57
	aug-cc-pVTZ-PP	-36.36	-62.71	-56.36	-47.25	-47.47	2.50	1.72	2.79	2.34	2.36
MP2	LANL2DZ	-31.49	-34.59	-36.85	-39.36	-26.85	2.44	1.96	2.75	2.19	2.35
CCSD(T)	LANL2DZ	-31.49	-34.59	-36.85	-24.14	-26.85	2.44	1.96	2.50[e]	2.19	2.35
MP2	LANL2DZ	-32.51[a]	-	-	-	-38.74[a]	2.44[a]	-	-	-	2.27[a]
Δ*H* (Experiment)	-32.51[a]	-52.10[b]	-38.18[c]	-	-37.28[d]	-	-	-	-	-	

Note: from references, [a](Ho *et al.*, 1997), [b](Meyer *et al.*, 1995), [c](Steckel, 2005), [d](Y.-M. Chen & P. B. Armentrout, 1993) , [e](Steckel, 2005).

core potential for the metal atom (ECP) (Leszczynski, 2006) was combined with the 6-31g(d) basis set. The binding energies of the divalent metal cations with GO using the four initial ion positions are presented in Table 2, with BSSE corrections in parentheses. ΔE_{bind} of all studied complexes were decreased by ~3-7 kcal/mol after the BSSE corrections, similarly to results found in many systems (Ozutsumi, Koide, Suzuki, & Ishiguro, 1993). The GO model contained epoxy and hydroxyl groups at which each divalent cation was initially placed at positions 1-4 (Figure 1). The interaction of the divalent metal ion with GO is favorable at C-O-C and OH groups (Ogata *et al.*, 2014). From Table 2, the order of binding strength of cation-GO systems on the GO sheet chosen from the lowest energies of each cation (among initial positions 1-4) was Cu^{2+} (-361.91) > Zn^{2+} (-281.06) > Hg^{2+} (-277.52) > Cd^{2+} (-241.24), with BSSE correction. The binding energy of Cu^{2+} on the GO sheet was much lower than those of Hg^{2+}, Cd^{2+} and Zn^{2+}, in correspondence with the shorter binding distance (*d* of 0.62 Å).

The smaller cation can approach the GO sheet more closely than larger cations and the order of these distances is consistent with the ΔE_{bind} values, namely Cu^{2+} > Zn^{2+} > Hg^{2+} > Cd^{2+}. In most cases, Cu^{2+} and Hg^{2+} have only one position on the GO sheet after optimization. Therefore, these ions only have a single binding energy. In contrast, Zn^{2+} and Cd^{2+} have two positions on the GO sheet after optimization, and consequently have more than one binding energy.

3.2 Adsorption of Cu^{2+} cations on the GO sheet

X-ray photoelectron spectra (XPS) (Hu *et al.*, 2013) of the initial GO and the GO complexes are shown in Figure 3. The spectrum of the epoxy C-O-C group on the GO surface is 286.5 eV. The differences include a halved intensity of the peak due to the epoxy group by the Cu^{2+} cation. It is evident that the epoxy group can also convert to a hydroxyl group. This result can be confirmed by quantum calculations. The picture insert shows that the functional groups of GO have been destroyed by the Cu^{2+} metal cation. The right hand side of Figure 3 illustrates the angle (α) between the C-C-O of the epoxide group on bottom of the GO surface. This changed from about 60° to 110° after Cu^{2+}-GO complex formation. This result shows good correlation of the experimental results (Hu *et al.*, 2013).

The Cu^{2+} cation has the strongest interaction with the oxygen atoms of functional groups on GO, based on the evidence in Table 3. The distance R_1 for Cu^{2+} of 2.124 Å is in agreement with a previous study of transition metal binding to benzene (Bauschlicher, Partridge, & Langhoff, 1992) and

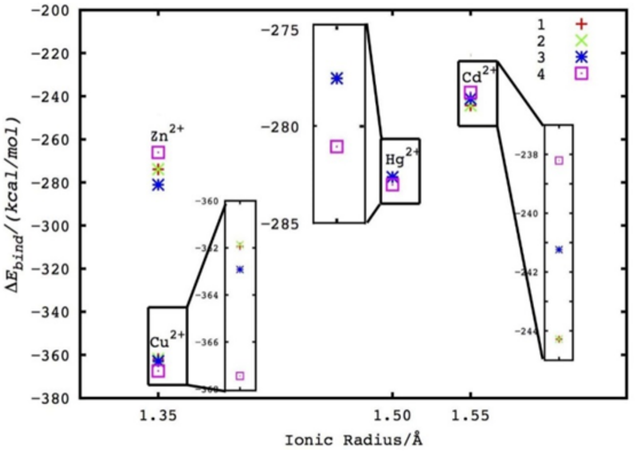

Figure 2. Binding energies (ΔE_{bind}) of four divalent metals at 4 positions on the GO sheet calculated using the B3LYP/6-31g(d)/LANL2DZ basis set.

Table 2. Results for divalent metal adsorption on graphene oxide, (the shortest distance between the metal atom and the GO plane) [Å] and binding energy (ΔE_{bind}, kcal·mol^{-1}) of the divalent metal on the GO surface with and without BSSE corrections using the 6-31g (d) basis set. The values in parentheses are the binding energies with BSSE correction

positions	ΔE_{bind}			
	Cd^{2+}<1.55>	Cu^{2+}<1.35>	Hg^{2+}<1.50>	Zn^{2+}<1.35>
1	-248.86(-244.29)	-369.74(-361.94)	-280.31(-277.53)	-280.36(-273.89)
2	-246.08(-241.24)	-370.24(-362.92)	-280.31(-277.52)	-288.43(-281.06)
3	-248.85(-244.28)	-369.69(-361.86)	-280.30(-277.50)	-280.36(-273.88)
4	-239.69(-238.21)	-371.73(-367.44)	-282.13(-281.04)	-267.78(-266.10)

with X-ray data (Ozutsumi *et al.*, 1993) showing 1.97 Å. The smaller cation can approach the GO sheet more closely than larger cations and the order of these distances is consistent with the ΔE_{bind} values, namely $Cu^{2+} > Zn^{2+} > Hg^{2+} > Cd^{2+}$. In most cases, Cu^{2+} and Hg^{2+} have only one position on the GO sheet after optimization. Therefore, these ions only have a single binding energy. In contrast, Zn^{2+} and Cd^{2+} have two positions on the GO sheet after optimization, and consequently have more than one binding energy.

The goal of this study is to examine the behavior of divalent metal cations on a GO sheet. Therefore, we evaluated the optimized parameter of GO complexes as the binding distance ($R_{1,2,3}$) and an angle β, defined as angle of O-M^{2+}-O (Figure 4), after the full optimization was performed. The binding distance ($R_{1,2,3}$) is that between M^{2+} and the functional groups, including two epoxy groups and a hydroxyl group, on the surface of the GO sheet (Figure 4). $R_{1,2,3}$ and β were shown in Table 3. The binding distances, R, for Cd^{2+}, Cu^{2+},

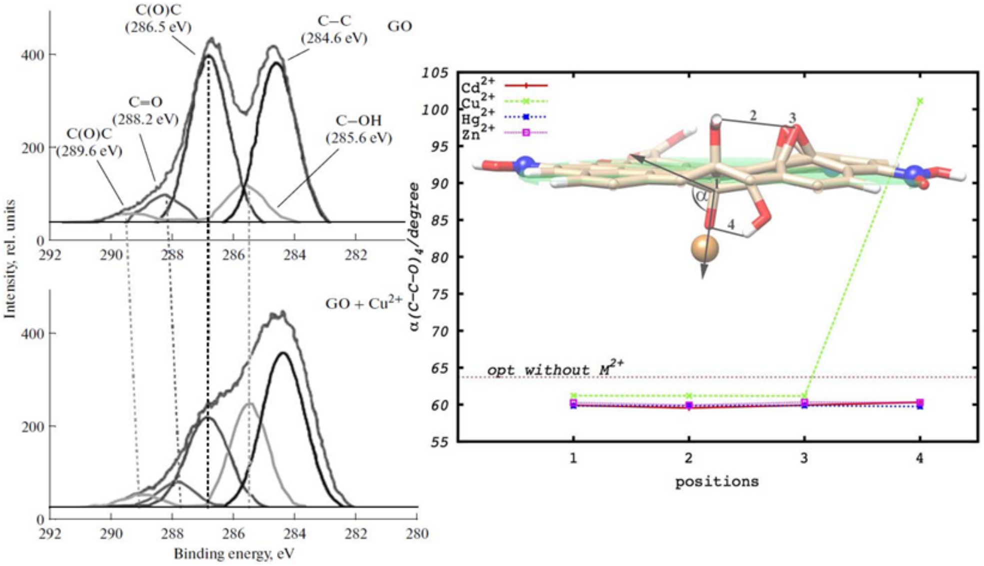

Figure 3. X-ray photoelectron spectra (C1s) of GO and GO-Cu^{2+} (Laure, Tkachev, Buslaeva, Fatushina, & Gubin, 2013) (left) and the angle α relate to divalent cation adsorption (right).

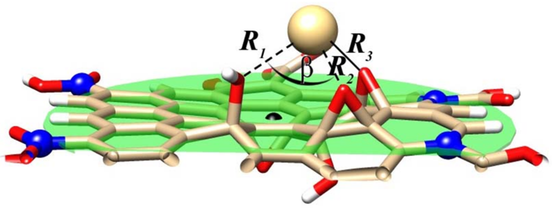

Figure 4. Angle (b) and distances (R_1-R_3) for divalent metal cation adsorption with respect to functional groups of the GO sheet.

Table 3. Binding distance, R (Å), and angles (β) and (φ) between divalent metal cations and the GO surface.

Metal	Positions	P_1	R_2	R_3	β	φ
Cd^{2+}	1	2.323	2.533	2.967	59.98	45.75
	2	2.411	2.636	2.686	58.91	57.80
	3	2.323	2.533	2.965	60.00	45.78
Cu^{2+}	1	2.124	2.561	2.184	58.15	64.33
	2	2.125	2.556	2.186	58.11	64.43
	3	2.124	2.561	2.186	58.10	64.28
Hg^{2+}	1	3.242	3.583	3.783	58.59	28.52
	2	3.240	3.583	3.779	58.57	28.53
	3	3.240	3.578	3.774	58.59	28.74
Zn^{2+}	1	2.093	2.215	3.023	60.41	53.38
	2	2.180	2.363	2.637	59.06	68.51
	3	2.094	2.217	3.015	60.40	53.53

Hg^{2+}, and Zn^{2+} were 2.323, 2.124, 3.240, and 2.093 Å, respectively.

4. Conclusions

We performed a systematic DFT investigation of the adsorption of Cd^{2+}, Cu^{2+}, Hg^{2+} and Zn^{2+} on a GO surface. Geometries and energies of adsorption demonstrated interaction of the divalent metal with the functional groups on the GO surface. The binding efficiency of the metal ions to the GO surface increased in the following order: $Cu^{2+} > Hg^{2+} > Zn^{2+} > Cd^{2+}$. The binding energies of Cu^{2+} are much lower than those of Hg^{2+}, Cd^{2+} and Zn^{2+}, and the corresponding binding distances are much shorter. These are the first calculations of the structures of GO-M^{2+} complexes. The Cu^{2+} cation has the strongest interaction with the hydroxyl and epoxy functional groups, while the two epoxy groups are the main active oxid es of GO for adsorption of the other cations. The epoxy group may also be converted to a hydroxyl group by Cu^{2+}adsorption. However, bonding in these systems may be quite different because of interactions with *d* orbitals on the metal, and further experiments and higher level calculations are needed to confirm these structures. Understanding the behavior through which divalent metal cations adsorb on the GO surface is useful for design of effective control technologies for control of heavy metal pollution in industrial settings. Future work should therefore consider the effect of aqueous solutions to allow these findings to be applied for treatment of industrial waste by GO.

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