First-principles study of the interaction between reduced graphene oxide and nickel hydroxide

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Abstract: A series of reduced graphene oxide (rGO) sheet models with various oxygen-containing groups (carbonyl, epoxyl, and hydroxyl groups) were designed and the interactions between these rGO sheets and nickel hydroxide were studied using first-principles DFT (B3LYP) calculations. It is found that the adsorption energy of nickel hydroxide on rGO sheets is seriously dependent on the oxygen-containing groups on rGO. All the three oxygen-containing groups facilitate the adsorption of nickel hydroxide on rGO sheet. In particular, the adsorption between nickel hydroxide and rGO with epoxyl group is strongest among the series of rGO sheet models. In addition, the variations of atomic distances and charge distribution of the series of rGO sheets after absorbing nickel hydroxide were analyzed.

1 Introduction

Graphene, a single-layer carbon sheet with a honeycomb crystal lattice, has attracted tremendous research interest in recent years due to its exceptional properties such as the high carrier mobility at room temperature, large theoretical specific surface area, good optical transparency, high Young’s modulus, and excellent thermal conductivity [1]. Graphene is the thinnest material and can be viewed as a basic build block for constructing other carbon materials. For example, it can be rolled into carbon nanotubes or stacked into three-dimensional graphite. The low-cost and mass production of graphene derivatives, graphene oxide (GO) and reduced graphene oxide (rGO), offers the numerous possibilities for fabricating graphene-based functional materials [3]. The GO and rGO possess many reactive oxygen-containing groups, such as carbonyl, epoxyl, and hydroxyl groups, which can be used for further functionalization and regulating properties of GO and rGO sheets. Due to these additional advantages, GO and rGO are much easier and more flexible to integrate with various kinds of functional materials than graphene [6]. The nanostructured metal oxides or hydroxides are widely employed in applications like electrochemical energy conversion and storage, electronics, optics, solar energy harvesting, and so on [7, 13, 15]. In order to further enhance their properties, a great number of metal oxides or hydroxides nanostructures have been composites with graphene and its derivatives [8, 12, 16]. A synergistic enhancement effect was observed when coupling rGO with metal hydroxides. For example, the nickel hydroxide (Ni(OH)_2) nanoparticles were anchored on the rGO surface by a chemical deposition method [10]. The Ni(OH)_2@RGO nanocomposite exhibits superior performances in Ni-MH batteries and lithium-ion batteries (LIBs). One reason was that the introduction of rGO into Ni(OH)_2@RGO nano-
composite enabled both H⁺ (in Ni-MH battery)/Li⁺ (in LIBs) and electron to migrate and reach each active nanoparticle and to complete insertion/extraction reaction. Similar results were also observed in metal oxides, such as NiO [2], MnO₂ [4], TiO₂ [17], Fe₃O₄ [11], Co₃O₄ [14] and so on. For those composites, an understanding of the interactions between the metal oxides/hydroxides and rGO at atomic level is very crucial for fabricating high performance and reliable functional materials. However, there are few reports on the issue till now. In this work, the adsorption of nickel hydroxide on graphene and three rGO models with different oxygen-containing groups (carbonyl, epoxyl, and hydroxyl groups) is studied using first-principles DFT (B3LYP) calculations. The variations of atomic distances and charge distribution of the series of rGO sheets after absorbing nickel hydroxide were also analyzed.

2 Calculations
Fig. 1 shows the models of graphene sheet (GS, model A) and rGO sheets with different oxygen-containing groups (model B, C, and D). In model B, one hydroxyl group was anchored on C1 atom of rGO sheet. In model C, one epoxyl group was anchored on C1 atom of rGO sheet. In model D, one carbonyl group and one hydroxyl group were anchored on the adjacent C1 and C4 atoms of rGO sheet.

![Figure 1. Models of GS (model A), rGO sheet with one hydroxyl group (model B), rGO sheet with one epoxyl group (model C), and rGO sheet with one carbonyl group and one hydroxyl group (model D).](image)

All these GS, rGO model structures, and the rGO sheets adsorbed with Ni(OH)₂ were optimized at B3LYP level with 6-31G* basic set except Ni at LANL2DZ. The adsorption energies (ΔE_ads) were calculated according to the following equation:

\[ ΔE_{ads} = E_{total} - E_{rGO} - E_{Ni(OH)₂} \]  

(1)

In the above equation, \( E_{total} \), \( E_{rGO} \), and \( E_{Ni(OH)₂} \) correspond to the total electronic energy the rGO adsorbed with Ni(OH)₂, the electronic energy of the isolate rGO, and the electronic energy of the isolate Ni(OH)₂, respectively. All the calculations were carried out by using the Gaussian 09 program [5].

3 Results and Discussion
Table 1 compared the selected C-C bond lengths of the GS and rGO model structures. The optimized GS shows a perfect planar conformation due to the strong conjugation effect. While the 3 rGO models exhibit obvious local distortion because of the destruction of \( sp^2 \) hybridization of carbon atoms binding with oxygen-containing groups. Moreover, the C-C bond lengths adjacent to the oxygen-containing group in the three rGO models become longer as compared to the GS. Among the three rGO models, model D shows the most obvious elongation of C-C bond length. This elongation of C-C bond length suggests that the conjugation degree of rGO sheets decreases.
Table 1. Selected C-C bond length of the GS and rGO sheets with different oxygen-containing groups. The corresponding atoms' serial number is indexed in Figure 1.

| C-C bond | model A | model B | model C | model D |
|----------|---------|---------|---------|---------|
| C1-C2    | 1.4196  | 1.5064  | 1.5197  | 1.5039  |
| C1-C3    | 1.4292  | 1.5069  | 1.4723  | 1.5093  |
| C1-C4    | 1.4196  | 1.5064  | 1.4695  | 1.5275  |

The optimized geometries of GS, rGO one hydroxyl group, rGO with one epoxyl group and one hydroxyl group after absorbing Ni(OH)$_2$ are presented in Fig. 2. It can be seen that the GS remains planar conformation after absorbing Ni(OH)$_2$ (Fig. 2a). The distance between Ni(OH)$_2$ and the GS surface is 2.03 Å and the adsorption energy is 22.75 kJ/mol. In addition, the C-C bond lengths in GS have almost no changes after absorbing Ni(OH)$_2$. The very large distance between Ni(OH)$_2$ and the GS surface and the small adsorption energy indicate that there is little chemical adsorption between Ni(OH)$_2$ and GS. In other words, the GS will have little influence on the electronic properties of Ni(OH)$_2$.

For the rGO with one hydroxyl group (model B), Ni(OH)$_2$ tends to form bond with the O atom in hydroxyl group (Fig. 2b). The distance between Ni(OH)$_2$ and the hydroxyl group anchored on rGO is 2.138 Å, suggesting that Ni(OH)$_2$ is much closer to rGO than GS. The adsorption energy is -14.43 kJ/mol, which indicates that the adsorption between Ni(OH)$_2$ and rGO with one hydroxyl group is strong under the influence of complexation interaction between the Ni atom in Ni(OH)$_2$ and the O atom in hydroxyl group.

For the rGO with one epoxyl group (model c), the distance between Ni(OH)$_2$ and the epoxyl group anchored on rGO is 2.043 Å (Fig. 2c). The adsorption energy is 7.33 kJ/mol, which is 15.42 kJ/mol lower than that (22.75 kJ/mol) for GS, suggesting that the epoxyl group also facilitates the adsorption of Ni(OH)$_2$ on rGO. For the rGO with one carbonyl group and one hydroxyl group, Ni(OH)$_2$ tends to form bond with the carbonyl group (Fig. 2d). The distance between the Ni atom in Ni(OH)$_2$ and the O atom in epoxyl group is 1.802 Å, a littler shorter than that in rGO with one hydroxyl group. The adsorption energy is -20.23 kJ/mol and it is the lowest value in the three systems containing rGOs with different oxygen-containing group, suggesting that very strong interaction exists between the Ni atom in Ni(OH)$_2$ and O atom in carbonyl group.

Figure 2. The optimized geometric structures of (a) GS, (b) rGO with one hydroxyl group, (c) rGO with one epoxyl group, and (d) rGO with one carbonyl group and one hydroxyl group after absorbing Ni(OH)$_2$ optimized at 6-31G* level except Ni at LANL2DZ, using DFT (B3LYP) method.
The charge distributions over GS and rGO sheets after adsorbing Ni(OH)₂ are analyzed as shown in Fig. 3. For GS, the adsorbing of Ni(OH)₂ has little effect on the charge distribution over GS. The net charges of Ni(OH)₂ is -0.211 e, indicating that electrons transfer from Ni(OH)₂ to graphene are not effective. When Ni(OH)₂ is adsorbed with the hydroxyl group on rGO (model B), the net charges of Ni(OH)₂ is -0.276 e. There is obvious electrons transfer from the Ni in Ni(OH)₂ to the O in hydroxyl group. When Ni(OH)₂ is adsorbed with the epoxyl group on rGO (model C), the net charges of Ni(OH)₂ is -0.239 e. However, there is little charge transfer between the Ni in Ni(OH)₂ and the O in epoxyl group, which is very similar to the case of NS adsorbed with Ni(OH)₂. When Ni(OH)₂ is adsorbed with the carbonyl group on rGO (model D), the net charges of Ni(OH)₂ is -0.102 e. There is obvious electrons transfer from the Ni in Ni(OH)₂ to the O in carbonyl group.

Figure 3. The charge distributions of (a) GS, (b) rGO with one hydroxyl group, (c) rGO with one epoxyl group, and (d) rGO with one carbonyl group and one hydroxyl group after absorbing Ni(OH)₂ optimized at 6-31G* level except Ni at LANL2DZ, using DFT (B3LYP) method.

4 Conclusions

The interactions between rGO sheets with different oxygen-containing groups (carbonyl, epoxyl, and hydroxyl groups) and nickel hydroxide were investigated using first-principles DFT (B3LYP) calculations. The optimized GS show a perfect planar conformation. The introduction of oxygen-containing groups on GS results in obvious local distortion due to the destruction of sp² hybridization of carbon atoms in GS. After adsorbing Ni(OH)₂, the GS remains planar conformation and the distance between Ni(OH)₂ and the GS surface is up to 2.03 nm. Moreover, the adsorption energy (22.75 kJ/mol) is smallest among the 4 model systems, indicate that there is little chemical adsorption between Ni(OH)₂ and GS. The introduction of oxygen-containing groups on GS facilitates the adsorption of Ni(OH)₂ on rGO sheets. The calculated adsorption energies for Ni(OH)₂ on rGO with one hydroxyl group, rGO with one epoxyl group, rGO with one carbonyl group, and one hydroxyl group are -14.43 kJ/mol, 7.33 kJ/mol, and -20.23 kJ/mol, respectively. So, there are strong interactions between the Ni atom in Ni(OH)₂ and O atom in hydroxyl group and carbonyl group on rGO. Charge distribution analysis revealed that the adsorbing of Ni(OH)₂ on GS or rGO with one epoxyl group has little effect on the charge distribution over GS or rGO. However, for rGO with hydroxyl group and/or carbonyl group, there is obvious electrons transfer from the Ni in Ni(OH)₂ to the O in hydroxyl group or carbonyl group.
group. The above results could provide a theoretical guidance for the preparation and performance optimization of graphene-based organic/inorganic hybrid materials.

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