

Density functional theory studies on the nano-scaled composites consisted of graphene and acyl hydrazone molecules

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Abstract. Graphene, which is the first obtained single atomic layer 2D materials, has drawn a great of concern in nano biotechnology due to the unique property. On one hand, acyl hydrazone compounds belonging to the Schiff bases have aroused considerable attention in medicine, pharmacy, and analytical reagent. However, few understanding about the interaction between graphene and acyl hydrazone molecules is now available. And such investigations are much crucial for the applications of these new nano-scaled composites. The current work revealed theoretical investigations on the nano-scaled composites built by acyl hydrazone molecules loaded on the surface of graphene. The relative energy, electronic property and the interaction between the counterparts of graphene/acyl hydrazone composites are investigated based on the density functional theory calculations. According to the obtained adsorption energy, the formation of the nano-scaled composite from the isolated graphene and acyl hydrazone molecule is exothermic, and thus it is energetically favorable to form these nano composites in viewpoint of total energy change. The frontier molecular orbital for the nano composite is mainly distributed at the graphene part, leading to that the energy levels of the frontier molecular orbital of the nano composites are very close to that of isolated graphene. Moreover, the counterpart interaction for the graphene/acyl hydrazone composites is also explored based on the discussions of orbital hybridization, charge redistribution and Van der Waals interaction.

1. Introduction

Acyl hydrazone compounds are organic matter that belongs to the Schiff bases with great concern, which can be obtained by the condensation of hydrazide and ketone or aldehyde. Usually they exhibit strong coordination ability due to the various sites to coordinate. Also most Schiff bases possess good biological activities, such as anti-tumor and antibacterial [1]. With the aid of Schiff bases, the transamination can be achieved in biochemical reaction [2-4]. The C=N double bond in Schiff is found to be the effect group, and plays an important role in antibacterial activity. Therefore, Schiff bases currently have aroused considerable attention in medicine, pharmacy, and analytical reagent [1,5]. Compared with the ordinary Schiff bases, acyl hydrazone compounds are more stable, and exhibit even stronger biological activity. Besides, the oxygen and nitrogen atoms in acyl hydrazone molecules could be involved in the formation of hydrogen bonding networks of biochemical systems. In such a way, the acyl hydrazone compounds are good candidate in various physical chemical processes, such as resistance to high blood sugar, antitumor, antifungal and immune inhibitors [6-8].



On the other hand, graphene, which is the first obtained single atomic layer 2D materials, has drawn a great deal of attention due to the state-of-the-art potentials in physics, chemistry, bio-nanotechnology and pharmacy [9-14]. Currently graphene have been utilized in many practical fields. Shirzadmehr et. al developed graphene-based sensor composition. They demonstrate that the sensor is highly selective for heavy metal ions determination with very low limit, such as Hg^{2+} and Ag^+ [11-12]. Along with a rise in the number of patents related to the graphene, its industrial applications have been dramatically increased, especially in pharmaceutical science and targeted drug delivery [15-19]. Because graphene possesses very large specific surface area which can be either the both edges and the top or bottom surfaces, therefore, its loading capacity is much higher than that of others. Dai et al. studied the polyethylene glycol loaded with nano-scaled graphene as anticancer drug carriers, and the drugs are interacted with the graphene by non-covalent bonding [17]. Zhang studied the functionalized graphene that can efficiently load two anticancer drugs, and has the specificity of breast cancer cells. The two anticancer drugs combined loading of the cancer cells have great toxicity, so as to more effectively to kill cancer cells [18]. Yang reported that oxide graphene can efficient load doxorubicin hydrochloride. And then the drug release can be controlled under different pH [19].

The current work presents a quantum chemical study on the nano-scaled composites made of acyl hydrazone molecules loaded on the surface of nanoscale graphene. The adsorption energy, electronic structure and the interaction nature between the counterparts of graphene/acyl hydrazone composites are investigated. And a solid understanding of the structure, energy, electronic property and interaction of the counterparts is much crucial for the construction new nano-scaled composite and also their applications. We expect that the current work here would be helpful to further studies of the acyl hydrazones drugs and graphene.

2. Models and Computational Details

As shown in Figure 1, several acyl hydrazone molecules (denoted as *mol-1* – *mol-3*) are adopted as the model compounds in this work. These acyl hydrazone molecules can be obtained by the modification of pyridine and carboxylic acid. It is noticed that the three molecules studied here are isomers with different connecting sites for the pyridine rings. As for the nano-scaled graphene, a layer structure that contains 120 carbon atoms, is built with 8 carbon atoms and 15 carbon atoms along two axes of the surface. The surface area is $16.5 \text{ \AA} \times 18.0 \text{ \AA}$. The C–C bond length in the six-membered rings is 1.42 \AA . The dangling bonds at the edges are terminated by hydrogen atoms in our model. It can be seen that the similar treatment has been used in previous theoretical studies [20-21].

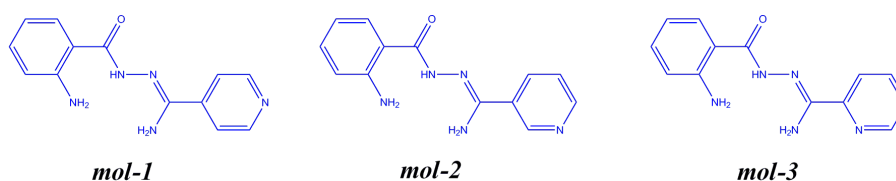


Figure 1. Models of the acyl hydrazone molecules in this work.

We are aware that various possible configurations of acyl hydrazone molecules may exist when they are adsorbed on graphene surface. In order to get more reasonable configurations for the absorption models, molecular dynamics (MD) simulations are conducted with the aid of reactive force fields (ReaxFF) developed by Mattsson and co-authors [22]. We performed MD simulations at 300 K with each for 5 ps. The MD simulations are under the both constant temperature and volume condition, and the time step size is set as 1 fs. Different initial models are also considered to start the MD simulation. By using this strategy, the configurations are obtained as shown in Figure 2, and then computed by the quantum chemical methods.

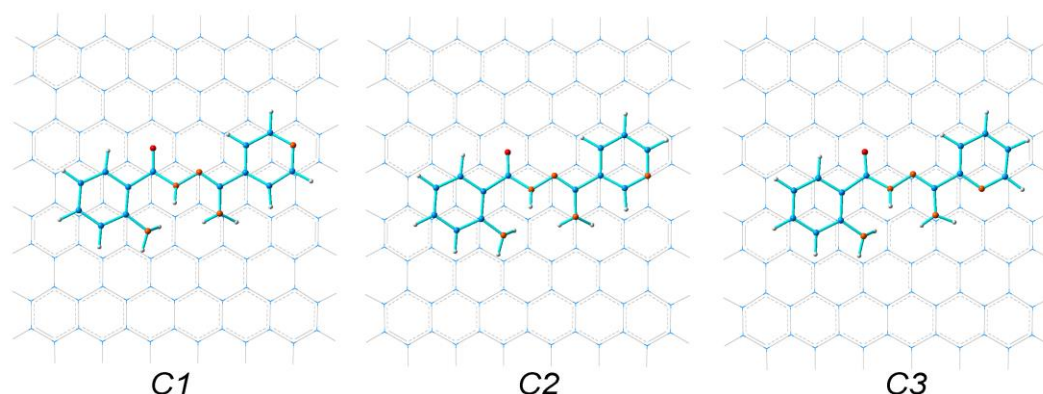


Figure 2. Structures of graphene/acyl hydrazone composites with fully geometrical optimization.

In this work the quantum chemical calculations are performed based on the Kohn-Sham density functional theory (DFT). M06-2X method [23] proposed by Truhlar and co-authors is selected as the exchange-correlation functional for all DFT computations. This selection is based on the fact that M06-2X method is more accurate to explore the system with non-covalent bonding, which may be very crucial for the nano-scaled composites in this work. All calculations are conducted by using the linear combination of atomic orbital (LCAO) technique with *Gaussian09* code [24]. For all computations, self-consistent field molecular orbital (SCF-MO) method under the framework of DFT at the 6-31G (*d*, *p*) basis set theory level is adopted.

3. Results and Discussion

3.1. Relative Energy

In order to study the energetic effects in the formation of the graphene/acyl hydrazone composites, the adsorption energy (E_{ads}), which is the energy difference of the adsorption process, is calculated by:

$$E_{\text{ads}} = E(\text{composite}) - E(\text{graphene}) - E(\text{mol}) \quad (1)$$

where $E(\text{composite})$ represents the total energy of the composite, and $E(\text{graphene})$ and $E(\text{mol})$ are the energies of isolated graphene and acyl hydrazone molecule with their minimum energy structures respectively. A negative E_{ads} corresponds to a stable adsorption. The obtained results are listed in Table 1.

Table 1. Obtained adsorption energy (E_{ads}), the HOMO and the LUMO of the nano composites.

structures	E_{ads} (eV)	HOMO (eV)	LUMO (eV)
C1	-1.357	-4.175	-3.651
C2	-1.343	-4.175	-3.652
C3	-1.323	-4.144	-3.620
graphene	/	-4.121	-3.621
mol-1	/	-7.315	-0.510
mol-2	/	-7.220	-0.343
mol-3	/	-7.005	-0.382

It is observed that the values of E_{ads} are below zero for all three graphene/acyl hydrazone composites studied in the current work. Recall that the formation of the nanoscaled composite from the isolated graphene and acyl hydrazone molecule is exothermic when $E_{\text{ads}} < 0$. Thus it is energetically favourable to form these graphene/acyl hydrazone composites in viewpoint of total energy change. The calculated values of E_{ads} are -1.357, -1.342 and -1.323 eV for **C1** – **C3**, respectively. Among them, the composite **C1** is the most exothermic to load the acyl hydrazone molecules on the surface of graphene due to the most negative E_{ads} . Nevertheless, the differences

between E_{ads} of the three composites are not evident (less than 0.1 eV). For a comparison, E_{ads} of the composites made of graphene and benzene or pyridine are also calculated with the same method. The obtained results for them are only -0.319 and -0.313 eV, respectively. These values are obviously smaller than those of **C1** – **C3**. As the acyl hydrazone molecules studied in this work, they contain both benzene and pyridine structures. The summation of E_{ads} for benzene and pyridine on graphene, however, is -0.632 eV, which is still only about 50% for those of **C1** – **C3**. This fact implies that the interaction between graphene and other parts of acyl hydrazone (with the exclusion of benzene and pyridine rings) is also important to adsorption energy.

3.2. Electronic Property

It is well-known that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are much crucial when the reactant is involved with chemical reactions [25], and thus the descriptions of the frontier molecular orbital (FMO) of the nano composites is necessary. The energy levels of the FMOs graphene/acyl hydrazone composites are listed in Table 1. It is quite clear here that HOMO and LUMO energy levels of **C1** – **C3** quite close to each other and vary very little (less than 0.03 eV). For a comparison, the isolated graphene flat and the acyl hydrazone molecules in this work are also calculated, and the obtained results are listed in Table 1. It is observed that both HOMO and LUMO energy levels of **C1** – **C3** are very close to that of isolated graphene, whereas far from those of the acyl hydrazone molecules. As a result, the FMO energy levels of composites change a little when the acyl hydrazone molecules are loaded on the surface of graphene. From this point, we may conclude that the FMO of the graphene/acyl hydrazone composites would be mainly derived from the graphene flat, other than from acyl hydrazone molecules.

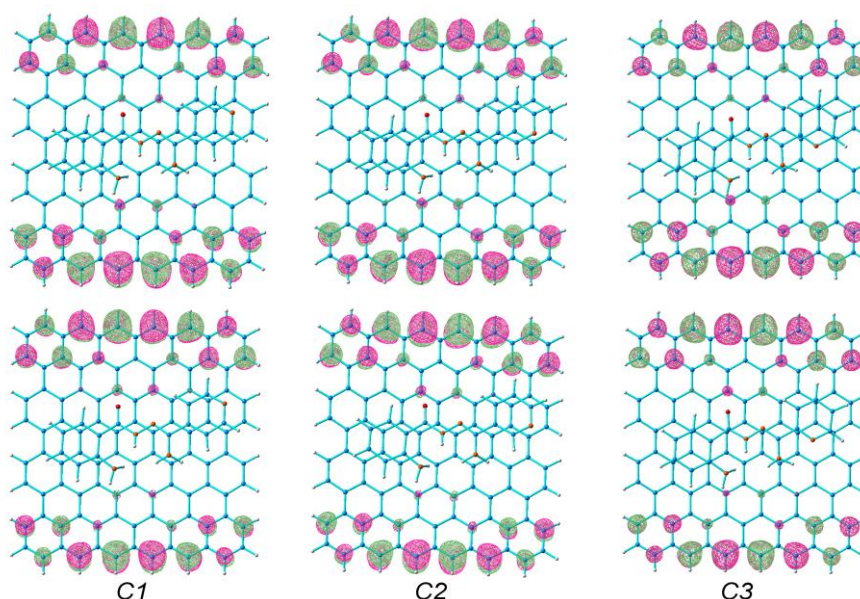


Figure 3. HOMO (top) and LUMO (bottom) of the composite **C1** – **C3**.

To confirm this assumption, the distributions of HOMO and LUMO for composite **C1** – **C3** are sketched in Figure 3. It is obvious that FMOs of the pure graphene and composite **C1** – **C3** all exhibit much localization at the edge regions of graphene part. Nearly no distribution is observed at the acyl hydrazone molecule. This feature is nearly the same as that of the isolated graphene flat. According to the frontier molecular orbital theory, the graphene flat is thus the dominating part when the graphene/acyl hydrazone composites are involved in chemical reactions.

3.3. Counterpart interaction

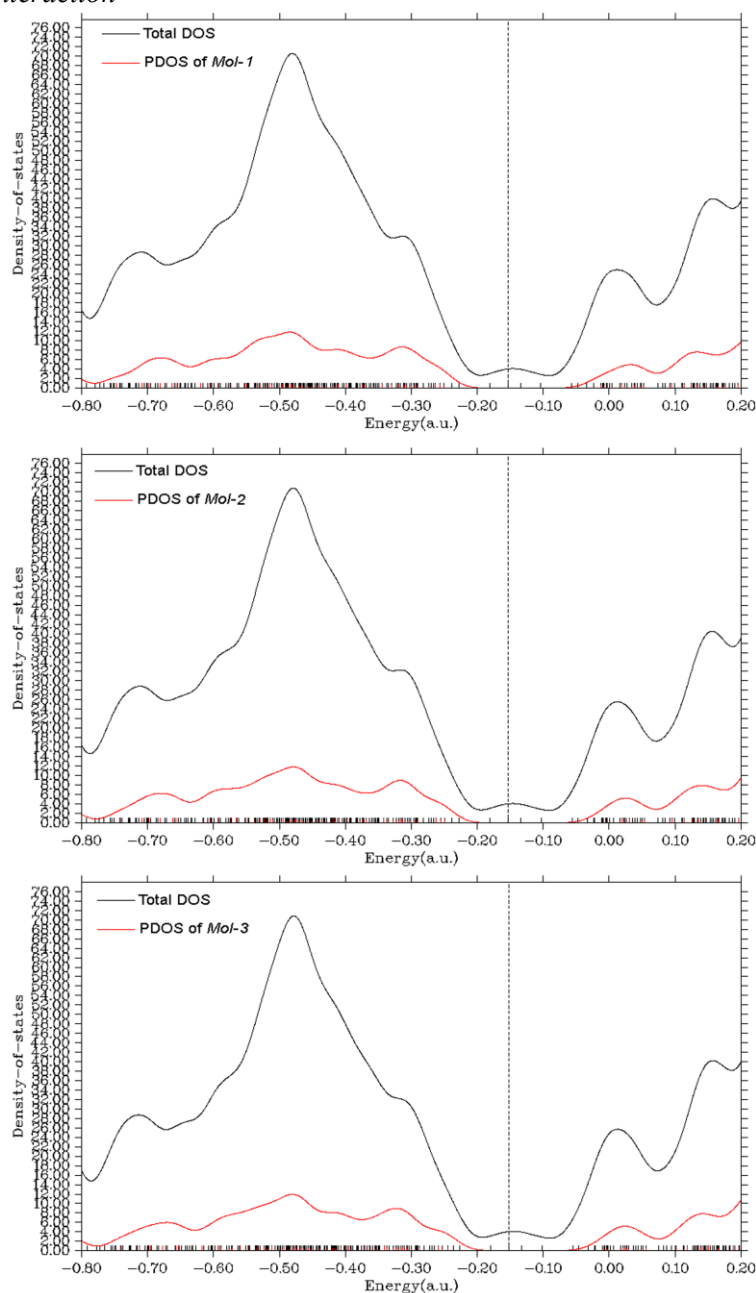


Figure 4. Total density of states and projected density of states of the composite *C1 – C3*.

In the current work, the graphene/acyl hydrazone composites can be considered as the acyl hydrazone molecules loaded on the graphene surface. And the understanding of the interaction of the counterparts is very crucial for the construction of the nano composites. Thus the investigation of the counterpart interaction for the graphene/acyl hydrazone composites is necessary. Firstly, we focus on the orbital hybridization for the counterpart. This can be analysed based on the projected density of states (PDOS) and total density of states (DOS), as shown in Figure 4. It is found that most parts of DOS are consisted with both graphene flat and acyl hydrazone molecules. This means that the orbital hybridization dose occur for the graphene/acyl hydrazone composites. Nevertheless, the DOS near the

FMOs are dominated by the graphene part, which agrees with the results of FMO analyses mentioned above.

Then we turn to the charge redistribution when the composites are formed by the nano graphene and acyl hydrazone molecules. It is observed that the electronic charge transfer from acyl hydrazone molecules to the graphene part can take place for these nano composites. The amounts of charge transfer are 0.027, 0.025 and 0.019 e respectively for **C1** – **C3** on the basis of the population based on Mulliken analysis. These values of charge transfer are much larger than 0.005 (or 0.007) e for that of the composites made of graphene and benzene (or pyridine). To give a videotext description for the charge redistribution, Figure 5 shows the electronic density difference of **C1** – **C3** relative to the isolated counterparts. It is observed that charge redistribution is mainly spreading at the interlayer space where oxygen and nitrogen atoms are located.

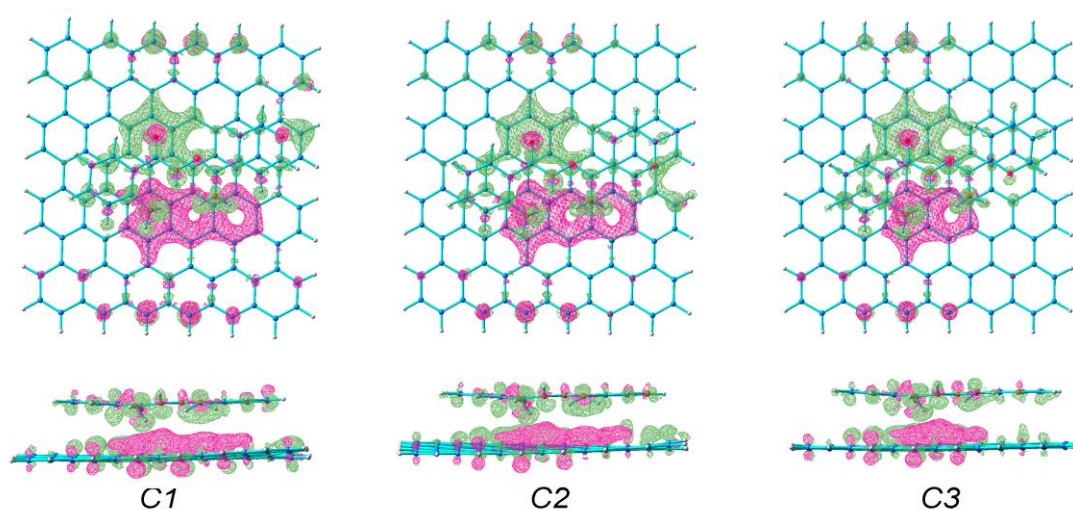


Figure 5. Top view (top) and side view (bottom) of the obtained electronic density difference of the composite **C1** – **C3**.

We also noticed that the acyl hydrazone molecules are loaded on the graphene surface in the nano-scaled composites. Thus Van der Waals interaction may also be important for the counterpart interaction. The nearest distances between the counterparts are calculated to be 3.098, 3.095 and 3.081 Å, respectively for composite **C1** – **C3**. These values are very close to the distances of Van der Waals interaction for carbon, nitrogen and oxygen atoms if their Van der Waals radii are considered to be 1.65, 1.55 and 1.60 Å, respectively. We are also aware that these distances are much longer than the covalent bond lengths between carbon, oxygen and nitrogen atoms. Thus these results indicate the Van der Waals interaction, not the covalent bonds, between the counterparts of the graphene/acyl hydrazone composite.

4. Conclusion

In summary, we have studied the nano-scaled composites composed of graphene and acyl hydrazone molecules based on DFT calculations. The absorption configurations were determined by means of the MD simulations. Then the relative energy, electronic property and the interaction between the counterparts of the nano-scaled composites are calculated and discussed. According to the obtained adsorption energy, the formations of the nano-scaled composites from the isolated graphene and acyl hydrazone molecules are always exothermic in view point of total energy change. This fact indicates that the formation of these nano composites is energetically favorable. Among them, composite **C1** is the most stable. The results of FMO analysis show that both HOMO and LUMO of these nano composites are mainly derived from the graphene flat, rather than from the acyl hydrazone molecule.

Thus graphene is the dominating part when the graphene/acyl hydrazone composites are involved in chemical reactions ~~pointing~~ in view point of FMO theory. The counterpart interaction for the graphene/acyl hydrazone composites is also investigated. It is observed that orbital hybridization, charge redistribution and Van der Waals force are important for the interaction between the counterparts of these nano-scaled composites.

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