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Research paper

Theoretical investigation of the weak interaction between graphene and alcohol solvents

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ABSTRACT

The dispersion of graphene in five different alcohol solvents was investigated by evaluating the binding energy between graphene and alcohol molecules using DFT-D method. The calculation showed the most stable binding energy appeared at the distance of ~3.5 Å between graphene and alcohol molecules and increased linearly as changing the alcohol from methanol to 1-pentanol. The weak interaction was further graphically illustrated using the reduced density gradient method. The theoretical study revealed alcohols with more carbon atoms could be a good starting point for screening suitable solvents for graphene dispersion.

1. Introduction

Graphene has attracted great attention as a novel 2D material in the last decade [1,2]. Thanks to the unique structure and outstanding mechanical, thermal and electrical properties, graphene has great potential application in varied areas such as electronics, optoelectronics and biomedicine [3–5]. The dispersion of graphene in solvents is an important issue because solvent is crucial for the liquid-phase-production and application of graphene [6,7]. The decoration of oxygen-containing groups can improve the dispersion [8,9], however, the thermal instability of graphene oxide due to the functional groups requires the dispersion of pristine graphene in solvents [10]. Coleman group achieved high-yield production of graphene by liquid-phase exfoliation of graphite in N-methylpyrrolidone (NMP) [11], but the high boiling point of NMP limits its usage. Browne et al. used a simple solvent exchange method to achieve the dispersion of graphene in ethanol from NMP, which can enable broader application of dispersed graphene [12]. Furthermore, theoretical calculations have also been carried out to investigate graphene dispersion in solvents. Coleman and co-workers conducted statistical analysis for the dispersion of graphene in 40 solvents and shown good solvents for graphene are characterized by Hildebrand and Hansen solubility parameters [13]. Blankschetin et al. found that the dominant barrier for graphene aggregation was the last layer of confined solvent molecules using molecular dynamics simulations [14].

The dispersion of graphene in solvent is related with the interaction between graphene and solvent molecules, therefore, DFT calculation should be crucial to study the dispersion of graphene in solvents [15–17]. However, there is lack of DFT work to investigate the interaction between graphene and solvent because the DFT calculation is inaccurate for London dispersion [18]. Recently Grimme et al. adopted the dispersion correction method (DFT-D) which could be used to accurately describe the London dispersion [19]. Furthermore, Yang and co-workers developed an approach to detect the weak interaction between molecules by calculating the reduced density gradient (RDG) [20]. These works provide new and accurate methods to study the weak interaction of graphene and solvent molecules.

To reveal the dispersion of graphene in alcohol solvents, DFT-D calculation was carried out to study the weak interaction between graphene and solvent molecules by varying the number of carbon atoms from one to five (i.e., methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol). The influence of dispersion correction and solvent molecule orientation on the weak interaction was demonstrated. The calculation revealed the binding energy of alcohol molecules on graphene was linearly related with the number of carbon atoms in the alcohol molecules. The RDG calculations graphically showed the weak interaction between graphene and alcohol molecules. According to the calculation, alcohols with more carbon atoms could be good candidates for graphene dispersion.

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2. Methods

The interaction between graphene and alcohol solvents is evaluated by calculating the binding energy (E_b) of alcohol molecules on a graphene fragment as reported in our previous work [16]. The graphene fragment contains 66 carbon atoms and 22 hydrogen atoms and the optimized C—C bond length is 1.43 Å which is consistent with previous research [21]. The graphene fragment is put in XY plane and the alcohol molecule is put at varied distance away from graphene surface in Z direction. The geometry of graphene and alcohol molecules are fixed in the calculation. E_b is obtained as

$$E_b = E_{m-graphene} - E_m - E_{graphene}$$

where E_m, $E_{graphene}$, and $E_{m\text{-}graphene}$ are the energy of an isolated molecule, graphene, and molecule-graphene system respectively.

The calculations were performed using the Gaussian 09 program [22] at the B3LYP/6-311+G(d,p) level, where the D3 dispersion correction was used to better describe the weak interaction between graphene and solvent molecules [23] and the PCM mode was applied to include the solvent effect [24]. The basis set superposition error (BSSE) was applied to correct the binding energy [25].

The D3 correction developed by Grimme et al. has been proved to give reasonable and accurate description for the weak interaction between molecules [23]. The dispersion energy could be calculated as

$$E_{disp}^{DFT-D3} = -\frac{1}{2}\sum_{A\neq B}\sum_{n=6,8} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{damp,n}(R_{AB})$$

where R_{AB} is the internuclear distance of an atom pair AB, C_n^{AB} is the averaged nth-order dispersion coefficient, s_n is the global scaling factor, $f_{damp,n}$ denotes the damping function used to determine the range of dispersion correction which is described as

$$f_{damp,n}(R_{AB}) = -\frac{1}{1+e^{-\gamma(R_{AB}/s_{r,n}R_0^{AB}-1)}}$$

where R_0^{AB} is a cut-off radius for atom pair AB.

The plots of the electron density (ρ) and reduced density gradient were generated using Multiwfn program [26].

3. Results and discussion

To evaluate the effect of dispersion correction on the interaction between alcohol molecule and graphene, the binding energy of ethanol or butanol molecule on graphene was investigated with or without the dispersion correction. In the calculation, the molecule was set as parallel to the graphene surface. As shown in Fig. 1a, the dispersion correction is quite crucial to describe the weak interaction between graphene and ethanol or butanol molecule. For ethanol molecule on graphene, the binding energy without the dispersion correction is 0.007 eV, and increases to be −0.271 eV after considering the dispersion correction, which agrees well with the results by Lazar's work [21]. The binding energy of butanol on graphene increases from −0.030 eV to −0.458 eV after dispersion correction. The results reveal that the DFT calculation gives poor description to van der Walls interaction, where the dispersion correction must be considered.

The orientation of molecule on graphene has significant influence on the binding energy. To demonstrate the influence, the binding energies of ethanol molecule with varied orientation on graphene are compared. Four typical orientations with optimal geometry are shown in Fig. 2. The result of binding energy is shown in Fig. 1b, which indicates the ethanol molecule with parallel orientation on graphene has the largest binding energy of −0.271 eV. As a comparison, the binding energies for the other three orientations are −0.257 eV, −0.139 eV and −0.186 eV respectively. The results for other alcohol molecules are similar, therefore, we focus on the alcohol molecules with parallel orientation on graphene in this work.

To investigate the interaction between graphene and alcohol molecules, we select five different alcohol molecules with carbon atom number from one to five, i.e., methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, with the orientation parallel to graphene. The binding energy at different sites of the graphene surface as a function of the distance between the weighted center of the molecule and the graphene surface is shown in Fig. 3a. The results clearly show that the most stable conformations all appear at the distance around 3.5 Å and the binding energy increases when the carbon atom number increases from one to five. Methanol molecule has the maximum binding energy of −0.185 eV, while it increases to −0.271 eV, −0.368 eV, −0.458 eV and −0.538 eV for ethanol, 1-propanol, 1-butanol, and 1-pentanol molecule respectively. Furthermore, the binding energy shows linearly relationship with carbon number in the molecule as shown in Fig. 3b. To be a good solvent for graphene dispersion and application, E_b should have a suitable value [16]. A small E_b would cause a serious aggregation of graphene in solvent because graphene sheets tend to agglomerate. However, a large E_b would result in the difficulty to remove solvent for graphene application. For a better comparison, we also calculated the binding energies for N,N-Dimethylformamide (DMF) and water molecule with graphene respectively, because DMF is a good solvent for graphene dispersion while water is not [16,27]. The result shows the binding energies for DMF and water are −0.44 eV and −0.095 eV respectively. As a result, alcohols with more carbon atoms could be a

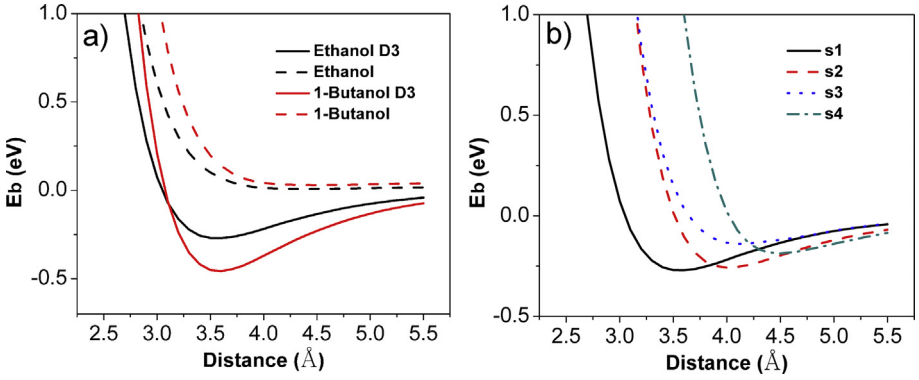

Fig. 1. (a) Binding energy (E_b) of ethanol and 1-butanol molecules at different sites of the graphene surface as a function of the distance between the weighted center of the molecule and the graphene surface. E_b is calculated with or without D3 correction. (b) E_b of ethanol molecules on graphene surface with different orientations.