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Defect-induced selective oxidation of graphene: A first-principles study

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ABSTRACT

Controlled oxidation of graphene is extremely important for nanopatterning and chemical functionalization. It is generally assumed in experiments that the oxidizing agent in the liquid-phase oxidation first attacks the defective sites in carbon lattices. To explore how the oxidation in the graphene sheet first begins, we have investigated the oxidization process with the structural defect using the density functional theory. Ten reaction pathways in the frame of the transition state theory are considered. We find that the most preferential reaction locus is located at the center of defect. It has also been observed that the preexistence of hydroxyl functional group on the graphene surface substantially decrease energy barrier for oxidization. Such facilitation of oxidation due to hydroxyl can explain how the oxidation process continues after its first oxidation around defects. The uneven redistributions of electron density caused both by defect and by the hydroxyl functional group account for the mechanism of the oxidization process on graphene sheet. Our calculation fully verifies the experimental assumption and is consistent with the recent experimental observations.

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1. Introduction

The outstanding one-atom-thick 2D graphene, which is composed of the flat sp^2 hybridized bonds, has been intensively studied due to its miraculous physical and chemical properties [1–5]. It can find a wide application in the field of electronics, new energies, next-generation materials and biomedicine [1–5]. Nonetheless, after more than one decade of intensive research, the practical application of graphene is still a big challenge. For example, the zero band gap of graphene [3] has hindered its performance in nano electronics [4,5]. The hydrophobicity of graphene [6] has become the barrier for its application in chemical reactions and biomedicine.

In order to achieve practical applications, much effort has been devoted to nanopatterning [7–9] or chemically functionalizing graphene [10,11] for tuning its properties. For instance, the lithographic patterning [12] or etching method [8,13] can tailor the graphene sheet down to the width of ten nanometers, which results in an open band gap [9]. In comparison with physics approach,

chemical functionalization [10,11] has a greater advantage because of the ease to scale up in the production. Controlled oxidation reactions are useful for shortening [14] or unzipping [15,16] carbon nanotubes(CNTs) into graphene nanoribbons. Besides, the oxidized graphene sheet can cut [17,18] the sheet into nano-sized pieces. During these chemical oxidation [15,19], how the oxidizing agent, such as potassium permanganate, leads to breaking the carbon lattice remains unclear. It is generally assumed in experiments [14,15,17–19] that the initial attack of the oxidizing agent starts from the defective site of lattices. The defect-induced oxidization of graphite by the oxygen atoms or molecules has been studied [20–26] for the gas-phase oxidation. However, how the oxidizing agent in experiments [14,15,17–19], such as potassium permanganate, first induces the oxidation of the carbon lattice has not been investigated, which is crucial for chemical patterning or cutting of graphene.

In this paper, our results from first-principles calculations focus on the following two issues: (i) where the oxidizing agent triggers the oxidation reaction on graphene sheet (ii) and how the oxidation proceeds after the first oxidization attack. To understand the oxidation process with the oxidizing agent in experiments, we here study ten reaction pathways around the defective sites on graphene sheet from the transition state theory using the density functional method. We find that the Stone–Wales(SW) defect in graphene

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Table 1
Thermodynamic parameters and the reaction rate for the ten pathways of oxidization.

Type	Path	E_b (kcal/mol)	k_i/k_I	E_r (kcal/mol)	ΔG (kcal/mol)
The pristine	Path I	38.38	1.00	31.42	42.87
With −OH	Path II	10.35	1.05×10^{21}	−1.55	11.63
With the SW defect	Path III	12.30	4.26×10^{20}	−2.25	10.79
	Path IV	16.25	3.52×10^{16}	−9.44	3.16
	Path V	27.78	7.64×10^7	11.98	24.10
	Path VI	18.04	1.93×10^{15}	−7.51	5.69
With both the SW	Path VII	5.22	1.82×10^{24}	−7.76	−4.35
defect and −OH	Path VIII	4.24	1.69×10^{25}	−2.12	8.80
	Path IX	2.10	6.18×10^{25}	−2.58	8.30
	Path X	2.96	2.64×10^{25}	−25.29	−12.31

sheet can considerably reduce energy barrier for oxidation and enhance reaction rate significantly. The most preferential reaction site is identified among ten different reaction pathways. It is also observed that the preexistence of hydroxyl functional group on the graphene surface can substantially facilitate the reaction and thus promotes the continuous oxidation. Our calculations have clarified the problem where the oxidation on the graphene sheet begins and demonstrated how this reaction process continues. The results qualitatively agree with the recent experimental [19] observations.

2. Models and computational details

To model the oxidization process on the graphene, we first consider a pristine graphene sheet $C_{50}H_{18}$ with the fifty carbon atoms saturated by the hydrogen atoms at the edges as shown in Fig. 1(a). The termination of the hydrogen atoms at the edges [21] is reduce the size effect.

Experimental and theoretical studies [27–32] have shown that the main oxidizing agent [29] is MnO_4^- for oxidation processes of C=C bonds and also demonstrate that the first step of the reaction of MnO_4^- with the C=C bond is the key and rate-limiting step. Since the oxidation reactions of MnO_4^- with either alkenes or graphene involve the breaking of C=C bonds, we here design the reaction processes of graphene oxidation by the oxidizing agent MnO_4^- to mimic the oxidation of graphene sheet.

To further explore the oxidization process with the structural defects of graphene, we consider a graphene sheet with the Stone–Wales(SW) defect [33–35], which is generated by rotating one of sp² bonds with 90° as illustrated in Fig. 1(b). In order to eliminate the impact of high symmetry, we employ the unsymmetrical geometry of the graphene sheet in Fig. 1(b), where the SW defect is not located in the center. There may also be other types of defects [33–35] such as vacancies etc. But the dangling bonds in vacancies will become the formation of pentagons [35] after optimization. Thus we focus on oxidation of the pentagon defect here. In addition, there usually exists some pre-oxidized groups [27–30] like −OH and −O− on the surface in the realistic oxidization process such as the Hummers approach [36]. To simulate the continuous oxidation, we therefore have investigated the reaction processes of graphene oxidation by MnO_4^- with the pre-existence of the oxidized groups −OH as schematically shown in Fig. 1(c).

During our calculations, the reactions between the MnO_4^- ion and the graphene sheet were simulated using the B3LYP functional [37] with the mixed basis set 6-31G(d)/LANL2DZ. The 6-31G(d) [38] basis set was employed for the O, C, and H atoms. Due to the presence of the transitional metal Mn atom, we choose the pseudopotential-based basis set LANL2DZ [39–41] for the manganese. The self-consistent field (SCF) tolerance is set to 1.0×10^{-5} hartree. The B3LYP/6-31G(d) approach has been commonly used in carbon-based nanostructures [42] and can predict qualitatively correct values of reaction energies or barriers in carbon fragments. We have further tested the reliability of the chosen

B3LYP/6-31G(d)/LANL2DZ approach and the SCF tolerance during our simulation. All the calculations were performed in the Gaussian 09 package [43].

First, all geometrical configurations of graphene sheet (including functional group −OH) and the oxidation agent MnO_4^-, as well as the product of their complex, are separately optimized. Then we calculate their vibrational frequencies to make sure that there is no negative vibrational frequency in all optimized configurations and that the convergence of minimum structural energy is reached. The transition-state theory [44] is further utilized to analyze the reaction mechanism of graphene oxidation by permanganate (MnO_4^-). The transition state is verified by visual inspection of the vibration modes and is confirmed to have only one imaginary frequency. Another calculation of the intrinsic reaction coordinate (IRC) is also performed to identify the minimum energy reaction pathway. The reaction energy E_r is obtained by subtracting the energy of reactants from the energy of products while the energy barrier E_b is the energy difference between the transition-state and the corresponding reactants. The change of Gibbs free energy ΔG between the reactants and the products is also derived to illustrate the spontaneity of reaction. To compare the rate of reaction among different reaction pathways, the reaction rate constant k is calculated [44] with the formula $k = \kappa \cdot (k_B T/h)(Q_{ts}/Q_r)exp(-E_b/RT)$. Here E_b is the energy barrier and T is the reaction temperature. The notation k_B, h and R denote the Boltzmann constant, the Planck constant and the universal gas constant, respectively. The tunneling correction κ is estimated as $\kappa T = 1 + \left(h\nu^{\neq}/k_B T\right)^2/24$ using the Eckwart potential, where $\nu^{\neq}$ is the imaginary vibrational frequency of the transition state. The Q_{ts} and Q_r are the partition function for the transition-state structure and the reactants, respectively. They are thermodynamically defined as $Q_{ts,r} = \prod_n \exp(-h\nu_n/(2k_B T))/(1 - exp(-h\nu_n/(k_B T)))$, where ν_n is the frequency of each vibrational mode.

3. Results and discussion

To illustrate the oxidization process in the frame of the conventional transition state theory, the relevant structures of reactants, transition state and products of the oxidation of pristine graphene for Path I as an example are shown in Fig. 2, respectively. Although small distortions of geometry exist in the product of graphene sheet with the presence of the SW defect, we have verified such deformation is not very serious in $C_{50}H_{18}$ because of the hydrogen termination of the graphene sheet.

The calculated energy profiles for the oxidation reaction by MnO_4^- are demonstrated in Fig. 3, including the oxidation of the intact pristine grapheme (Path I), the graphene surface with the pre-oxidized hydroxyl groups at the first-neighbor site of oxidation loci (Paths II), the graphene surface with the SW defects (Path III–VI)