



## Si Doping Induced Hydrophobic to Hydrophilic Transition on Graphene: a First Principles Study

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The dissociative adsorption of a H<sub>2</sub>O molecule on Si-doped graphene is investigated by using first principles calculations. It is found that the dissociative energy barrier is reduced from 3.6 eV on pristine graphene to 0.5 eV on Si-doped graphene, which indicates that this dissociative adsorption can occur smoothly at room temperature. Therefore, doping Si into graphene can convert graphene from hydrophobic to be hydrophilic, which is important for its potential applications in electronic devices.

### 1. Introduction

Graphene has attracted enormous interests due to its novel electronic, thermodynamic and mechanical properties since it was first experimentally fabricated in 2004 [1]. The potential applications of graphene significantly depend on the surface wettability, which is mainly determined by the hydrophobic/hydrophilic character. It is well known that graphene is strongly hydrophobic. The hydrophobic graphene surface can reduce possible liquid deposition and prevents contamination of advanced nanoelectromechanical systems. However, controllable manipulation of the hydrophilic properties of graphene has plenty of applications, such as electrode materials of supercapacitors [2] and biomaterials supports [3].

Some groups have reported on controlling the hydrophilicity of graphene films by changing the concentration of water and acetone during synthesis [4]. However, the process mentioned above is complicated and needs further improvements. It is well known that doping of graphene is usually applied to tune the reactivity of graphene [5]. Since the H<sub>2</sub>O molecule can dissociate on SiC, we expect that doping Si may induce the change of the wettability of graphene due to the production of hydrophilic OH group [6]. In this work, we perform a systematic density functional theory (DFT) calculations on the dissociative adsorption of a H<sub>2</sub>O molecule on graphene doped with Si to understand the doping effect on the wettability of graphene.

### 2. Calculation methods

All calculations are implemented by Dmol<sup>3</sup> code [7]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional is employed to describe exchange and correlation effects [8]. A double numerical plus polarization (DNP) is employed as the basis set. The convergence tolerance of energy of 10<sup>-5</sup> Ha is taken (1 Ha = 27.21 eV), and the maximal allowed force and displacement are 0.002 Ha and 0.005 Å, respectively. It was reported that the selection of exchange-correlation functional has small effect on the calculated energy barriers [9]. Linear synchronous transition/quadratic synchronous transit (LST/QST) [10] and nudged elastic band (NEB) [11] tools in Dmol<sup>3</sup> are used to investigate the minimum energy pathway for water dissociative adsorption on

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graphene. The simulation cell consists of a 4×4 graphene supercell with a vacuum width of 20 Å above the layer to minimize the interlayer interaction. The  $k$ -point is set to be 5×5×1, and all atoms are allowed to relax according to previous reports. The DFT+D method within the Grimme scheme is used to consider the van der Waals forces [12].

For a H<sub>2</sub>O adsorbed on graphene before and after dissociative adsorption, the adsorption energy  $E_{ad}$  is determined by,

$$E_{ad} = E_{\text{H}_2\text{O}/\text{graphene}} - (E_{\text{graphene}} + E_{\text{H}_2\text{O}}) \quad (1)$$

where  $E_{\text{H}_2\text{O}/\text{graphene}}$ ,  $E_{\text{graphene}}$  and  $E_{\text{H}_2\text{O}}$  are total energies of the H<sub>2</sub>O/graphene system, the isolate graphene and a H<sub>2</sub>O molecule in the same slab, respectively.

### 3. Results and discussion

#### 3.1 The geometric structure of graphene

The atomic structure before and after Si doping is shown in Fig. 1. It is shown that the Si atom replaces one C atom and moves out of the plane graphene as shown in Fig. 1(b). The distance between dopant atom and graphene is  $h_{\text{Si}} = 1.20$  Å, which is consistent with the reported result with  $h_{\text{Si}} = 1.457$  Å [13]. The C-Si bond length is  $l_{\text{C-Si}} = 1.76$  Å, which was reported to be 1.767 Å [14]. In addition, Fig. 1 also shows the atomic charge near the doped Si atom obtained by Mulliken analysis. It is shown that the Si atom is positive charged and forms an electron-deficiency position. Therefore, Si atom changes the electron distribution in graphene, and thus changes the reactivity for the interaction between small molecules and graphene.

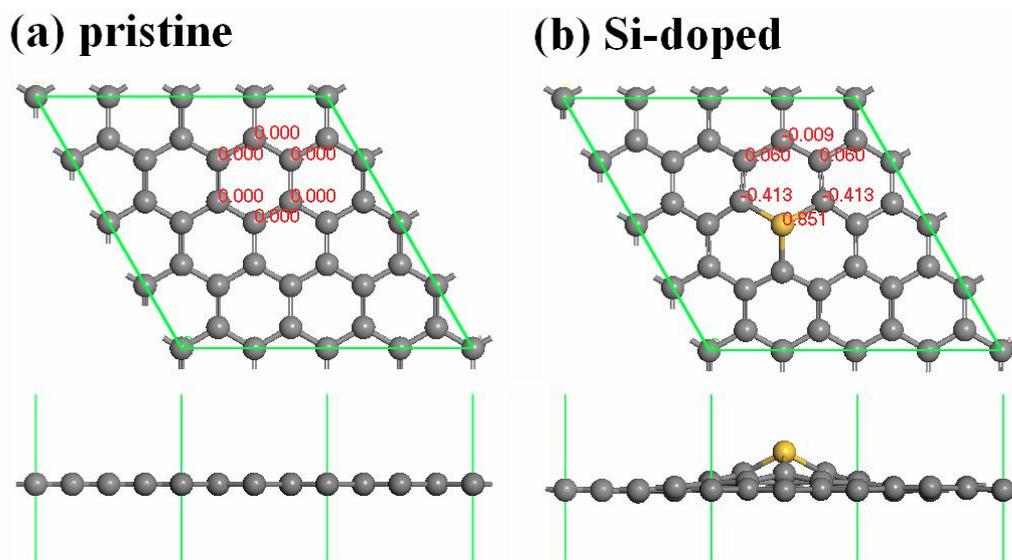


Fig. 1. The most stable configurations of pristine graphene (a), and Si-doped graphene (b). The atomic charge near the dopant obtained by Mulliken analysis is also given. The grey and yellow atoms are C and Si, respectively.

#### 3.2 Dissociative adsorption of a H<sub>2</sub>O molecule on pristine graphene

For a H<sub>2</sub>O molecule adsorption on pristine graphene, the favorable adsorption site of the H<sub>2</sub>O is at the hollow site with two OH bonds pointing down to the graphene surface with adsorption energy of -0.1 eV as shown in the Fig. 2(a), which is consistent with Ref. 15. This configuration is adopted as the initial structure in the subsequent transition state search calculations. For the H<sub>2</sub>O dissociative adsorption on graphene, the most favorable



configuration is that H and OH are chemisorbed on the face-by-face carbon atoms in the six-member ring with adsorption energy of 2.5 eV, as shown as the FS in Fig. 2(a). After LST/QST and NEB calculations, it is found that the reaction barrier  $E_{\text{bar}}$  is 3.6 eV. This  $E_{\text{bar}}$  value is similar to the reported result of 3.599 eV [16]. Therefore, the dissociative adsorption of water on pristine graphene is difficult and the pristine graphene is strongly hydrophobic.

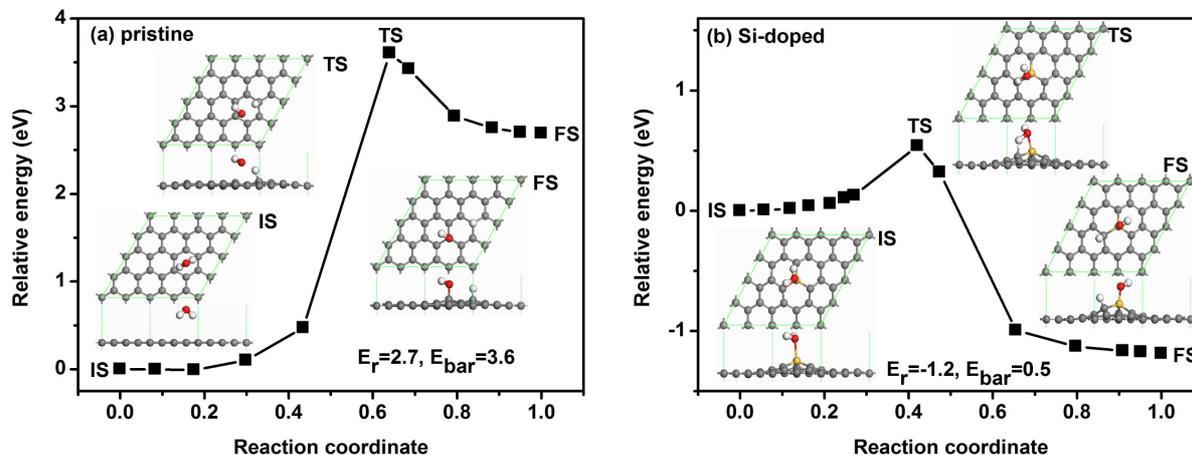


Fig. 2. The reaction pathway of a  $\text{H}_2\text{O}$  molecule dissociative adsorption on pristine and doped graphene. IS, TS and FS represent initial structure, transition structure and final structure, respectively. The energy of IS is taken to be zero. The units of  $E_{\text{bar}}$  and  $E_r$  are eV, where  $E_{\text{bar}}$  is the energy barrier and  $E_r$  is the reaction energy. The grey, white, red and yellow atoms are C, H, O, Si in this figure and below, respectively.

### 3.3 Dissociative adsorption of a $\text{H}_2\text{O}$ molecule on Si-doped graphene

The obtained adsorption energy  $E_{\text{ad\_IS}}$  between a  $\text{H}_2\text{O}$  molecule and the Si-doped graphene is -0.4 eV and the Si-O bond length  $D_{\text{Si-O}}$  is 2.126 Å, which indicates that the  $\text{H}_2\text{O}$  molecule chemically binds to the Si atom on Si-doped graphene as shown as IS in Fig. 2(b). This structure is the initial structure in the subsequent transition state search calculations as shown in Fig. 2(b). For the dissociative adsorption of  $\text{H}_2\text{O}$  molecule on the Si-doped graphene, the adsorption energy  $E_{\text{ad\_FS}}$  for the dissociative chemical adsorption is -1.7 eV and this structure is the final structure (FS) in Fig. 2(b). It is found that the Si atom transfers electrons to the C atoms nearby and is positively charged as shown in Fig. 1(b), which is preferable for the adsorption of negatively charged OH. Meanwhile, C atoms near the dopant with negative charges are preferable for the adsorption of positively charged H atom, which makes the dissociative adsorption of the  $\text{H}_2\text{O}$  molecule on graphene more stable.

After LST/QST and NEB calculations, the detailed reaction pathway and the energy barrier for the dissociative adsorption of a  $\text{H}_2\text{O}$  molecule on the Si-doped graphene system is shown in Fig. 2(b). It is found that  $E_{\text{bar}}$  of the electron-deficiency system doped with Si dopant decrease from 3.6 eV in pristine graphene system to 0.5 eV. In addition, the reaction process is exothermic on Si-doped graphene with negative reaction energy  $E_r$  of -1.2 eV. It has been reported that surface reactions at ambient temperature may occur when  $E_{\text{bar}} < 0.75$  eV [17]. We also consider the larger doping concentration of 12.5% with  $2 \times 2$  graphene supercell, which shows that the dissociative energy barrier of  $\text{H}_2\text{O}$  on doped graphene is 0.6 eV. Under this doping concentration, the entire graphene surface can be considered being hydrophilic, while the basic lattice parameters of graphene remain. Therefore, doping Si into graphene can facilitate the dissociative adsorption of  $\text{H}_2\text{O}$  on graphene, which induces the transition of graphene from hydrophobic to hydrophilic spontaneously at room temperature.

## 4. Conclusion



In summary, the effect of Si dopant on the dissociative adsorption of H<sub>2</sub>O molecules on graphene is investigated by using first principles calculations. The Si-doped graphene can efficiently decrease the dissociative barrier of H<sub>2</sub>O molecules on graphene and change the wettability of graphene from hydrophobic to hydrophilic spontaneously at room temperature, which is important for its potential applications, such as in supercapacitors and biomaterials.

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