



## Effect of External Electric Field on the Application of Graphene

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External electric field, which is often encountered in practical applications, can induce substantial alterations in materials with respect to chemical potentials and electronic properties. In this work, based on first-principles calculations, it presents the effect of an external electric field on inducing the dissociative adsorption of H<sub>2</sub> and H<sub>2</sub>O molecules for the application of graphene as hydrogen storage materials and in electronic devices, respectively.

### 1. Introduction

Graphene with unique electronic, thermal, and mechanical properties, has been regarded as one of the most promising candidates for the next generation of electronic materials and hydrogen storage materials [1]. Pristine graphene is not a good hydrogen storage material because of the very weak interactions between hydrogen and graphene through the van der Waals interaction [2]. Hydrogenation of graphene is alternative promising way to store atomic hydrogen with hydrogen storage capacity up to 7.7 wt%. In addition, hydrogenation of graphene can also open the band gap of graphene, which is desirable for its application in electronic devices [3-5]. However, the hydrogenation reaction has high energy barrier [4], which we are trying to reduce in this work. In addition, in some application, for example as electrode materials of supercapacitors and as biomaterials supports, it is desirable that graphene is hydrophilic in order to improve the wetting between graphene and polar electrolytes or biological molecules [6,7].

External electric field  $F$ , which is often encountered in practical applications, could induce substantial alterations in materials with respect to their geometry, binding energies, vibrational spectra, chemical potentials and electronic properties [8]. For example, Zhou et al. found that the H-C bond in graphane could increase under an electric field, and finally H atoms at one side of graphane would be desorbed with increasing  $F$  [9]. Therefore, based on density functional theory (DFT) calculations, external electric field is considered in this work to apply to the graphene system to seek the possibility of lowering the energy barrier of hydrogenation and facilitating the transition of graphene from hydrophobic to hydrophilic through the dissociative adsorption of H<sub>2</sub>O molecules on graphene.

### 2. Computational Methodology

The DFT calculations were performed using the DMOL3 code [10]. The generalized gradient approximation (GGA) with revised Perdew-Burke-Ernzerhof (RPBE) functional was employed as the exchange-correlation functional [11]. A double numerical plus polarization (DNP) was used as the basis set, while the DFT semicore pseudopotentials (DSPP) core treatment was employed to include relativistic effects that replaces core electrons by a single effective potential. Spin polarization was considered in the calculations. The convergence tolerance of the energy was set to 10<sup>-5</sup> Ha (1 Ha = 27.21 eV), and the maximum allowed force

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and displacement were 0.02 Ha and 0.005 Å, respectively. To investigate the dissociative adsorption of H<sub>2</sub> or H<sub>2</sub>O molecules on graphene surface, linear synchronous transition /quadratic synchronous transit (LST/QST) [12] and nudged elastic band (NEB) [13] tools in the DMOL3 code were used. These methodologies have been demonstrated as fantastic tools to search for the structure of the transition state (TS) and the minimum energy pathway. In the simulations, three-dimensional periodic boundary conditions were imposed, and all the atoms are allowed to relax. We minimized the interlayer interaction by allowing a vacuum width of 18 Å normal to the layer. The supercell used to investigate the dissociative adsorption of H<sub>2</sub> and H<sub>2</sub>O molecules on graphene is shown in Figs. 1 and 3, respectively. Different size of supercell is used for two reactions for demonstrating the results clearly. The size of the supercell has only very limited effect on the final results.

### 3. Results and discussion

#### A. Electric field induced hydrogenation of graphene

Fig. 1 shows the favourite atomic structure before and after hydrogenation. Before hydrogenation, the H<sub>2</sub> molecule is physically adsorbed at the hollow site of graphene as shown in Fig. 1(a). The distance between the H<sub>2</sub> molecule and the graphene layer  $d_{\text{H}_2\text{-graphene}}$  is 2.612 Å with adsorption energy  $E_{\text{b-H}_2} = -0.153$  eV, which are consistent with other simulation results of  $d_{\text{H}_2\text{-graphene}} = 2.635$  Å and  $E_{\text{b-H}_2} = -0.159$  eV in Ref. [2]. For the case of atomic hydrogen adsorption on graphene, the favourable configuration is two H atoms adsorbed on two face-by-face carbon atoms in the same hexagon as shown in Fig. 1(b), which is consistent with the reported DFT result [14].

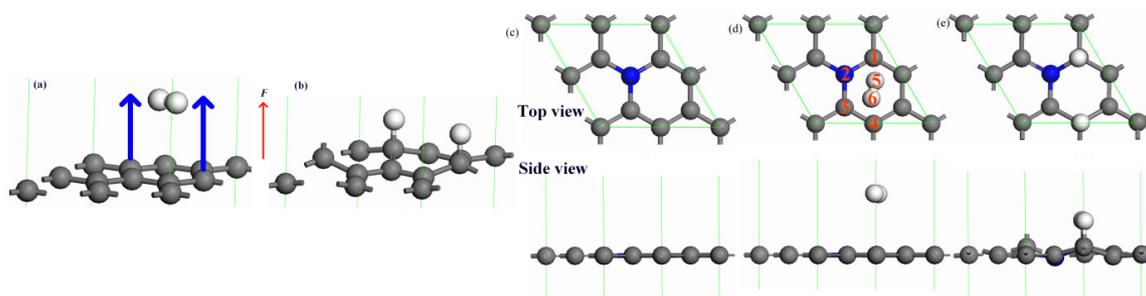


Fig. 1. The atomic structure of a H<sub>2</sub> molecule physical adsorption on pristine graphene (a), dissociative adsorption on pristine graphene (b), N-doped graphene (c), a H<sub>2</sub> molecule physical adsorption on N-doped graphene (d), and dissociative adsorption on N-doped graphene (e). The gray, white and blue balls are C, H and N atoms, respectively. The direction of the electric field is indicated by the arrow.

The energy minimum pathway for a H<sub>2</sub> molecule dissociative adsorption on graphene, that is from the structure of Fig. 1(a) to that of Fig. 1(b), is shown in Fig. 2(a). This dissociative adsorption reaction barrier  $E_{\text{bar}}$  is 2.734 eV, which is a little smaller than 3.3 eV found by others [14]. Regarding TS, the H<sub>2</sub> molecule is dissociated into two free H atoms without any binding with the C atoms. From Fig. 2(a), it is known that this reaction requires two steps: the H<sub>2</sub> molecule is dissociated into two free H atoms, then the two H atoms are bound to the two C atoms. Step one needs an energy of 2.7 eV to overcome the barrier and the second step releases an energy of 1.9 eV. Therefore, the dissociation of H<sub>2</sub> is the rate-limiting step, hydrogenation of graphene is very difficult to realise due to the high energy barrier.

The effect of electric field on this reaction is investigated. The results show that  $E_{\text{bar}}$  decreases as the intensity of  $F$  increases. When  $F$  reaches -0.02 au (1 au =  $5.14 \times 10^{11}$  V/m),  $E_{\text{bar}}$  is negative to be -0.222 eV as shown in Fig. 2(b), which means that there is no energy barrier from IS to state 2. Thus, such a negative electric field can act as a catalyst to significantly speed up the hydrogenation process of graphene. However, the second step that two H atoms chemically adsorb on C atoms requires a high energy, which prevents the



hydrogenation of graphene. Alternatively, the free H atoms are considered to automatically bind with the C atoms once removing the electric field after H<sub>2</sub> dissociation since there is no potential barrier after TS as shown in Fig. 2(a). In addition, experiment has also indicated that the graphene layer can be automatically hydrogenated by free H atoms [15].

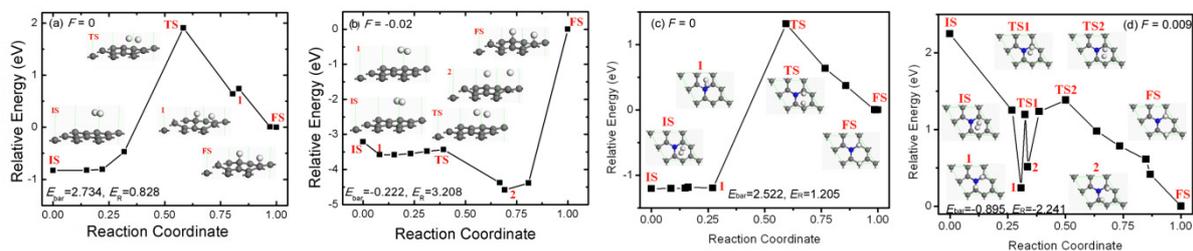


Fig. 2. The reaction pathway of a H<sub>2</sub> molecule that undergoes a dissociative adsorption on pristine and N-doped graphene under different electric field. (a) and (b) in pristine graphene system, (c) and (d) in N-doped graphene system. IS, TS, FS, and 1 and 2 represent initial structure, transition structure, final structure, and energy minimum states 1 and 2, respectively. The energy of FS is taken to be zero. The unit of  $F$ ,  $E_{\text{bar}}$ , and  $E_{\text{R}}$  are atomic unit and electron volt, respectively, where  $E_{\text{bar}}$  is the energy barrier and  $E_{\text{R}}$  is the reaction energy.

Doping N into carbon nanotube was reported to reduce the energy barrier of hydrogen molecule adsorption [16]. Therefore, the effect of N doping of graphene on the dissociative adsorption of a H<sub>2</sub> molecule is considered here. The favourable atomic structure of N-doped graphene, a H<sub>2</sub> molecule physical adsorption of N-doped graphene, and a H<sub>2</sub> molecule dissociative adsorbed on N-doped graphene is shown in Figs. 1(c)-1(e). It shows that the planar structures remain after N doping and with H<sub>2</sub> physical adsorption, and the H<sub>2</sub> molecule is located on the hollow site of the carbon hexagon. Fig. 2(c) shows the pathway of the H<sub>2</sub> molecule dissociative adsorption on N-doped graphene.  $E_{\text{bar}}$  is 2.522 eV, which is a little smaller than 2.734 eV for the H<sub>2</sub> molecule dissociative adsorption on pristine graphene. When considering the electric field effect, we find that  $F$  reduces the barrier significantly. When  $F = 0.009$  au as shown in Fig. 2(d), both  $E_{\text{bar}}$  and  $E_{\text{R}}$  are negative. Therefore, the electric field can induce molecular hydrogen dissociative adsorption in the N-doped graphene. In other words, the electric field and N doping are catalyzers for graphene hydrogenation.

## B. Electric field manipulated reversible transition from hydrophobic to hydrophilic

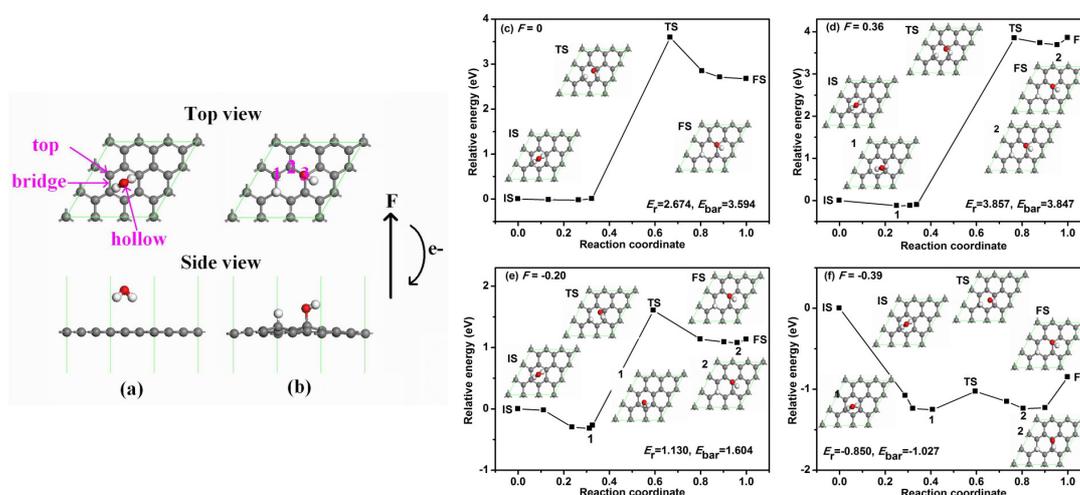


Fig. 3. Initial (a) and final structure (b) for a H<sub>2</sub>O molecule dissociative adsorption on graphene. Reaction pathway of a H<sub>2</sub>O molecule dissociative adsorption on graphene under different electric field,  $F = 0$  (c),  $F = 0.36$  (d),  $F = -0.2$  (e), and  $F = -0.39$  (f). The red balls are O atoms. The unit of  $F$  is  $\text{V}/\text{\AA}$ .

To understand the transition of graphene from hydrophobic to hydrophilic, which is



induced by the dissociative adsorption H<sub>2</sub>O molecules on graphene, the reaction is studied by DFT calculations. The initial structure is shown in Fig. 3(a) where a H<sub>2</sub>O molecule is physically adsorbed at the hollow site of C ring, while the final structure is shown in Fig. 3(b) where the H atom and HO group take the two face by face sites. The reaction pathways under different electric field are also shown in Fig. 3. It is known that the reaction barrier for the H<sub>2</sub>O molecule dissociative adsorption is as high as 3.594 eV when without electric field as shown in Fig. 3(c). However, in the presence of an negative electric field as shown in Figs. 3(e) and 3(f), both  $E_{\text{bar}}$  and  $E_r$  decrease and they are even to be negative when  $F = -0.39 \text{ V/\AA}$ . The presence of the chemically adsorbed hydrophilic OH group makes graphene hydrophilic. When removing the electric field after dissociative adsorption, the reaction of  $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$  is considered, which is from FS to IS in Fig. 3(c). The reaction barrier and reaction energy are  $E_{\text{bar}} = 0.921 \text{ eV}$  and  $E_r = -2.534 \text{ eV}$ , respectively. As  $E_{\text{bar}} > 0.75 \text{ eV}$ , which is believe that this reaction hardly occurs at ambient temperature. However, if a positive electric field is applied as shown in Fig. 3(d),  $E_{\text{bar}}$  and  $E_r$  of the reaction from FS to IS are respectively  $-0.006$  and  $-3.717 \text{ eV}$ . Therefore, the electric field can act as the switch to realise the reversible transition of graphene from hydrophobic to hydrophilic.

#### 4. Conclusion

The dissociative adsorption of a H<sub>2</sub> and a H<sub>2</sub>O molecule on graphene is investigated through DFT calculations for its potential application as hydrogen storage materials and in electronic devices. It is found that applying an external electric field can act a catalyst for the hydrogenation of graphene, which is a promising way to store hydrogen in its atomic form. Applying an external electric field can also induce the dissociative adsorption of H<sub>2</sub>O molecules on graphene to realise the reversible transition of graphene from hydrophobic to hydrophilic, which is essential for applications in supercapacitors and in biomaterial supports.

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