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Theoretical study on the removal of adsorbed sulfur on Pt anchored graphene surfaces

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ABSTRACT

The adsorption and dissociation reactions of hydrogen sulfide (H_2S) on the Pt atom anchored graphene (Pt-graphene) surfaces were investigated by first-principles calculations. It is found that the atomic S has stronger interaction with the Pt atom, while the SH and H_2S species are weakly bound on the Pt-graphene surfaces. The adsorption of S-based species can regulate the electronic structure and magnetic properties of Pt-graphene systems. Besides, the calculated results show that the formation of SH and H from the H_2S ($H_2S \rightarrow SH + H$) is rather easy and further the hydrogenation reaction generates the hydrogen molecular (H_2), as well as leaving the SH anchors on the Pt atom ($SH + H + H \rightarrow SH + H_2$). Moreover, the preadsorbed S atom with the presence of H atoms can be converted into other species (SH or H_2S) and thus inhibit the sulfur deposition on the Pt-graphene surfaces, which is expected to prevent the sulfur poisoning on graphene-based anode materials and boost the efficiency of fuel cells.

Introduction

Fuel cell is considered to be an attractive alternative to conventional power generators, due to its high efficiency in energy production and low degree of pollution emission [1,2]. Many fuels contain sulfur in different forms and concentrations, which is converted into gaseous hydrogen sulfide (H_2S) upon reforming [3]. The S-based species tend to accumulate on the active sites and increase the resistance to electrochemical oxidation of the fuel [4–6]. Further, the strongly binding of sulfur compound and small activation energies in the decomposition reaction of H_2S make the sulfur poisoning a serious problem on the anode materials [7]. So, it is essential to identify the incipient surface phases resulted from the poisoning process and consequently find the way to avoid sulfur poisoning.

As we know, the decomposition of H_2S is the most dominating step in the sulfidation process, and sulfur deposition can be effectively reduced by preventing the adsorption and

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dissociation of H_2S [8]. To overcome sulfur poisoning, the researchers investigated the reaction mechanisms of adsorption, diffusion, and dissociation of H_2S molecule on different metal surfaces [9–12]. Some studies focused on the new materials that can enhance the resistance against sulfur poisoning [5,8,13]. Graphene as a novel carbon allotrope exhibits many fascinating physical and chemical properties [14–16]. The catalysts are desired to disperse finely on graphene-based materials [17–20], because the graphene-supported catalysts display high catalytic activity as compared with the traditional metal substrates [21], which have wide applications in spintronic devices, gas sensors and catalytic electrodes [22–26].

Generally, the platinum (Pt) as electrode catalysts exhibit high activities in methanol oxidation reactions [27–29]. Especially, graphene-supported Pt catalysts as anode materials show high electrocatalytic activity and long-term durability [18,30–32]. Recently, the experimental results shown that the single metal atom can be successfully doped in graphene [33,34]. The metal Pt impurities in graphene exhibits the high stability [35,36] and chemical reactivity [37]. For example, the single-atom Pt anchored on different graphene substrates displays high catalytic property for CO oxidation [38–40]. Hence, the Pt-graphene complex is expected to guide the development of new sulfur-tolerant anode materials.

Although the newly developed materials for sulfur-tolerance are still focused on the traditional Ni/YSZ (yttria-stabilized zirconia) cermet anodes [3,41], it is desirable to gain a better understanding about the reaction mechanism of sulfur-based species (including H_2S, SH and S) on graphene substrates. Recently, the sensing performances [42,43] and catalytic decomposition of H_2S into gaseous S [44] and hydrogen (H_2) on semiconductor [45,46] or metal substrates [47] were performed, yet there is a lack of study on the adsorption stability and formation processes of H_2S and its intermediates (SH, S and H) on metal-graphene complex.

In this work, we explored the role of single-atom Pt anchored graphene surfaces (Pt-graphene) in the formation and dissociation mechanisms of H_2S molecule. The adsorption energies, electronic structures and magnetic properties of H_2S and its various intermediates (SH, S and H) on the Pt-graphene surfaces were investigated. At the anode, the fuels are oxidized, releasing H^+ ions, which may affect the predicted reaction pathway and generate products. To the best of our knowledge, only a few theoretical studies have been reported about the reaction mechanism between H_2S and its intermediates on the metal-graphene complex, which would be useful on designing the S-resistant catalysts.

Computational model and methods

Spin-polarized density functional theory (DFT) calculations were performed by the Vienna *ab initio* simulation package (VASP) [48,49] with the projector augmented wave (PAW) pseudo-potentials [50] and the generalized gradient approximation of Perdew, Burke, and Ernzernhof (PBE) function [51]. The C $2s^2 2p^2$, Pt $5d^9 6s^1$, S $3s^2 3p^4$ and H $1s^1$ states are treated as valence electrons. The Kohn-Sham orbitals were expanded in terms of plane waves basis sets with an energy cutoff of 450 eV, and the convergence criterion for the electronic self-consistent iteration was set to 10^{-5} eV. The graphene layer and the adsorbates are free to relax until the self-consistent force drops to below 0.02 eV $Å^{-1}$. The distance between the graphene sheet and its images is set to 15 Å, which leads to negligible interactions between the systems and their mirror images. As references, the geometrical parameters of H_2S, SH and S were computed in a 15 × 15 × 15 $Å^3$ cubic box. The calculated lattice constant of graphene is 2.47 Å, which quite approximates to the experimental value of 2.46 Å [52]. The optimized C–C bond lengths are 1.43 Å. The graphene supercell was then built based on the calculated lattice constant. The graphene sheet was represented using a hexagonal supercell containing 32 carbon atoms, with a *p* (4 × 4) structure in the *x*-*y* plane. The Brillouin zone integration was sampled using a 3 × 3 × 1 Γ-centered Monkhorst-Pack (MP) grid and a Γ-centered MP grid of 15 × 15 × 1 was used for the final density of states (DOS) calculations.

Bader charge analysis [53] was used to evaluate the atomic charges and electron transfer in the reactions. Adsorption energies and site preferences for each type of H_2S, SH, S and H were tested on the Pt-graphene surfaces, and the corresponding most favorable configurations are shown in Fig. 1. The climbing image nudged elastic band method (CI-NEB) [54–56] was employed to investigate the saddle points and minimum energy paths (MEPs) for the reaction pathways and barriers of reactive adsorbates on the substrate. A number of intermediate images are constructed along the reaction pathways between the initial state (IS) and the final state (FS), and the spring force between adjacent images was set to be 5.0 eV $Å^{-1}$. Images are optimized until the forces on each atom are less than 0.02 eV $Å^{-1}$. The energy barriers are calculated using the initial state as a reference.

The adsorption energy (E_{ads}) of one atom or molecule (*A*: Pt, H_2S, SH and S) on a substrate (*B*: graphene or Pt-graphene) is calculated by the following expression:

$$E_{ads} = E_A + E_B - E_{AB} \quad (1)$$

where $E_{A(B)}$ represents the total energy of *A* (*B*), and E_{AB} represents the total energy of the system with adsorbate(s).

Results and discussion

Adsorption geometry and stability

We have explored various possible adsorption sites of each adsorbate (including H_2S, SH or S) on Pt-graphene surfaces, and the corresponding configurations and adsorption energies (E_{ads}) are shown in Fig. 1 and Table 1. For the Pt/pri-graphene, it is found that H_2S molecule favors an adsorption pattern with the S atom adsorbs on the top site of Pt atom (E_{ads} = 0.59 eV) and the corresponding adsorption height (the vertical distance between gas molecule and Pt atom, $d_{Pt\text{-}gas}$) is 2.20 Å, as shown in Fig. 1(a). The H–S–H angle (97.7°) of the adsorbed H_2S is slightly changed as compared to the free H_2S molecule (91.5°). As shown in Fig. 1(b)–(c), the adsorbed SH and S are placed at the top sites of the Pt atom with large E_{ads} (3.32 and 4.17 eV), and the corresponding $d_{Pt\text{-}gas}$ is 2.19 and 2.11 Å, respectively. Bader charge analysis shows that the