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Synergistic effect of nitrogen and sulfur co-doped graphene as efficient metal-free counter electrode for dye-sensitized solar cells: A first-principle study

Yang Liu *, Yanxiang Wang, Xiaonan Zheng, Ya Wang

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150080, People's Republic of China

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ABSTRACT

The carbon materials, as one of the Pt-free alternative materials, have been extensively used for the counter electrodes of dye-sensitized solar cells. In this study, a series of functionalized graphenes with doping N or/and S atoms in different configurations are investigated with density functional theory to reveal their different electrocatalytic activity in the process of I_2 adsorption. The results show that the adsorption energy and the transferred charge between the substrate and adsorbed I_2 on the surface of N/S co-doped graphene are much bigger than that of N or S monodoped graphene. The enhanced adsorption activity of the former essentially results from the synergistic effect by co-doping with N and S atoms in promoting the positive charge density distribution of active centers and increasing the number of active sites. It is also found that the charge and spin distributions features are two reliable benchmarks for evaluating the physical or chemical adsorption activity of materials and guiding the design of high-performance counter electrodes materials for dye-sensitized solar cells.

1. Introduction

Solar energy is one of the most abundant and renewable resources, and varies of photovoltaic devices and technology have been developed to take use of it [1–4]. Due to the low-cost, simple fabrication, and high power-conversion efficiency, dye-sensitized solar cells (DSSC) have received widespread attention in recent years [5–12]. In order to improve the power-conversion efficiency of DSSC for commercial application, continued efforts were made on searching promising counter electrode materials to replace the traditional and high-cost platinum [13–20]. The carbon materials, such as carbon nanotube, graphene, graphite etc, as one of the Pt-free alternative materials, have been studied and applied extensively for the DSSC [19,21–32].

Functionalizing carbon materials by introducing various heteroatoms has been confirmed to be significantly effective for improving the electrocatalytic efficiency [23,32–35]. Recently, more interest has been paid on the dual-doping with two different atoms. Wang et al. synthesized the nanotubes containing both boron and nitrogen atoms which show high efficiency as metal-free electrocatalyst electrode for oxygen reduction reaction [36,37]. Many research groups reported the nitrogen and sulfur co-doped graphene electrocatalyst with the improved activity for oxygen reduction reaction [38–40], hydrogen evolution reaction [41], or I_3^- reduction reactions [42]. Bai et al. synthesized the three-dimensional nitrogen and sulfur co-doped graphene networks by a one-step hydrothermal method, and the DSSC with that exhibits an efficiency of 9.46% [43]. Therefore, more and more experimental evidences have shown that co-doping is promising approach to enhance the catalyst performance of carbon material counter electrode.

Besides the experimental explorations, the theoretical studies with the first-principle quantum chemical methods have been extensively performed. As an effective tool for revealing the catalytic mechanism and designing high-performance counter electrodes for DSSC, the first-principle study could provide meaningful guidance for further experimental investigations. On the basis of the calculated adsorption energies of a series of low-cost semiconducting materials, Hou et al. successfully screened out the rust (α-Fe_2O_3) to possess comparable electrocatalytic activity as platinum counter electrode, and this prediction was further confirmed in experiment [17]. Zhang et al. investigated the catalytic mechanism of N or S doped graphene for oxygen reduction reaction in fuel cells [34,44], and revealed that the doping atom introduces high spin density or charge density, improving the

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* Corresponding author.
E-mail address: yang.liu@hit.edu.cn (Y. Liu).

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electroncatalytic activities for oxygen reduction reaction. Liang et al. reported the synergistic effect in enhancing the oxygen reduction performance due to the formation of a large number of active C atoms by the dual-doping of N and S atoms [38]. Denis revealed a stable configuration of N/S co-doped graphene with N and S replacing a C—C bond, and further investigated its electronic properties and chemical activity [45,46]. However, the catalytic mechanism of the N/S co-doped graphene in I_3^- reduction reactions in DSSC is not completely clarified. Moreover, in the cases mentioned above as well as most of previous theoretical studies, the graphene cluster model containing limited atoms was commonly employed for simulating local effect of material surface, while the periodic supercell model of graphene was less used. Inspired by this, a theoretical study by constructing a series of periodic functionalized graphene models is performed to investigate the electronic properties and chemical activity of graphene with doped heteroatoms, aiming at revealing the synergistic effect of N/S co-doping in graphene. A fundamental understanding of I_3^- reduction mechanism at various functionalized graphene surfaces is helpful for the design of new-type doped carbon materials with high electrocatalytic performance for solar cells.

2. Simulation methods and models

The spin-polarized density functional theory (DFT) calculations with Perdew-Burke-Ernzerhof (PBE) functional [47] were performed by Vienna ab initio simulation package (VASP) [48,49]. The projected-augmented wave (PAW) method was used to treat the interactions between the core and valence electrons [50,51]. The wavefunction at each k point was expanded in plane wave basis sets with a kinetic cutoff energy of 350 eV. The energy and force convergence criterion for geometrical optimization were set to be 1.0×10^{-6} eV and 0.01 eV/Å, respectively. The integration of the Brillouin zone was conducted with a $5 \times 5 \times 1$ Monkhorst–Pack grid centered at Γ-point. A (5×5) supercell was constructed to model the infinite graphene sheet. In the perpendicular direction to the surface, a vacuum layer as large as 15 Å was used to minimize periodic interactions. The DFT-D2 approach [52] was performed to consider the van der Waals interaction in the energy calculations. Bader analysis [53] was employed to quantitatively describe the charge distribution and charge transfer upon adsorption.

The adsorption energy is defined as follow:

$$E_{ads} = E(sheet) + E(I_2) - E(I_2/sheet)$$

where E(sheet) is the total energy of pristine or doped graphene sheet, $E(I_2)$ is the total energy of free I_2 molecule, and $E(I_2/sheet)$ is the total energy of I_2 adsorbed on the pristine or doped graphene.

3. Results and discussion

3.1. Adsorption activity

The overall I_3^- reduction reaction occurring on the counter electrode for DSSC could be described as $I_3^- + 2e^- \rightarrow 3I^-$. As the first step, the I_3^- dissociates to $I_2 + I^-$ in solution very fast [6], and then I_2 discomposes into two I^- ions by accepting the transferred electrons from the surface of counter electrode. Therefore, the adsorption ability of different electrode materials for I_2 is definitely one of the key factors to determine the catalytic efficiency for the I_3^- reduction reaction. If the adsorption ability is too weak, it is not benefit for the I_2 molecule approaching to the electrode surface; while if it is too strong, the I^- leaving in the desorption reaction process will be hindered. In this section, the adsorption abilities of different electrode materials are gauged in the respects of the adsorption energy, the I—I bond elongation of the stable adsorbed structures, as well as the capability of extracting electrons for I_2 from the material surface.

Ten patterns including pristine and N or/and S doped graphene are constructed as computational models to investigate the adsorption activity toward I_3^- reduction reaction. The doping configurations include the popular chemical status of N or S heteroatom which were detected by X-ray photoelectron spectroscopy [35,39,43]. As shown in Fig. 1, they are pristine graphene (G), substitutionally S-doped based on the single-vacancy graphene (S_1-G) and double-vacancy graphene (S_2-G), graphite N-doped graphene (N_1-G), pyridine N-doped graphene (N_2-G), as well as the N/S co-doped graphene with N and S in different relative positions (N_1/S_1-G, N_1/S_1-G*, N_2/S_1-G, N_2/S_1-G*, N_2/S_2-G). Without and with the "*" presents the two atoms are doped simultaneously in the same hexagon and adjacent hexagon, respectively. With respect to the structural change of graphene by doping heteroatom, the N and S dopants show distinguished features. When N atom is doped, the material surface is still planar as pristine graphene. However, in S_1-G a hump around S atom appears which makes the surface deformed. It is worth mentioning that in the N_2/S_2-G, the dopants replace two neighbored C atoms, but they remain non bonded by adopting a pyridinic N and —S— configurations, which was reported before [45,46].

Table 1 lists the adsorption energies for I_2 on the surfaces of graphene-based materials we studied and the geometrical parameters of the adsorbed structures. During the search for the most favorable adsorbed structures, many possible adsorption statuses are considered as initial guess, i.e., the I_2 is placed at different sites of the surface or different orientation (parallel or perpendicular to the surface). Basically, two kinds of adsorption behaviors are determined. At G, S_1-G, S_2-G, N_1-G, N_1/S_1-G, N_1/S_1-G* and N_2/S_2-G, the I_2 is physically adsorbed with the distance of 3.5–3.8 Å to the surface. In these cases, the parallel adsorption orientation is popular, such as in G, N_1-G, S_2-G, N_1/S_1-G, N_1/S_1-G*, while the perpendicular adsorption is preferred in S_1-G and N_2/S_2-G. On the surfaces of N_2-G, N_2/S_1-G, N_2/S_1-G*, the I_2 is chemically adsorbed accompanying with the dissociation into two I atoms, i.e., one I bonds with C atom of material surface with bond length of ~2.1 Å, and the other I is solely adsorbed above the surface. Because of the strong chemical adsorption character in latter cases, their adsorption energies are much higher than those of former ones. By referring to the adsorption energy range from about 0.33 to 1.20 eV for good catalysts in literature [17], the calculated adsorption energies in this study are all in the rational range. In addition, it is found that the doped graphenes we studied usually have higher adsorption energies than the pristine graphene with either physical or chemical adsorption behavior. It indicates that the doping by introducing N or/and S to graphene is usually advantageous for the adsorption of I_2. Particularly, one can see from Table 1 that the adsorption energies for I_2 on the surface of N/S co-doped graphene are always higher than that doped with only N or S atom. With respect to the physical adsorption patterns, the adsorption energy for N_1/S_1-G, N_1/S_1-G*, and N_2/S_2-G elevates to 0.72–0.81 eV, respectively, in comparison with that for N_1-G (0.58 eV) and S_1-G (0.47 eV). For the cases of chemical adsorption, the adsorption energies of N_2/S_1-G, N_2/S_1-G* are about 0.2 and 0.6 eV higher than those of N_2-G and S_1-G, respectively. As a common sense, different position of material surface possess different ability for adsorption, and the area with relatively strong adsorption ability is so-called "active center" (or active sites). By taking N_1/S_1-G* as an example, the adsorption energy at the N or S active center is calculated to be 0.74 and 0.52 eV, respectively. They are higher than the adsorption energy in monodoped N_1-G (0.58 eV) or S_1-G (0.47 eV), respectively. It indicates the synergistic effect of co-doping graphene in enhancing the adsorption ability in contrast to the monodoped graphene.