Metal-free Si-doped graphene: A new and enhanced anode material for Li ion battery

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ABSTRACT

Anode materials with large reversible capacity, small volume expansion, high mobility and low cost are urgently demanded in portable electronics. Herein, we have tried to seek a new and excellent material for Li ion batteries. Because of the synergetic effect of Si and graphene, Si-doped graphene with divacancy structure has been found to be the best candidate. On the one hand Si component can improve the storage capacity and facilitate the Li atom diffusion, on the other hand, the stable frame structure of graphene can reduce the expansion effect simultaneously, contributing to its long-time stability. The reversible capacity can be increased to 1171 mA h/g or even more just by one Si atom doping, with only 0.4% volume expansion. Simultaneously, the foreign Si impurity can decrease the barrier of Li diffusing compared to its counter-part pristine graphene. Therefore, it is reasonable to design Si-doped graphene serving as a new and promising Li ion battery anode.

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1. Introduction

Li ion battery has been employed widely in portable electronics, such as laptops, camcorders and mobile devices, because it has a much higher energy density than other rechargeable batteries [1,2]. The traditional Li metal anode shows an inherent high specific capacity of 3860 mA h/g [3], however, considering the safety and dendrite formation during recharging, there are still many challenges for its commercial application at present. Very recently, graphite has been widely selected as an anode material owing to its high diffusivity of Li ions and high stability through Li intercalation [4]. However, the biggest disadvantage of graphite is its low specific capacity of 372 mA h/g, where every six carbon atoms just support one Li atom for the Li-intercalated case to form the composite of LiC_6 [5].

Li ion battery with high energy and power densities is highly desired. Graphene, which is composed of one monolayer of carbon atoms with honeycomb lattice, has attracted enormous attention because of its ultra large surface area, excellent electrical conductivity, good chemical stability, as well as low manufacturing price [6–8]. Both sides of the graphene sheets could anchor the energy carriers Li, facilitating its potential application in electronic storage devices [9]. It has been demonstrated experimentally to have a good cyclic performance and a specific capacity of 460 mA h/g after 100 cycles [10,11], in addition, Yoo et al. obtained a high specific capacity of 540 mA h/g on graphene nanosheets [12]. To achieve a more enhanced Li reversible capacity, the pristine graphene has been modified and functionalized further. Oxidized graphene nanoribbons were obtained by unzipping pristine multi-walled carbon nanotubes, presenting a stable specific capacity of about 800 mA h/g [13]. N-doped graphene electrode exhibited reversible capacity of 1043 mA h/g in the first cycle and 872 mA h/g after 30 cycles [14]. A series of theoretical investigations have also been carried out to help understanding the nature Li interaction and exploring better anode materials. Graphene decorated fully by Li atoms with a graphane configuration Li_2C_2, where each carbon atom was pulled out of the plane by the attached Li atoms, was found to be a conductor, giving consequences to its application in Li storage [15]. However, it should not be easy to synthesize Li_2C_2 in experiment due to the larger binding energy at the hollow site [11]. High Li storage capacity of LiC_3 and good mobility have been predicted by density functional theory calculations on graphdiyne [16]. Graphene doped with pyridinic N atoms was found to be the most suitable for Li storage with a high storage capacity [17], furthermore, graphene doped with 4 pyridinic N atoms cluster exhibited strong force for Li adsorption as well as low barrier for Li diffusion

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It is reported that Li ion batteries with specific energy capacity as high as 4200 mA h/g using Si nanowires as anodes have been achieved [19], and the interstitial tetrahedral and hexagonal sites in Si nanocrystals are energetically stable positions and the saddle points for the Li diffusion pathway, respectively [20]. This high capacity of Si material is amazing, however, the practical use is hampered by its large volume expansion, causing pulverization, loss of electrical contact and early capacity fading [21]. To combine the advances of graphene and Si, some groups have mixed them together and obtained improved performance [22−26]. However, the Si part remained the nanoparticle morphology and the synergetic increase could just occur at the interfaces between graphene and Si particles, which limited their enhancement. Therefore, we are interested in the performance of Si-doped graphene (SiG), and curious about whether the doped Si atoms could increase the reversible capacity of pristine graphene and meanwhile, whether the frame structure of graphene could limit the volume expansion of Si. The investigation of the interactions between graphene and doped foreign elements is very interesting and popular [27]. To the best of our knowledge, the application of doped graphene in Li ion batteries is still in infancy and it is lacking excellent SiG reports in this area [28]. Considering the possible synergetic effect of this promising anode material, we have constructed its model using the density functional theory (DFT) based on several experimental reported SiG structures. By virtue of the reversible capacity, volume structural expansions and Li mobility barriers, we have tried to design and seek the best anode structure via Si doping.

2. Method of calculations

In this work, all the calculations have been carried out by the DFT scheme as implemented in the Gaussian 09 package [29]. The graphene model discussed here is based on the Sidik's structure and has been used well in our previous simulations, which is composed of 42 carbon atoms with 16 hydrogen atoms terminated at the edges [18,30]. All of the ground-states geometries were optimized by the B3LYP functional and there were no imaginary frequencies, demonstrating that all of the obtained structures were stable. The 6−31G* basis set was selected in all the below calculations, based on the previous study [31,32]. Both of them were suitable for large complex systems. Geometry optimizations were carried out until the gradient forces were smaller than a threshold value of 0.00045 Hartree and all of the simulations were performed with a (75, 302) pruned grid. The charge distribution was calculated through the Mulliken method and the bonding analysis was completed via the Natural Bond Orbital (NBO) method, respectively. The vibrational frequency calculations were corrected by a scale factor of 0.9614. In addition, the adsorption energy was calculated as:

$$E_{ads} = (E_{system} - E_{graphene} - n{*}E_{Li})/n$$

where n was the total number of the adsorbed Li atoms and E_{system}, $E_{graphene}$, and E_{Li} were the total ground state energies of Li adsorbed on graphene, free graphene and one isolated Li atom, respectively. In virtue of this definition, a more negative E_{ads} demonstrated that the interacting graphene-Li system was more stable. All of the adsorption energies were corrected by taking into account the effects of basis set superposition error estimated by using the counterpoise corrections method [33]. The diffusion energy barrier was calculated by seeking the transition state between the optimized initial and final geometries by the Synchronous Transit-Guided Quasi-Newton method.

3. Results and discussions

3.1. Constructing stable SiG models

This study was started from investigating the geometrical structures of graphene doped with Si atoms in different formats. Although there were some simulated studies about SiG in other applications, they almost just focused on the simple substitutional case [34−36]. Luckily, the Si impurity atoms in the graphene surfaces have been identified in experiment using annular dark-field imaging in a scanning transmission electron microscope recently [37]. Moreover, large scale synthesis has been realized and used in molecular sensing [28]. Based on these experimental results, we have considered the three observed and raised doping configurations here, according to Chisholm's findings [37]. All of their optimized structures were shown in Fig. 1, including substitutional graphene (SUG), divacancy graphene (DVG) and 5−7 reconstructed vacancy graphene (5−7 G). For the former SUG case, the doped Si atom would bond with its nearest three C atoms forming bonding lengths in the range of 1.75−1.76 Å, which were close to the reported 1.75 Å [36], indicating our obtained geometry was reasonable. In the side view, the sheet of SUG was obviously distorted, with the Si atom moving out of the plane forming a curved surface, and this was in accordance to the calculated Si−C bonds as they were longer than the original C−C bond of 1.42 Å. In the DVG model, two adjacent C atoms were replaced by one Si atom, remaining its previous symmetry. Its plane distortion was minimal, evidenced by its side view, which suggested its good stability and quite well structure. For the last 5−7 G, although doped by one Si atom as before, its deformed area was the largest and composed of several 5 and 7 atom rings. Correspondingly, its side views also displayed an obvious crispation compared to the DVG case.

In the SUG case, the three Si−C bonds have deviated from the planar sp² configurations and Zhao et al. thought Si atom preserved its sp³ character as in the bulk crystal [36]. While based on our NBO results as illustrated in Table 1, it could be achieved that the ratios of s and p components of the Si atom were all close to 1:2 for the three Si−C bonds here, demonstrating that the doped Si atom of SUG remained sp² character. As the graphene model used here was a symmetric configuration, only the top half of its data was given, omitting the small discrepancy between the two halves. This could be supported by the calculated Raman spectra too, as shown in Fig. 2, the intensity of G band of SUG was the strongest and also obviously stronger than that of DVG. It was well accepted that G band at about 1580 cm⁻¹ in Raman spectrum was a good indication for sp² hybridized C bonds, so this hybridized component still contributed mainly to its structural bonding in SUG model.

In addition, DVG was still a planar configuration and the NBO result showed a sp³ character for its doped Si atom, which was in line with the four Si−C bonding formation displayed in the optimized structure. For the last 5−7 G case, the bonding analysis as well as the obtained structure revealed its Si atom would be a sp² character with three Si−C bonds. Its surface was corrugated apparently, which might be due to the large strain induced by the more vacancies. After that, we wanted to study the performance of these three models in Li storage.

3.2. Structural distortion during Li adsorption on SiG models

Two Li atoms have been introduced into these complexes because both sides of the graphene surface could supply active sites to accommodate Li atoms. The obtained stable structures were illustrated in Fig. 3 and it could be found that the two Li atoms tended to adsorb on different sides of the graphene sheet for all of these cases. For the SUG model, Li atoms would combine to the