A combined theoretical and experimental study on the oxygenated graphitic carbon nitride as a promising sulfur host for lithium–sulfur batteries

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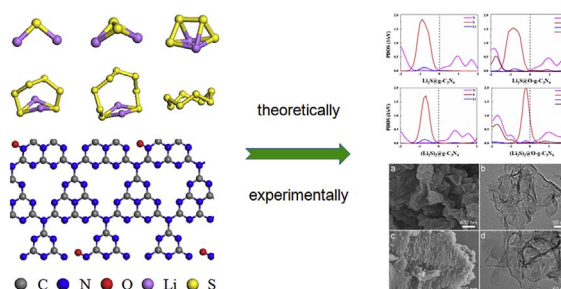[c] College of Optoelectronics Technology, Chengdu University of Information Technology, Chengdu, 610225, PR China
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HIGHLIGHTS

- The O-g-C_3N_4 material has better electrical conductivity than other 2D materials.
- The O-g-C_3N_4 material especially favors the adsorption of Li_2S_x species.
- The O-g-C_3N_4-S cathode exhibits excellent electrochemical performance.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

To effectively restrain the dissolution of soluble polysulfides and fully utilize the active sulfur materials in lithium-sulfur (Li-S) batteries, host materials with unique compositions and porous structures have been pursued. Herein, we have investigated the mechanism of the excellent activity of oxygenated g-C_3N_4 for Li-S batteries from theoretical perspective, and the further experiment confirms that our O-g-C_3N_4-S cathode exhibits much better electrochemical performance compared with those in previous reports. Our DFT calculations reveal that the oxygenated material has better electrical conductivity and stronger adsorption ability with the Li_2S_x species compared with the pristine g-C_3N_4 and other two-dimensional (2D) materials. Furthermore, we have confirmed experimentally that the O-g-C_3N_4-S composite cathode exhibits excellent electrochemical performance in Li-S batteries with high reversible discharge capacity of 1030 mAh g^{-1} after 100 cycles at 0.2 C, great rate capability with the discharge capacity of 364 mAh g^{-1} even at 5.0 C, and outstanding long-term cyclic stability with the discharge capacity of 465 mAh g^{-1} after 1000 cycles at 1.0 C (capacity decay was only 0.046% per cycle). Our results also suggest that theoretical study will play a significant role in predicting and screening novel materials with better performance.

1. Introduction

The requirements for the energy storage in some fields such as hybrid electric vehicles, portable electronic equipments, and grid-scale stationary storage are gradually increasing in recent years. To meet the demands, it is necessary to explore the advanced batteries with high

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energy density [1–3]. Among various energy storage technologies, lithium-ion batteries have dominated the market in portable electronics in the past years [4,5]. Nevertheless, the commercial application of the batteries is extremely hampered by the relatively low energy density and high cost [6,7]. In recent years, lithium-sulfur (Li-S) batteries with the advantages of high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}) have received widespread attention and are regarded as the promising candidates for the next-generation electrical energy storage systems [8,9]. Besides, in Li-S batteries, sulfur is one of the nontoxic and the most abundant materials in earth, which also make them the attractive and low cost competitors [10,11]. Despite these considerable advantages, there are still some key challenges for the commercialization of Li-S batteries up to now, such as the poor electrical conductivity of sulfur and easily dissolution of polysulfides during the charge/discharge processes, which could lead to the loss of active sulfur, low discharge capacity and even poor cycle performance of Li-S batteries upon cycling [12,13].

To address these problems in Li-S batteries, several strategies have been developed [11,14–16]. One effective strategy is to compress sulfur into carbon materials with unique features, such as porous, hierarchical and hollow nanostructures, which synergistically enhances the electrical conductivity of the sulfur cathode, traps the soluble polysulfide intermediates, and accommodates the volume variation of sulfur cathode [17–20]. Indeedly, micro/mesoporous carbon [21], macroporous carbon [22], and carbon nanotube/hollow carbon nanofiber [23] have been demonstrated with significantly enhanced lithium storage properties. For instance, Nazar et al. employ the bimodal-carbon spheres to encapsulate nanostructured sulfur, achieving a high and relatively stable discharge capacity [24]. The advantage of the optimized bimodal-carbon spheres is that the smaller pores can entrap the sulfur while the larger pores can facilitate electrolyte's access throughout the structure. Besides the physical confinement of polysulfides by utilizing the unique structures of carbon materials, chemical confinement of polysulfides through the chemical interaction has been considered as another reliable strategy because it does not depend on the nanostructures of host materials [25–27]. Moreover, this method can effectively suppress the dissolution of polysufides in organic electrolytes [28,29] and the diffusion of these soluble polysufides between the positive and negative electrodes [30]. Thus, numerous efforts have been made to search for the better materials for the anchoring of polysulfides.

Recently, polar host materials based on metal oxides (TiO$_2$ [10], SiO$_2$ [14], MnO$_2$ [31], etc.) have achieved much successes in the confinement of polysulfides due to the effective binding via chemical interactions and the surface-mediated redox reactions. Unfortunately, most of these polar hosts are insulated materials that cannot transport electrons, or in the form of either 2D nanosheets or nanocrystals with low surface area that cannot physically confine the polysulfides [32], which inevitably compromises the rate capability and even the specific capacity. As demonstrated in previous reports, the oxygenated functional groups and the doped nitrogen (N) on two-dimensional (2D) materials (e.g., graphene and phosphorene) possess strong chemical interactions with lithium polysulfides, which can maintain the good sequestration of the polysulfides in these carbon hosts [20,33,34]. Therefore, inspired by these considerations, we have anticipated whether the oxygenated graphitic carbon nitride (i.e., O-g-C$_3$N$_4$) material possessing both oxygenated functional groups and enriched nitrogen content could be the candidate for enhancing the Li-S performance of sulfur cathode.

The recent report demonstrates that the graphene-like oxygenated carbon nitride (OCN) host cathode can retain improved reversible capacity during long term cycles at high current density, which displays a specific capacity of 808 mAh g^{-1}, 517 mAh g^{-1} at 1.0 C, and 447 mAh g^{-1} after cycling 500 cycles at 0.5 C [35]. In the present work, the electrochemical performance of the oxygenated g-C$_3$N$_4$ has been investigated by combining both density functional theory (DFT) and

experimental studies. DFT calculations reveal that the material has a potential application in Li-S batteries due to the better electrical conductivity and the stronger adsorption with the Li$_2$S$_x$ species compared with the pristine g-C$_3$N$_4$. Furthermore, we have also successfully synthesized the oxygenated g-C$_3$N$_4$ in experiment and proved that the O-g-C$_3$N$_4$-S composite cathode exhibits high discharge capacity, great rate capability and outstanding cyclic stability, which further confirms our theoretical prediction. The approach adopted in our work is more facile and efficient for preparing O-g-C$_3$N$_4$, the synthesized material is thinner and better dispersive compared with Ref. [35], which can introduce much more oxygen and is critical for improving the performance of Li-S batteries.

2. Material and methods

2.1. Theoretical calculations

Density functional theory (DFT) was employed to calculate the adsorption energy (E_{ads}) between the substrates (g-C$_3$N$_4$ and O-g-C$_3$N$_4$) and the polysulfides, which was defined by

$$E_{ads} = E_{s-sub} - E_s - E_{sub}$$

where E_{s-sub}, E_s, and E_{sub} are the energy of the polysulfides_substrate, polysulfides, and substrate, respectively. The DFT calculations were performed by using the Vienna Ab-initio Simulation Package (VASP) [36,37]. The interactions between ion cores and valence electrons were described by the Blöchl's all-electron-like projector augmented wave (PAW) method [38,39]. The exchange correlation functional was approximated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) method [40]. The electron occupancies were determined according to the Fermi scheme with the energy smearing of 0.1 eV. The cut-off energy of 400 eV was used. All geometries were optimized until the energy and the self-consistent force were converged to 1.0 × 10^{-5} eV/atom and 0.01 eV/Å, respectively. The Brillouin zone integration was sampled with a 3 × 3 × 1 k-point grid using the Monkhorst-Pack method. A vacuum space as large as 15 Å between repeated single-layer g-C$_3$N$_4$ was used along the c direction normal to the catalyst surface to avoid periodic interactions. The (2 × 2 × 1) supercell surface model of g-C$_3$N$_4$ with a lattice parameter of 14.26 × 14.26 Å (containing 24 C and 32 N atoms, respectively) was adopted in this work. During the geometry optimization, all atoms were allowed to relax. A semiempirical DFT-D2 force-field approach [41,42] was employed to describe the van der Waals (vdW) interactions accurately in our calculations, which influenced the adsorption of Li$_2$S$_x$ species on the substrates.

2.2. Chemicals

All the chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd, and were of analytical grade and used without further purification.

2.3. Synthesis of O-g-C$_3$N$_4$ material

The oxygenated material was obtained by calcining the g-C$_3$N$_4$ in the tube furnace at the temperature of 300 °C for six hours under air with the heating rate of 2 °C min^{-1}.

2.4. Characterizations

Field-emission scanning electron microscopy (SEM) images were collected on a JEOL JSM-6480 scanning electron microscope. Transmission electron microscopy (TEM, JEM-2100), scanning TEM (STEM) images and energy dispersive X-ray spectroscopy (EDX) mapping profiles were taken on a JEOL JEM-2100F transmission electron microscope using an accelerating voltage of 200 kV. The powder X-ray