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Facile synthesis of N and S co-doped graphene sheets as anode materials for high-performance lithium-ion batteries

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ABSTRACT

A simple and cost-effective approach is proposed to synthesize the nitrogen (N) and sulfur (S) co-doped graphene sheets. X-ray photoelectron spectroscopy reveals that the content of N and S atoms is 5.42% and 0.52%, respectively, indicating that N and S have been successfully incorporated into the graphene sheets. The resulting co-doped graphene sheets exhibit excellent electrochemical performance when they are employed as anode materials for lithium-ion batteries. A superhigh initial reversible capacity of 1016 mAh g^{-1} at a current density of 100 mA g^{-1} was obtained. More significantly, even at an extremely high current density of 20 A g^{-1}, the as-prepared co-doped graphene still delivers a high capacity of about 250.1 mAh g^{-1}. The improved electrochemical performance is due to the two-dimensional structure, the large quantity of edge defects, and the synergistic effect of N and S atoms. The results indicate that the co-doped graphene sheets could be promising candidate for high-performance lithium-ion batteries materials.

1. Introduction

Lithium-ion batteries (LIBs) with high energy density, long cycling life and excellent safety have been proposed as one of the most promising energy storage devices for hybrid electric vehicles and electric vehicles in recent years [1]. But graphite, the commercial anode material, possesses low theoretical specific capacity (372 mAh g^{-1}) and low lithium diffusion coefficient (10^{-7}~10^{-10} cm^2 s^{-1}), which restricts the further application in LIBs [2]. Therefore, it is imperative to design and synthesize novel anode materials for high-performance LIBs.

Graphene, a two-dimensional sheet of sp^2-hybridized carbon, has considered to be a promising anode material for lithium-ion batteries owing to its high specific capacity and fascinating electronic properties [3–5]. However, the irreversible stacking of graphene sheets always occurs during the lithiation/delithiation process due to the strong van der Waals interactions. As the results, the agglomeration will significantly decrease the lithium storage active sites and inevitably affect the electrochemical properties of the graphene electrode. Tremendous efforts have been dedicated to address the above problem, including heteroatom doping [6–10] and porous structure design [11–14]. Experiments and theoretical calculation have proved that heteroatom doping could effectively modify the electronic property and chemical reactivity of graphene, which leads to the dramatically enhanced electrochemical performance of LIBs [6–10,15–17]. Meanwhile, the heteroatoms (nitrogen, sulfur, phosphorus and boron etc.) in the graphene frameworks are also able to break the inertness of the graphene layer and increase the disorder degree, thus improving the specific capacities and rate properties. A particularly exciting example is N-doped graphene that exhibits the enhanced electrochemical performances for lithium storage by taking advantage of its more active sites and higher electrical conductivity than the pristine graphene [6,7,10]. Besides, recent investigations demonstrated that co-doping (especially N and S) is more effective in comparison with mono-heteroatom doping, since the co-doped graphene can induce more powerful active regions on the graphene surface and the lithium electroactivity [18–23]. Moreover, N and S co-doped graphene has been extensively applied in various fields, such as electrocatalysis [24–27], supercapacitors [28,29], Li-oxygen batteries [30], sensors [31], lithium-sulfur batteries [32,33] and LIBs [22,23].

In general, there are two major synthetic routes to fabricate the N and S co-doped graphene materials. One is by pyrolyzing foreign atoms- and carbon-containing precursors directly [27]. The other is

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by postsynthesis treatment of graphene-based materials with reactive heteroatom sources [24–26,29–31]. The latter approach is regarded to be a feasible method due to the large-scale preparation and controllable co-doping by adjusting the ratio of graphene-based materials and dopants [23–26]. Unfortunately, the route of the post-treatment of graphene is complicated and of high cost under high-pressure conditions [29–31]. Thus, to further improve the performance of LIBs, a facile and cost-effective approach of N and S co-doped graphene needs to be proposed urgently.

Herein, we report a facile and versatile synthetic method to prepare the N and S co-doped graphene sheets by thermal treatment of graphene sheets, benzyl disulphide and melamine. By this means, the unique N and S co-doped graphene sheets retain the intrinsic physicochemical characteristics of graphene and possess more active sites due to the synergistic effect of N and S. The electrochemical performance of the obtained material was investigated. It is expected that the as-prepared N and S co-doped graphene sheets as anode materials for LIBs exhibits excellent lithium storage performance.

2. Experimental

2.1. Materials preparation

N and S co-doped graphene sheets (NSG) were synthesized by a simple thermal annealing approach involving graphene sheets, benzyl disulphide and melamine. The graphene sheets were prepared by rapid thermal expansion method according to the previous report [5]. The detailed procedure is as follows: 0.05 g of graphene sheets were ultrasonically dispersed in acetone with 0.3 g of benzyl disulphide and melamine. Then the slurry was stirred at room temperature until the solvent totally evaporated to form a uniform solid mixture. The mixture was placed in the center of a quartz tube with argon gas atmosphere and heated to 900 °C at a heating rate of 3 °C/min. After the temperature was maintained for 1 h, the furnace was cooled to room temperature slowly. For comparison, the pristine graphene sheets (PG) were prepared under the same thermal treatment condition without adding melamine and benzyl disulphide.

2.2. Materials characterization

X-ray diffraction (XRD) pattern were recorded on a D8 Advance (Bruker) (Cu/Kα, $\lambda = 1.54056$ Å) at 293 K. Raman spectra were measured using a Horiba Jobin Yvon LabRam Aramis Raman spectrometer with a laser of 632.8 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Kratos Axis Ultra DLD using the mono Al Kα radiation (1486.6 eV) at a pressure of 5×10^{-9} torr. XPS data were analyzed using XPSPEAK software and binding energy corrections on high-resolution scans were calibrated by referencing the C 1s peak (284.8 eV). The surface morphology and the elemental distribution of the N and S co-doped graphene sheets were measured using a transmission electron microscopy (TEM) (FEI, Tecnai G^2 F30 S-Twin) and scanning electron microscopy (SEM) (HITACHI SU8220) equipped with an energy dispersive spectrometer (EDS) mapping. The Brunauer-Emmett-Teller (BET) specific surface area and porosity were determined by N_2 adsorption-desorption measurement (Autosorb-IQ2-MP). The pore size distribution was calculated by the density functional theory (DFT) method with the adsorption curves.

2.3. Electrochemical measurements

The electrochemical performances of the NSG and PG were investigated using coin cells (CR2025). The slurry contained the active materials (80 wt. %), Super P (10 wt. %), and poly(vinylidene fluoride) (PVDF, Kureha, Japan) binder (10 wt. %) in an N-methyle-2-pyrrolidone (NMP, Tianjin Kermel Chemical Reagent Co., Ltd., China) solvent was pasted on a copper foil. The copper foils with active materials were used as anode electrodes, while highly pure lithium foil was used as the counter electrode and reference electrode. The electrolyte was composed of 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1 by volume) (Beijing Institute of Chemical Reagents, China). The celgard 2325 membrane was used as the separator. The coin cells were assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents were below 1 ppm.

The cells were galvanostatically discharged and charged using a battery testing system (BTS, Neware Electronic Co., China) between 0.01 and 3.0 V. Electrochemical impedance spectra (EIS) of NSG and PG were measured at the electrochemical workstation (Zahner IM6ex). The frequency range was set from 0.1-10^5 Hz and the potential amplitude was 5 mV.

3. Results and discussion

To investigate the chemical compositions and element-bonding configurations in the NSG and PG, the XPS measurement was performed. As shown in Fig. 1a, the XPS survey spectrum of NSG contain four characteristic peaks located at ca. 165, 285, 400, and 533 eV, which correspond to S 2p, C 1s, N 1s, and O 1s, respectively. Apparently, nitrogen and sulfur signals can be observed in the XPS spectra of NSG, while no N and S signals were recorded for the XPS spectra of PG. The above results suggest that both N and S species have been successfully doped into graphene sheets by the thermal annealing method using graphene sheets, benzyl disulphide and melamine. The contents of N and S elements in the co-doped graphene sheets are calculated to be 5.42% and 0.52%, respectively.

Then, we analyzed the high-resolution C 1s, N 1s and S 2p peaks in the as-obtained NSG and PG. From Fig. 1b, the C 1s peak can be deconvoluted into five peaks for NSG and four peaks for PG. For C 1s spectrum of PG, the peak located at 284.8 and 285.0 eV can be attributed to C=C and C–C in sp^2-hybridized domains, while the peaks at 286.4 and 290.1 eV are related to C–O epoxy and hydroxyl groups, C=O carbonyl groups and O–C=O carboxyl groups. Similarly, for C 1s spectrum of NSG, the main peak at about 284.6 and 284.9 eV is related to the graphite-like sp^2 C, which indicates that most of the C atoms in the NSG are arranged in a conjugated honeycomb lattice [23–26]. In addition, the peaks at binding energies of 286.5 and 289.6 eV could be attributed to carbon atoms bound with oxygen atoms resulting in a formatting of such bounds as C–O, C=O and/or O–C=O. Compared with the C 1s spectrum of PG, a new peak at 285.6 eV is observed for NSG, which reveals the presence of C–S and C–N [23–26,32,33]. The results further justify that N and S heteroatoms have been doped into the graphene framework.

The complex N 1s spectra can be further split into three different peaks at the binding energies of about 398.4, 401.0 and 403.2 eV, corresponding to pyridinic-N, pyrrolic-N and graphitic-N, respectively [22,23,28,29]. As shown in Fig. 1c, the pyridine-like and pyrrolic-like nitrogen atoms are the main functional groups in the as-prepared co-doped graphene sheets. It is well known that the dominant pyridinic and pyrrolic N is beneficial for the enhancement of conductivity and reversible capacity for lithium-ion batteries [7,10].

The high-resolution S 2p peak can be resolved into three different peaks at binding energies of about 163.9, 165.0, and 167.7 eV (Fig. 1d). Two fitted peaks at ~163.9 and 165.0 eV can be assigned to the S $2p_{3/2}$ and S $2p_{1/2}$ of the –C–S–C– covalent bond of the thiophene-S owing to the spin-orbit couplings. Meanwhile,