One-step solid-state synthesis of sulfur-reduced graphene oxide composite for lithium-sulfur batteries

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Xiaozhong Zhou[*], Yujie Li, Guofu Ma, Qianru Ma, Ziqiang Lei[**]

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, PR China

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ABSTRACT

A novel sulfur-reduced graphene oxide composite was prepared via a facile one-step solid-state method. The composite was characterized by means of XRD, Raman, XPS, SEM, and TEM (HR-TEM) techniques. After being directly heated in the presence of sulfur powder, the freeze-dried graphene oxide was reduced, and a homogeneous composite containing sulfur simultaneously formed. The obtained composite display good electrochemical performance when used as a cathode for lithium-sulfur batteries.

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1. Introduction

Sulfur has been considered to be one of the most promising cathodes for the next-generation rechargeable batteries for its high energy density, natural abundance, low cost, and environmental friendliness [1]. Unfortunately, the practical realization of lithium-sulfur batteries suffers from low sulfur utilization and poor cycle life of the sulfur cathode due to the electrically insulating nature of sulfur and its discharge products (Li_2S), and the solubility of the reaction intermediates of polysulfides (Li_2S_x, $3 \leq x \leq 8$) [2]. Over the past few decades, research and development efforts have been made to address the above issues [3—5]. Of remarkable successes, fabricating sulfur-carbon composite cathodes with sulfur embedded within conductive carbon frameworks has been proven promising, such as graphene- or reduced graphene oxide-sulfur composites [6—13].

Graphene has become a research hotspot in the recent years owing to its superior electronic conductivity, large surface area, intriguing mechanical properties, and high reversible capacity [10,14—16]. Oxygen functional groups on the graphene oxide (GO) anchored sulfur species to the nanosheets through chemical adsorption, which results in the enhanced immobilization of later formed Li polysulfides and the improvement of cycle performance of the sulfur based cathode [6,7,17—19], which demonstrates a great potential of using graphene oxide to load sulfur as a novel cathode structure, although its conductivity is much lower than graphene [7,20]. However, most sulfur-reduced graphene oxide composites were synthesis by more complex process, including impregnating molten sulfur into reduced graphene oxide, the graphene oxide should be reduced in advance, and so on. Those synthesis strategies take time and energy, and were not conducive to large-scale production. It is still necessary to seek a general approach fabricate sulfur-graphene composites easily and eco-friendly. Herein, a facile one-step solid-state method was employed to prepare the sulfur/reduced graphene oxide (S@FD-rGO) composite by directly heating the ground mixture of sulfur powder and the freeze-dried graphene oxides (FD-GO). After heat-treating process, FD-GO was reduced, and a homogeneous composite containing sulfur simultaneously formed. The obtained composite was characterized by means of XRD, Raman, XPS, SEM, and TEM (high-resolution TEM) techniques. The performance and potential of the S@FD-GO materials as a cathode for lithium-sulfur battery was explored.

2. Experimental section

Materials and method: All reagents were analytical grade from Shanghai Aladdin Biochemical Technology Co. Ltd., Shanghai,

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* Corresponding author.
** Corresponding author.
   E-mail addresses: zxz20004@163.com (X. Zhou), leizq1958@hotmail.com (Z. Lei).

China, and were adopted as received without further purification. Graphene oxide (GO) was synthesized from natural graphite power by a modified Hummers' method [21]. In a typical experiment, 0.3 g GO was dispersed in 30 mL distilled water by ultrasonic dispersing method to form homogeneous suspension, and the suspension was subjected to freeze-drying for two days, yielding the FD-GO. Then the as-obtained FD-GO was mixed with sublimed sulfur by grinding, and the mixture was transferred into a 100 mL stainless-steel Teflon-lined autoclave. The autoclave was sealed and maintained at 155 °C for 4 h and 180 °C for another 4 h. After being naturally cooled to room temperature, a black solid, the final product (S@FD-rGO), was collected for characterization.

Physical characterization: The crystal structures, composition, and morphology of the as-obtained samples were examined by powder X-ray diffraction (XRD, Rigaku D/max 2400, operating with Cu K_α radiation of $\lambda = 0.15416$ nm, 40 kV, 150 mA), X-ray photoelectron spectra (XPS, PHI-5702 spectrometer with Al K_α X-ray radiation), field emission scanning electron microscopy (SEM, Ultra Plus, Carl Zeiss, Germany, operating at 5 kV), and transmission electron microscopy (TEM, FEI TECNAI TF20, operating at 200 kV), respectively. The carbon and sulfur contents were inspected using a Pyris Diamond thermogravimetric analyzer (TGA) (PrekinElmer, U.S.A.).

Electrochemical performances characterization: galvanostatic charge-discharge (GSCD) and cyclic voltammetry (CV) techniques were employed to evaluate the electrochemical performances of the as-prepared samples. The working electrodes were prepared by coating a copper foil substrate with a slurry composed of 60 wt% active material of S@FD-rGO or pure S, 20 wt% conductive additive of carbon black, and 20 wt% binder of polyvinylidene fluoride (PVDF). Then, the as-prepared electrode tapes were cut into discs with a diameter of 10 mm, followed by assembling them in a 2032-type coin cell in an argon-filled glove box with a lithium foil as the counter electrode and a Celgard 2400 polypropylene foil as the separator. The electrolyte used was a solution of 1 M lithium bis(-trifluoromethanesulfonyl)imide (LiTFSI) dissolved in an equivolume mixture of dimethoxyethane (DME) and 1,3-dioxolane (DOL) with 0.1 M LiNO₃ as additive. The coin cells were galvanostatically discharged and charged using a CT2001A battery tester (Wuhan Jinnuo Electronics Co., Ltd., China) in the voltage range of 1.0–2.8 V vs. Li⁺/Li at room temperature. The CV technique was performed in the voltage range of 1.0–2.8 V vs. Li⁺/Li at a scan rate of 0.2 mV s⁻¹ on an electrochemical work-station (Autolab PGSTAT128N, Metrohm, Switzerland) at room temperature.

3. Results and discussion

The phase and purity of the obtained samples S, FD-GO, and S@FD-rGO was determined by XRD, as shown in Fig. 1a. As same as the pure sublimed S, all the sharply feature peaks for as-obtained S@FD-rGO matches the characteristics of orthorhombic sulfur, which could be indexed with the JCPDS card No. 08-0247. Interestingly, it is worth noting that the peak position ($2\theta = 10°$) of FD-GO (Fig. 1a, red curve) vanishes, and a broad diffraction peak at $2\theta = 22°$ appeared, indicating that FD-GO was reduced during the synthesis process.

Raman spectra further provide additional evidences of the reduction of FD-GO. As shown in Fig. 1b, Raman spectra of FD-GO and S@FD-rGO both exhibit two broad peaks at 1336 cm⁻¹ and 1591 cm⁻¹, which in accordance with those of graphite, respectively. The D band is attributed to the defects or imperfections, reflecting the presence of disordered edges or boundaries in the rGO domains [22]. The higher D/G band intensity ratio (I_D/I_G) in S@FD-rGO ($I_D/I_G = 1.00$) than that in FD-GO ($I_D/I_G = 0.89$) means that most of the oxygen functional groups intercalated into the

interlayer spacing of FD-GO have been removed and a larger number of defects and disordered edge sites are introduced during heating treatment [23]. However, the characteristic sulfur peaks in the range 100–500 cm⁻¹ (inset Fig. 1b) did not appear in S@FD-rGO composite, indicating S₈ molecules loading in FD-rGO matrix [24].

The surface chemical composition and functional groups of the S@FD-rGO were identified by XPS in Fig. 1c. The deconvoluted C 1 s spectra of S@FD-rGO shows five peaks at 284.6 eV for C–C/C=C, 285.4 eV for C–S, 286.4 eV for C–O, 287.1 eV for C=O and 289 eV for O–C=O, respectively [25,26]. The fraction of carbon-carbon and carbon-sulfur bonding is about 71.9%, which is similar to the previously reported result for rGO [25]. This can be attributed to the efficient removal of oxygen functional groups from the GO by the one-step heat treating process and demonstrates the formation of FD-rGO. The successful loading of sulfur on rGO is also depicted by the S 2p spectrum of the S@FD-rGO (Fig. 1d), as characterized by the S $2p_{3/2}$ and $2p_{1/2}$ doublet with an energy separation of 1.2 eV and intensity ratio of ~2:1. The binding energy of S $2p_{3/2}$ peak is 163.7 eV, slightly lower than that of elemental sulfur (164.0 eV), which reveals the presence of thsssssssssse chemical bonding between sulfur and rGO [26], and the binding energy of S $2p_{1/2}$ peak is 164.9 eV. The peaks at 164.3 and 165.5 eV are attributed to the S–O bonds, and the peaks at 168.5 and 169.7 eV are ascribed to the sulphate species formed by sulfur oxidation in air [20,27]. Above analysis shows that FD-GO was reduced by molten S during the heat-treating process. Based on the data from both thermogravimetric analysis (Fig. 1e) and XPS, the S loading in the as-obtained S@FD-rGO composite is ca. 55.7 wt%.

The morphology of bare FD-GO and the as-obtained S@FD-rGO composite are depicted in Fig. 2. FD-GO is comprised of stacked sheets with a porous corrugated structure (Fig. 2a). As shown in Fig. 2b, after heat-treating with sublimed sulfur, the as-obtained S@FD-rGO composite consists of solid lumps, which is composed of nano-size sulfur particles embedded in rGO sheets (inset Fig. 3b). Fig. 2c and d shows the TEM images. It is clearly observed that there are many nano-sized particles on rGO sheets. The high-resolution TEM (HR-TEM) image in Fig. 2d illustrates the lattice of sulfur exposed plane (444) plane with d-spacing of 0.193 nm in the as-obtained S@FD-rGO composite. The corresponding fast Fourier transform (FFT) image inserted in Fig. 2d also verifies the crystallization of sulfur.

Nitrogen (N₂) adsorption isotherms and pore size distribution curves of both FD-GO and S@FD-rGO are shown in Fig. 3. FD-GO exhibits a type-IV isotherm with H4 type hysteresis loop, indicating a mesoporous structure with narrow pore size distribution (Fig. 3a, black curve) [28]. The BET specific surface area and the majority pore size of the FD-GO are 36.7 m² g⁻¹ and ca. 3.9 nm, respectively, as shown in Fig. 3. Moreover, the isotherm curves of both FD-GO and S@FD-rGO present sharp increase in the relatively high pressure region ($p/p_0 > 0.9$), indicating the existence of macropores derived from the accumulation of particles [29]. After the material was treated with sulfur, the N₂ adsorption isotherm curve (Fig. 4a, red curve) and the pore size distribution curve (Fig. 3b, red curve) of the S@FD-rGO composite significantly diminish, confirming the successful impregnation of sulfur into the pores, which is consistent with the result of TEM analysis.

The electrochemical performances of the as-obtained S@FD-rGO cathode for lithium-sulfur batteries were investigated by cyclic voltammogram (CV) and galvanostatic charge-discharge measurement. As shown in the first cathodic scan of the CV profiles (Fig. 4a), two main peaks around 2.3 and 2.0 V is clearly presented, corresponding to the transformation from cyclo-S₈ high-order lithium polysulfides (Li₂Sₙ, $n \geq 4$) and the sequential reduction of high-order lithium polysulfides into Li₂S₂ and Li₂S, respectively. In the subsequent anodic scan, only a strong oxidation peak around 2.5 V