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Nanosulfur/polyaniline/graphene composites for high-performance lithium–sulfur batteries: One pot *in-situ* synthesis

Ya Liu [a], Jun Zhang [a,*], Xiaochun Liu [b], Jinxin Guo [a], Lifei Pan [a], Hongfei Wang [a], Qingmei Su [a], Gaohui Du [a,*]

[a] *Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China*
[b] *National Center of Quality Supervision and Inspection of Automobile Spare Parts, Changchun 130012, China*

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ABSTRACT

A sandwich-structured nanosulfur@polyaniline/graphene (nanoS@PANI/G) composite was synthesized through a facile method: polyaniline is polymerized *in-situ* on graphene sheets and sulfur nanoparticles are deposited into polyaniline layer simultaneously. Such a hierarchical framework combines multiple advantageous features, including a continuous electrically conducting polyaniline@graphene network binding with sulfur nanoparticles, high flexibility accommodating volume expansion and porous space for adsorbing the polysulfides. The resulting composite delivers a high initial capacity of 1625 mA h g^{-1}, remaining a reversible capacity of ~600 mA h g^{-1} after 100 cycles, making it a promising cathode material for rechargeable lithium batteries with high energy density.

1. Introduction

Lithium–sulfur (Li–S) battery has attracted considerable attention in recent years due to the high theoretical capacity of sulfur (1672 mA h g^{-1}), which is the highest value for all known solid cathode materials for lithium batteries [1–3]. Sulfur is abundant, extremely low cost and environment friendly, making Li–S battery the most promising candidate for electric vehicles and energy storage systems for renewable energy. However, Li–S battery suffers severe capacity fading because of the poor conductivity of elemental sulfur, the dissolution of polysulfide products in the electrolyte and the deposition of insulating Li_2S_2 and Li_2S on the active surface of cathode [4,5].

In the past five years, great efforts have been made to overcome the poor cycling stability issue associated with the low conductivity of sulfur and the dissolution of polysulfides into the electrolyte, mostly through combining sulfur with some conductive matrix. Various carbonaceous materials including carbon nanotubes [6], mesoporous carbon [7], activated carbon [8] and graphene [9], and some conducting polymers such as polyaniline [10] polypyrrole [11] are used as the conductive matrix. Recently, ternary sulfur/conducting polymer/carbon composites with combined advantages of conductive polymers and carbon have also been reported by some groups [12–14]. Among the various carbonaceous materials, graphene based electrodes show enhanced electrochemical performance due to its high conductivity and flexibility [15,16]. Though with high conductivity, however, graphene fails to trap the polysulfides due its open structure, resulting in limited cyclic stability. Here we report a facile method to incorporate sulfur into polyaniline matrix with graphene sheets as the conductive skeleton. NanoS@PANI/G composites were synthesized by polymerization of polyaniline onto graphene oxide sheets combining with *in situ* deposition of sulfur nanoparticles. Aniline monomer was polymerized to polyaniline using graphene oxide (GO) as the oxidant, meanwhile GO was reduced to graphene, resulting a layered polyaniline/graphene composite. During the process, sulfur nanoparticles were embedded into the polyaniline/graphene composite by adding $Na_2S_2O_3$ in to the acidic suspension ($2HCl+Na_2S_2O_3=2NaCl+H_2O+S\downarrow+SO_2\uparrow$). Graphene works as conductive framework that is benefit for the sulfur utilization and the reactivity of the composite. PANI provides reaction chamber for sulfur particles and retards diffusion of polysulfides out of the electrode.

2. Experimental

NanoS@PANI/G composites were synthesized by a one pot *in situ* chemical oxidative polymerization process. Graphene oxide (GO) was prepared by a modified Hummer's method, and detailed

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* Corresponding authors. Tel.: +86 579 82283897; fax: +86 579 82282234.
E-mail addresses: zhangjun@zjnu.cn, zhangjun1985@gmail.com (J. Zhang), gaohuidu@zjnu.edu.cn (G. Du).

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synthesis process can be find in previous report [17]. First, 0.1 g GO was dispersed in 100 ml deionized water by ultrasonication for 30 min to form a uniform solution. Then, 1 ml aniline monomer dissolved in 50 ml 1 M hydrochloric acid was poured into the previously prepared solution and stirred for 24 h at 70 °C. During the reaction, 6.2 g $Na_2S_2O_3$ dissolved in 20 ml deionized water was dropped to above mixture. Finally, the precipitate was washed by water and ethanol twice respectively. The precipitate was dried by freezing drying.

The products were characterized using X-ray powder diffraction (XRD) on a Philips PW3040/60 X-ray diffractometer with Cu $K\alpha$ ($\lambda = 1.5418$ Å), scanning electron microscopy (SEM) on a Hitachi S4800 microscope, transmission electron microscopy (TEM) on a JEOL 2100F at 200 kV, X-ray photoelectron spectroscopy (XPS) on Thermo Scientific ESCALAB 250Xi, and thermogravimetric (TG) measurement on Netzsch STA 449C thermal analyzer. The as-prepared composite (75 wt%) was dispersed with acetylene carbon black (15 wt%), SBR glue (8 wt%) and carboxymethyl cellulose bind (2 wt%) in ethanol and deionized water to form a slurry. The slurry was coated on an aluminum foil (the average sulfur loading is 0.8 mg cm^{-2}) and vacuum dried at 60 °C. CR2025-type coin cells were assembled in an argon-filled glove-box with a lithium foil as the counter-electrode. The electrolyte is 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (volume ratio 1:1) with 0.1 M $LiNO_3$ additive. Cyclic voltammetry (CV) was carried out on a CHI604D electrochemistry workstation. The galvanostatic charge/discharge measurements were conducted on a NEWARE battery tester.

3. Results and discussion

The XRD patterns of GO, elemental sulfur, nanoS@PANI/G and PANI/G are shown in Fig. 1a. No obvious peak is observed for PANI/G composite, appearing as amorphous state. A characteristic peak is observed at 11° for GO, which disappeared for the nanoS@PANI/G composite, indicating that GO is reduced by aniline during preparation process. The peaks of nanoS@PANI/G composite are indexed to the characteristic peaks of sulfur (JCPDS: 08-0247). Comparing with elemental sulfur, the peaks of nanoS@PANI/G exhibit broadened width and weak intensity, suggesting small particle size. The average particle size of sulfur calculated using the Scherrer equation is about 48.1 nm. The sulfur contents calculated from TG curves (Fig. 1b) is about 53%. The composite exhibits sheet-like morphology with very thin thickness (Fig. 1c). TEM (Fig. 1d) exhibits that sulfur nanoparticles with diameter 20–50 nm are uniformly dispersed on the PANI/G conductive sheets.

The XPS spectra of nanoS@PANI/G composite are shown in Fig. 2. The typical doublet S2p peaks (Fig. 2a) at 163.2 and 164.4 eV are attributed to S2p$_{3/2}$ and S2p$_{1/2}$ core levels.[18] The binding energies of C 1s (Fig. 2b) distributed at 283.9, 285.0 and 287.9 eV could be attributed to the C=C/C–C in graphene, C–O and C=O groups on the surface of graphene, respectively [18]. The major composition of C=C/C–C in C 1s demonstrates that GO was reduced completely by aniline. N 1s spectrum (Fig. 2c) can be decomposed into two peaks (398.7 and 400.5 eV), which are assigned to the radical cationic nitrogen atoms and uncharged amine sites in PANI, respectively [19].

The CV curves of nanoS@PANI/G electrode are shown in Fig. 3a. During the first cathodic scan, two reduction peaks at around 2.25 and 1.82 V are observed. The lower reduction potential for the first cycle is attributed to the transformation from small molecule sulfur to S_8^{2-}. The interaction between sulfur and carbon/polyaniline also results lower reduction potentials. From the second to the fifth cycle, the reduction peaks shift to 2.35 and 2.0 V, respectively, indicating a reduced polarization of the cell. The two reduction peaks are ascribed to the open ring reduction of the cyclic S_8 to long chain lithium polysulfides ($n\mathrm{S}+2\mathrm{Li}^+ + 2\mathrm{e}^- \rightarrow \mathrm{Li}_2\mathrm{S}_n$, $(4 \le n \le 8)$) and the reduction of high order lithium polysulfides into lithium sulfides ($\mathrm{Li}_2\mathrm{S}_n + 2(n-1)\mathrm{Li}^+ + 2(n-1)\mathrm{e}^- \rightarrow n\mathrm{Li}_2\mathrm{S}$ $(n<4)$), respectively [18]. The broad anodic peaks at 2.45 V are attributed to the reversible stepwise reaction of lithium sulfide to metallic Li and S_8.

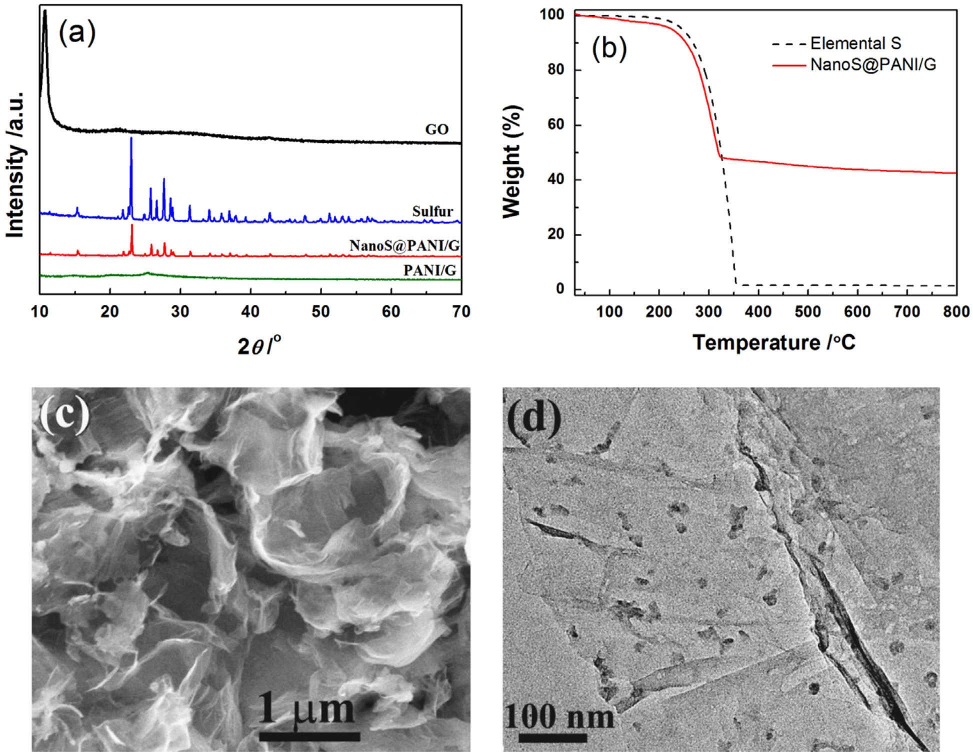

Fig. 1. (a) XRD patterns of GO, elemental sulfur, nanoS@PANI/G and PANI/G; (b) TG curves of the elemental sulfur and nanoS@PANI/G composites; (c) SEM and (d) TEM images of the nanoS@PANI/G composite.