Self-assembled graphene/sulfur composite as high current discharge cathode for lithium-sulfur batteries

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ABSTRACT

Hydriodic acid and self-assembly approach are used to fabricate graphene wrapped sulfur composite. The self-assembly process of the relative "large" graphene sheet and "small" sulfur is quite controllable, and the sulfur particles are completely enfolded by RGO sheets with a unique stacked structure .The RGO/S composite with 80 wt.% sulfur shows an initial discharge capacity of 865.1 mAh g^{-1} at 0.5 mA/cm^2. A high specific capacity of 720 mAh g^{-1} with a coulombic efficiency of 95% is achieved after 50 cycles of charge/discharge. The material also delivered a capacity of more than 580 mAh g^{-1} at 2 mA/cm^2 and can be recovered to 736 mAh g^{-1} when the rate is returned to 0.2 mA/cm^2, representing a promising cathode material for high current discharge lithium-sulfur batteries.

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1. Introduction

High capacity(theoretical specific capacity of 1675 mAh g^{-1}), utilization of sulfur as a cathode material has the advantages of natural abundance, low cost and environmental friendliness, which makes lithium-sulfur (Li-S) battery as one of the most promising alternative cathode materials for next-generation batteries [1–3]. In typical lithium-sulfur systems, sulfur undergoes reduction by lithium to generate a series of polysulfides Li$_2$Sn (8 ≥ n ≥ 2) to ultimately form Li$_2$S, which corresponds to 100% depth of discharge [4]. However, commercially viable Li-S battery has been gravely plagued by several issues, such as the poor conductivity of sulfur, the dissolution of lithium polysulfide intermediates Li$_2$Sn (2 < n ≤ 8) along with "shuttle effect", the precipitation of insoluble and insulating Li$_2$S$_2$/Li$_2$S on the electrodes and volumetric expansion [5,6].

To avoid these disadvantages, the supporting conductive agents were added to sulfur cathodes to improve the electric conductivity of sulfur and suppressing the loss of soluble polysulfide intermediates during cycling. Carbon based materials are the main choices. Many types of carbon materials have been developed as the matrix for the preparation of carbon/sulfur composites, such as carbon nanotube [7,8], carbon fiber [9–11], ordered mesoporous

carbon [12,13], porous carbon [14], carbon spheres [15], and graphene [16]. Graphene is favorable for its high surface area, good chemical stability and conductivity as one of the most promising conductive additives [17]. Recently, researchers have demonstrated that embedding sulfur in flexible reduced graphene oxide (RGO) sheets to form RGO/S anode materials promoted long cycle life of Li-S cell [18–20]. However, in order to guarantee the conductivity of S cathode for rate performance, the sulfur loading amount in these RGO/S composites is low and rarely reaches a high content level up to 80 wt.%. Generally, high sulfur content in cathodes means a high energy density of the battery. However, high sulfur content in cathodes makes polarization more severe and lead to poor rate performance, lower capacity, and decreased coulombic efficiency. Thus, increasing the sulfur loading in RGO/S composites while keeping the electrochemical performance of RGO based sulfur cathode is still a critical issue, especially RGO/S composites made by common sulfur melting or conductive layer coating methods so far [21,22]. Furthermore, a normal opened structure of RGO/S composite using sulfur melting route fails to trap the polysulfides, resulting in low coulombic efficiency and limited cyclic stability.

In this present work, a novel electrostatic self-assembly approach and an efficient reducing agent (hydriodic acid) previously reported were used to prepare RGO/S composites as cathode material for Li-S battery[23]. The closed structure, rich conductive network and flexible space of the produced RGO/S composites were good for immobilizing the polysulfide species,

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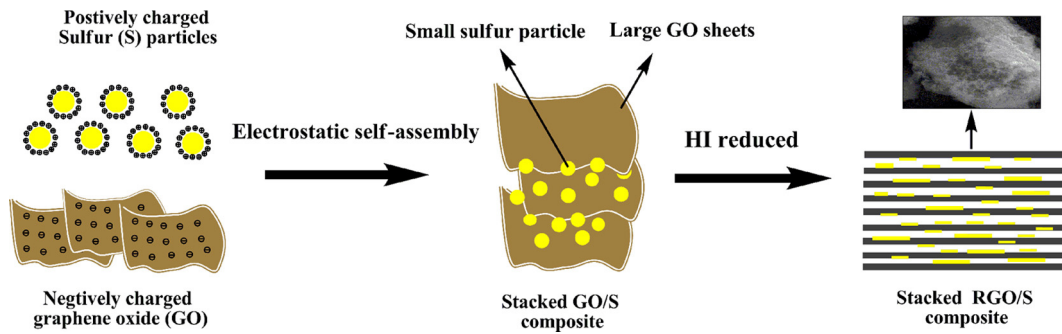*E-mail addresses:* yingh@nwpu.edu.cn, haiweiwufly@163.com (Y. Huang).

Fig. 1. Scheme representation of the synthesis step for the production of RGO/S composite.

charging transfer and accommodating the volumetric expansion during cycling. Therefore, the RGO/S cathode showed superior high current discharge performance.

2. Experimental

2.1. Sample Preparation

All chemicals used in this study were purchased from Sinopharm Chmical Reagent Co., Ltd China as an analytical reagent grade and used without further purification. Deionized water was used in all experiments.

Graphene oxide (GO) was prepared from natural graphite by the modified Hummers' method [24]. Sulfur nanoparticles were synthesized by adding concentrated HCl to an aqueous solution of $Na_2S_2O_3$ (500 ml, 0.16 M) containing a concentration of polyvinylpyrrolidone (PVP, Mw58 000, 0.4 M) [25]. In order to control the sulfur particle size, NaOH solution (1 M) was added to neutralize HCl and terminate the reaction after 1 h (We found that the size of sulfur is greatly affected by the reaction time, the longer reaction time, the larger particle size, thus NaOH solution was used to terminate reaction and control the size of sulfur particles). The sulfur particles were washed by centrifugation and vacuum dried

at 60 °C.The fabrication process of RGO/S composite is schematically shown in Fig. 1, in which Graphene oxide encapsulated sulfur particles were fabricated via the electrostatic interaction between positively charged poly(dially ldimethylammoniumchloride) (PDDA)-modified sulfur particles and negatively charged graphene oxide in aqueous solutions, and hydriodic acid was used to reduce GO. In a typical process,1 g PDDA-modified sulfur particles and 0.2 g GO were dispersed in 400 ml mixed solution of ethanol and water with the volume ratio of 1:1, respectively. Then, GO suspension was added into the PDDA-modified sulfur dispersion under mild magnetic stirring. The GO/S composites precipitate off gradually. After centrifugation and washing with ethanol, the products were dried in a vacuum oven at 60 ∘C for 12 h. Then, the produced GO/S composites was reduced for 1 h at 90 °C in 55% HI under mild magnetic stirring, after centrifugation and washing with ethanol, the RGO/S composite was collected and dried in a vacuum oven at 60 ∘C for 12 h.

2.2. Materials characterization

The surface morphology of the composites were performed by model Tecnai F30 G2 (FEI CO., USA) field emission transmission electron microscope (FETEM) and scanning
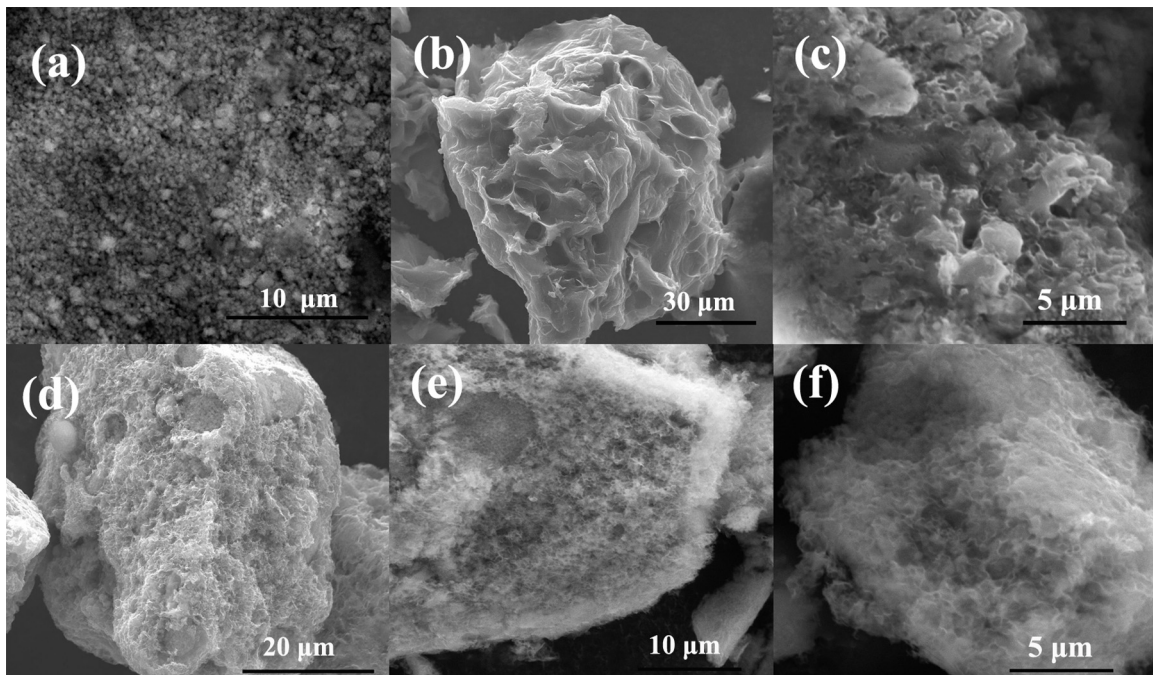

Fig. 2. SEM images of synthesized sulfur particles (a), GO/S composite (b, c) and RGO/S composite (d, e, f).