

Hydroxylated graphene-sulfur nanocomposites for high-rate lithium-sulfur batteries

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Introduction

Lithium-sulfur batteries are considered as a promising candidate for next-generation secondary batteries because of their high theoretical capacity, safe operating voltage (2.15 V vs. Li/Li⁺), and low cost. Nevertheless, lithium-sulfur batteries suffer from capacity fading, which limits their widespread application, due to the insulating nature of sulfur and its reduced products and the dissolution of intermediate lithium polysulfides.

To address these problems, carbon-based materials have been integrated with sulfur to enhance the conductivity and inhibit the polysulfide dissolution. Recently, graphene, a single-atom-thick carbon material with superior electrical conductivity and mechanical flexibility, has been successfully applied in lithium-sulfur batteries. While graphene-sulfur composite cathodes demonstrate promising electrochemical performance, their synthesis is usually complicated and challenging for large-scale application. On the other hand, the solution-based synthesis without heat treatment produces large crystalline sulfur particles, resulting in low utilization of active materials and poor rate performance. Herein, we report hydroxylated graphene nanosheets as a substrate to produce graphene-amorphous sulfur nanocomposites, exhibiting superior cyclability at high rates, by a facile *in situ* deposition method at room temperature.

Experimental

Synthesis of Hydroxylated Graphene Nanosheets (GNSOH). Pristine graphene nanosheets (1.0 g) were dispersed in aqueous NaOH solution (40 mL, 2 M) with the aid of ultrasonication (Sonics & Materials, Inc) for 30 minutes at room temperature. Next, the mixture was transferred into a stainless steel reaction autoclave (50 mL) with a polytetrafluoroethylene liner, heated to 180 °C for 2 h, and cooled to room temperature.¹ The reaction mixture was washed with methanol and de-ionized (DI) water until the pH reached 7.0 and dried in a vacuum oven at 50 °C.

Synthesis of Hydroxylated Graphene-S Nanocomposite (GNSOH-S): First, Na₂S₂O₃ (0.02 mol) was dissolved in de-ionized water (500 mL), followed by magnetic stirring for 5 minutes. Next, the as-synthesized hydroxylated graphene nanosheets (0.06 g) were suspended in the above solution to produce composites with different sulfur loadings. The mixture was ultrasonicated for 30 minutes. Concentrated hydrochloric acid (0.5 mL) was then added into the solution drop-wise to precipitate sulfur homogeneously on the hydroxylated graphene nanosheets. The reaction proceeded for 45 minutes before the product was filtered, washed with de-ionized water, and dried under vacuum at 50 °C.

Results and Discussion

X-ray photoelectron spectroscopy (XPS) analyses of the GNSOH and GNSOH-S nanocomposites are compared in Figure 1. The C1s spectrum of the GNSOH shows an overlap of three peaks at 284.3, 284.6, and 286.0 eV, which can be ascribed to the graphitic carbon, sp² carbon (C=C), and hydroxylated carbon (C-OH), respectively.² In

contrast, the GNSOH-S nanocomposite has a C1s spectrum with reduced intensity, due to the sulfur coverage on the graphene surface. In particular, the peak intensity of the hydroxylated carbon drops significantly, implying possible partial cleavage of the C-OH bond during the sulfur precipitation reaction and formation of a carbon bond with a less electronegative atom, *e.g.*, a C-S bond with a binding energy of 285.7 eV.²

The electrochemical performance of the GNSOH-S nanocomposite was evaluated with CR2032 coin cells, with the results shown in Figure 2. High initial discharge capacities of 1,277, 1,136, and 815 mAh g⁻¹ were obtained, respectively, at C/2, 1C, and 2C rates. Even after 100 cycles, reversible capacities of 1,021 (C/2), 955 (1C), and 647 mAh g⁻¹ (2C) were retained with a capacity retention of as high as 84 % and Coulombic efficiency of ~100 % during cycling. This improvement could be attributed to (i) the homogeneously distributed hydroxyl groups, which aid the formation of an amorphous sulfur layer attached to the graphene and retention of polysulfides, (ii) sulfur nanoparticles, which provide short pathways for ion and electron transport, and (iii) the unique sponge-like morphology of GNSOH-S that allows complete electrolyte penetration and absorbs the strain from cycling-induced volume changes. We believe that the GNSOH-S nanocomposite generated through this facile chemical deposition method is a promising cathode material for high-rate lithium-sulfur batteries.

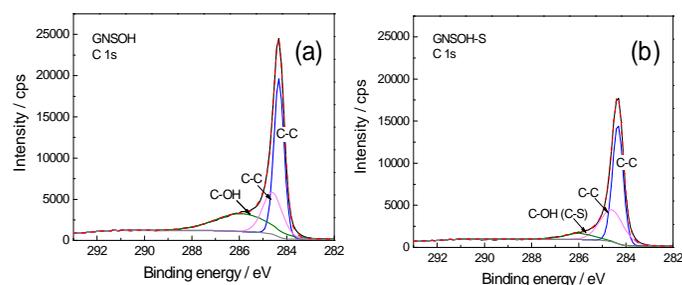


Fig. 1. High-resolution C1s XPS spectra of the (a) GNSOH and (b) GNSOH-S nanocomposites.

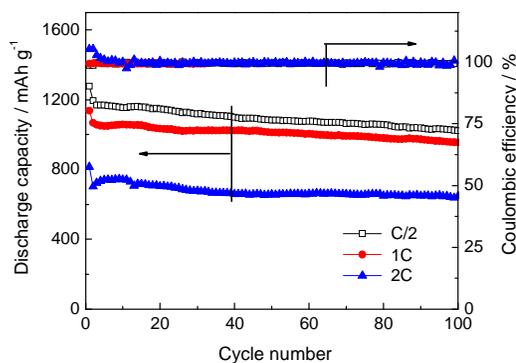


Fig. 2. Cycle performance of the Li-S cells with the GNSOH-S nanocomposite cathode at C/2, 1C and 2C rates at room temperature.

References

1. D. Yang, G. Guo, J. Hu, C. Wang and D. Jiang, *J. Mater. Chem.*, **18**, 350 (2008).
2. L. Zhang, L. Ji, P.-A. Glans, Y. Zhang, J. Zhu and J. Guo, *Phys. Chem. Chem. Phys.*, **14**, 13670 (2012).