



Full length article

N-doped yolk-shell hollow carbon sphere wrapped with graphene as sulfur host for high-performance lithium-sulfur batteries

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ARTICLE INFO

Article history:

Received 12 May 2017

Received in revised form 19 June 2017

Accepted 28 June 2017

Available online 1 July 2017

Keywords:

Lithium-sulfur battery

Hollow carbon sphere

Graphene

Nitrogen doping

ABSTRACT

N-doped yolk-shell hollow carbon sphere wrapped with reduced graphene oxide (rGO/N-YSHCS) is designed and fabricated as sulfur host for lithium-sulfur batteries. The shuttle effect of polysulfides can be suppressed effectively by the porous yolk-shell structure, graphene layer and N-doping. A good conductivity network is provided for electron transportation through the graphene layer coupled with the unique yolk-shell carbon matrix. Such unique structure offers the synthesized rGO/N-YSHCS/S electrode with a high reversible capacity (800 mAh g⁻¹ at 0.2 C after 100 cycles) and good high-rate capability (636 mAh g⁻¹ at 1 C and 540 mAh g⁻¹ at 2 C).

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1. Introduction

To satisfy the urgent requirements of energy storage for electric vehicles (EVs) and hybrid electric vehicles (HEVs) as well as other energy conversion systems [1,2], lithium-sulfur (Li-S) batteries have attracted much attention owing to the high theoretical capacity of sulfur (1675 mAh g⁻¹), resulting in a high energy density (2600 Wh kg⁻¹), which is almost four times higher than that of commercial lithium-ion batteries [3]. Additionally, the other advantages of sulfur, such as with low cost and environmental friendliness, further promote the rapid development of Li-S batteries [4–6]. However, sulfur and its final discharge products (Li₂S and Li₂S₂) suffer from the shortages of low electrical conductivity and large volume change (>80%) during the lithiation/delithiation processes. Specially, the shuttle effect of polysulfide intermediates (Li₂S_n, 4 ≤ n ≤ 8) result in the rapid capacity attenuation and poor high-rate performance of Li-S batteries [7–9].

To overcome the low electrical conductivity and the shuttle effect of sulfur species, various novel nanostructures have been designed for sulfur host [10–12]. Among the efforts, carbonaceous

materials (such as carbon nanotubes [13,14], carbon nanofibers [15,16], graphene [17–19], porous [20] or hollow [21,22] carbon spheres) have been extensively developed, owing to their special nanostructures, unique surface chemical properties and high electrical conductivity [23]. For example, sulfur was inserted among the graphitic layers of multi-walled carbon nanotubes by capillary force, which exhibits a high reversible capacity of 670 mAh g⁻¹ at 100 mAh g⁻¹ after 60 cycles [24]. When graphene was wrapped on the surface of poly-ethylene-glycol coated sulfur nanoparticles, the resultant composite delivered a high and stable specific capacity of 600 mAh g⁻¹ at 0.5 C after 100 cycles [25]. The graphene-coated mesoporous carbon/S composite also obtained an improved reversible capacity of 734 mAh g⁻¹ at 0.5 C after 100 cycles than that of the counterpart without graphene [26]. Meanwhile, some researchers focus on introducing metal oxides (such as TiO₂ [27,28], MnO₂ [29] and BaTiO₃ [30]) or sulfides (such as FeS₂ [31], CoS₂ [32] and SnS₂ [33]) into the sulfur host to further suppress the shuttle effect of polysulfides by chemical affinity. For instance, when BaTiO₃ nanoparticles were added into the hollow carbon nanospheres [30], the electrode delivered a discharge capacity of 835 mAh g⁻¹ at 0.2C after 100 cycles, which was two times higher than that of the counterpart without BaTiO₃ nanoparticles. When 10 wt% SnS₂ nanoparticles with size of 6 nm were distributed into the hollow carbon nanosphere, the synthesized hybrid retained a high capacity of 924 mAh g⁻¹ after 200 cycles at 0.2 C [33].

Heteroatom doping (N, B and P) is another approach to improve the electrical conductivity of carbonaceous materials as well as

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the chemical affinity with sulfur species [34,35], especially the N-doping. The pyridinic N and pyrrolic N can improve the chemical affinity of carbon based host with polysulfides [36], and the quaternary N can facilitate the electrical conductivity of carbonaceous material [37]. For example, when N heteroatom was doped into mesoporous carbon to immobilize sulfur species, the N-doped carbon/sulfur composite exhibited a high capacity of 3.3 mAh cm^{-2} at 0.7 mA cm^{-2} after 100 cycles [38], because the N-doping can promote the formation of S–O bonds between sulfur and oxygen-containing functional groups of mesoporous carbon.

Hollow carbon sphere (HCS), as an ideal sulfur host, has been extensively investigated because of its obvious advantages, such as a high volume for sulfur storage, a large free space for sulfur expansion, porous structure for sulfur impregnation and a high electrical conductivity for electronic transportation [39]. For example, the sulfur loading of synthesized HCS with foam-like shell was as high as 70 wt% [40], and the reversible capacity of the corresponding electrode retained at 780 mAh g^{-1} under a current density of 1 A g^{-1} after 300 cycles. However, the electrical conductivity of the sulfur accommodated in the interior space of HCS is unavoidably quite low, because the diameter of the reported HCSs are always larger than 200 nm. Additionally, the chemical affinity between nonpolar carbon shell and polar lithium polysulfides is very weak, leading to the lithium polysulfides easily diffuse out of the porous carbon shell [41].

Herein, a novel graphene wrapped and N-doped yolk-shell HCS (denoted as rGO/N-YSHCS) hybrid was designed and successfully synthesized as sulfur host, using dopamine as the carbonaceous and nitrogen precursor. The wrapped graphene layer coupled with the yolk-shell structure not only can provide a good conductivity network for electron transportation, but also can act as a dual-barrier to alleviate the shuttle effect of polysulfides. Meanwhile, the N-doping can improve the immobilization of polysulfides as well as the Li^+ diffusion. Thus, the resultant rGO/N-YSHCS/S composite exhibits a high reversible capacity (800 mAh g^{-1} at 0.2 C after 100 cycles) and excellent high-rate performance (540 mAh g^{-1} at 2 C).

2. Experimental

2.1. Synthesis of rGO/N-YSHCS hybrid

The N-YSHCS was prepared using dopamine (DA) and tetraethyl orthosilicate (TEOS) as raw materials in an alcohol-water system with $\text{NH}_3 \cdot \text{H}_2\text{O}$ as catalyst. In a typical synthesis, 0.1 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added in a mixture of ethanol (12 ml) and deionized water (40 ml), then 200 mg DA and 0.5 ml TEOS was dissolved in the system. The mixture was constantly stirred at room temperature for 36 h. Subsequently, the PDA@ SiO_2 @PDA composite was dried overnight at 60°C and carbonized under N_2 atmosphere at 800°C for 2 h. Finally, the silica was etched by 10 wt% HF for 12 h to obtain the N-YSHCS. For comparison, 0.5 ml ammonia aqueous solution was added into the system to form silica spheres, then DA was introduced to obtain the N-doping HCS (N-HCS).

200 mg graphene oxide (GO), prepared by Hummers method, were dispersed in 100 ml deionized water by ultrasonication for 2 h. Subsequently, 0.5 g PDA@ SiO_2 @PDA composite was added into 50 ml GO dispersion and vigorously stirred. After centrifugation and vacuum drying, the GO/PDA@ SiO_2 @PDA composite was carbonized at 800°C for 2 h and etched by HF to get the rGO/N-YSHCS hybrid.

2.2. The preparation of rGO/N-YSHCS/sulfur composites

The as-prepared rGO/N-YSHCS and sublimed sulfur were grinded with a mass ratio of 1:2, then sealed in a vacuum glass

tube. The glass tube was heated at 155°C for 10 h and then 300°C for 2 h, resulting the rGO/N-YSHCS/sulfur hybrid.

2.3. Materials characterization

The morphology and microstructure of the samples were examined by scanning electron microscopy (SEM, JEOL-7100F), transmission electron microscopy (TEM, JEOL-2100F) and X-ray diffraction (XRD Rigaku D/max2550, Cu $\text{K}\alpha$). The surface composition was measured by X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD) and the sulfur content was determined by the thermogravimetric analysis (TG, TA company Q600 Analyzer). The N_2 adsorption and desorption isotherms were taken on a Quadrasorb SI analyzer at 77 K, and the pore size distribution were obtained by the Barrett-Joyner-Halenda (BJH) model. Raman spectra was recorded on Raman spectrometer (Spex 1403).

2.4. Electrochemical measurements

Electrochemical measurements were tested using CR2016 coin-type cells. The working electrode were composed of active material, carbon black and polyvinylidene fluoride (PVDF) with a mass percent of 80:10:10. The slurries were uniformly pressed onto Al current collector, dried at 80°C for 12 h, then cut into small pieces with a diameter of 1.2 cm. The active sulfur mass loading on each electrode was about $0.4\text{--}0.6 \text{ mg cm}^{-2}$. Lithium foil was used as the counter electrode and Celgard 2300 as the separator. The electrolyte was composed of 1 M bis (trifluoromethane) sulphonamide lithium salt (LiTFSI) dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume) with 0.1 M LiNO_3 additive. The cells were assembled in an Ar-filled glove box. The galvanostatic charge-discharge tests were carried on an Arbin BT-2000 electrochemical workstation. Cyclic voltammetry (CV) was performed from 1.7 to 2.7 V at a scanning rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was measured with an electrochemical working station (Gamry Instrument, USA). The cycled electrode chips were obtained in the glove box and washed with DME solvent for several times. Then the chips were dried in the glove box overnight and transferred in a sealed container for structural observation.

3. Results and discussion

The typical fabrication of rGO/N-YSHCS hybrid is schematically illustrated in Fig. 1. The N-YSHCS was initially fabricated using dopamine and TEOS as raw materials. Briefly, the aqueous solution of dopamine and TEOS were simultaneously added in the alcohol-water system with $\text{NH}_3 \cdot \text{H}_2\text{O}$ as catalyst. Then the obtained PDA@ SiO_2 @PDA composite was dispersed into deionized water and mixed with GO dispersion. Subsequently, the obtained GO/PDA@ SiO_2 @PDA composite was carbonized at 800°C and then etched by HF, giving the rGO/N-YSHCS hybrid. Finally, the sulfur was impregnated into rGO/N-YSHCS hybrid to obtain the rGO/N-YSHCS/S composite by melt impregnation.

As shown in Fig. 2a, the as-prepared N-YSHCS fabricated with 0.1 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ has regular uniform spherical morphology with an average diameter of $\sim 600 \text{ nm}$. A typical yolk-shell structure can be clearly observed (Fig. 2b), where the porous spherical honeycomb-like carbon exists in the interior of N-YSHCS with a diameter of 200 nm. If the PDA@ SiO_2 @PDA spheres were oxidized in air at 550°C for 5 h, hollow SiO_2 sphere can be obtained (see Supporting information, Fig. S1), which further illustrates that the synthesized N-YSHCS has a yolk-shell structure (Fig. 2b). The yolk-shell structure can be controlled by adjusting the ammonia aqueous solution and the sequence of process steps. For example, if much more ammonia aqueous solution (0.5 ml) was added into the formed

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