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# Facile large-scale synthesis of core–shell structured sulfur@polypyrrole composite and its application in lithium–sulfur batteries with high energy density

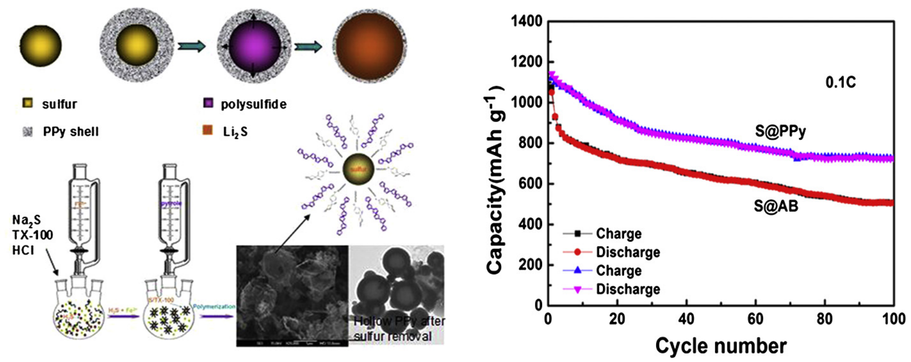
Yanping Xie [a], Hongbin Zhao [a,b,]*, Hongwei Cheng [c], Chenji Hu [a], Wenying Fang [a], Jianhui Fang [a], Jiaqiang Xu [a,]*, Zhongwei Chen [b]

[a] College of Science, Shanghai University, 99 Shangda Road, Shanghai 200444, China
[b] Department of Chemical Engineering, University of Waterloo, 200 University Avenue, Waterloo N2L 5G5, Canada
[c] State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering, Shanghai University, 149 Yanchang Road, Shanghai 200072, China

## HIGHLIGHTS

- The core–shell structured S@PPy composite is obtained by *in situ* polymerization of PPy on sulfur spheres.
- The homogenous PPy layer prevents diffusion of polysulfide and volume expansion.
- $PO_4^{3-}$ doping is helpful to improve the conductivity of the S@PPy cathode.
- High C-rate performance and cycling stability are obtained on the S@PPy cathode.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this context, we report a novel one-pot synthesis of S@Polypyrrole core–shell spheres as the cathode material in lithium–sulfur battery, designed by polypyrrole (PPy) wrapping on the formed nano-sulfur via the facile wet chemical strategy. The in-situ polymerized PPy layer in this special structure is helpful to inhibit aggregation of sulfur particles with small size, the polysulfide dissolution and shuttling, and offer fast and efficient transport of electron/lithium ion within the electrode. Besides, the flexible PPy layer effectively accommodates the volume expansion. PPy with partial $PO_4^{3-}$ doping was also employed to improve cycling stability and C-rate performance of S@PPy composite by exchanging $Cl^-$ with $PO_4^{3-}$. Thus, the sulfur electrode with a high sulfur loading of 80% delivered an initial discharge capacity of 1142 mA h g$^{-1}$ and maintained a high capacity of 805 mA h g$^{-1}$ after 50 cycles at 0.1 C. The corresponding capacity retention over 100 cycles was about 65%, with a limited decay of 0.3% per cycle. Even at a high current density of 1.5 C, the composite still exhibited a high discharge capacity of about 700 mA h g$^{-1}$. This results mean that the designed electrode can achieve a high practical specific energy density of more than 400 W h/kg, far beyond the commercial $LiCoO_2$ batteries. Due to low cost, facile large-scale synthesis and superior electrochemical performance of S@PPy cathode with high sulfur loading, this work will provide a very promising method to further promote the Li–S batteries in the practical application of portable electronic devices, electric devices and energy storage system.

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* Corresponding authors at: College of Science, Shanghai University, 99 Shangda Road, Shanghai 200444, China.
*E-mail addresses:* hongbinzhao@shu.edu.cn (H. Zhao), xujiaqiang@shu.edu.cn (J. Xu).

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## 1. Introduction

Recently, the invention of rechargeable lithium-ion (Li-ion) battery technology has made the great breakthrough in electronic device and scalable electrochemical energy storage systems over the last several decades [1–5]. In particular, rechargeable Li–S battery has been considered as a promising high energy storage system and has attracted more attention among many researchers, due to its high theoretical specific capacity of 1675 mA h $g^{-1}$ based on a reversible redox reaction between sulfur and lithium [6–10]. For Li–S batteries with an average voltage of 2.15 V, a high specific energy density of about 2600 W h/kg could be obtained, several times higher than those reported in conventional lithium-ion batteries, such as $LiCoO_2$ and $LiFePO_4$ cathode [11,12]. In addition, due to other merits such as inexpensive, non-toxicity and abundance of sulfur, Li–S batteries will make it possible for the practical application in next generation efficient and green energy power systems [13–15]. Unfortunately, for its natural defects of the inherent low electrical conductivity, soluble polysulfide intermediated ($Li_2S_{4-8}$) in organic electrolyte and the marked volume change of sulfur (~80%) upon lithium ion insertion/extraction, the sulfur electrode still need to overcome these problems before its wide application [16–19].

To overcome the above problems, recently many reports focused on improving its conductivity with various kinds of carbon, including graphene, graphite, mesoporous carbon, et al. [20–24]. These reports pay more attention on enhancing the cycling performance by designing carbon with microporous and modified chemical groups [20,24]. However, the number of the reports that conductive polymers are used in Li-ion and Li–S batteries is not too much. But the conductive polymers really contribute to enhance the conductivity and then improve the cycling performance in Li-ion [25–28] and Li–S battery [29–37]. For example, polyaniline (PANi) [29] and polypyrrole (PPy) [30–34] have been used as attractive hosts for confining sulfur due to their special structure and properties in rechargeable Li–S batteries. For instance, Gao et al. [29] reported that carbon/sulfur composite coated the conducting polymer PANi highly improved the electrochemical performance of the batteries. The outer coating strategy can effectively confine polysulfide dissolution into the electrolyte and offer fast ion/electron transportation. Among these S/conductivity polymers, a core–shell structured sulfur cathode by coating conductive polymer on the sulfur electrode, has been under close investigation by many research teams. The special core–shell structure may offer effective electrochemical contact, shorter ion/-electron transport path, and accommodate volume change [30,32]. However, most reported strategies for the preparation of the core–shell structured sulfur cathode often lead to particles agglomeration and growth, which makes its practical application hindered. Furthermore, a facial and homogenous conductive polymer layer has seldom been well obtained [35,36].

Herein, we reported a facile one-pot chemical method to synthesize a stable core–shell S@Polypyrrole (S@PPy) composite in large scale, which consists of spherical sulfur particles and uniform conductive PPy outer layer. In this work, the designed S@PPy composite with nano-sized sulfur spheres of 150 nm, smaller than that previously reported, and uniform coating layer of PPy was obtained without heat treatment and template in the synthesis process. PPy is electrochemically active, stable and moderately elastic for lithium ion insertion/extraction in the electrochemical reaction [33,37,38]. Because the PPy layer with a thickness of about 60 nm uniformly wrapped on sulfur particles, the aggregation and the size of spherical sulfur particles were effectively controlled through one-pot synthesis. In such a rational core–shell structure, the outer flexible PPy layer was mainly intended to further improve the conductivity of sulfur electrode, relieve the shuttling effect and increase the stability of the structure of the composite during cycling. In addition, the PPy layer with $PO_4^{3-}$ doping was also introduced into the sulfur cathode to enhance the cycling stability performance. As the cathode, the as-designed S@PPy composite with core–shell structure in Li–S battery establishes superior comprehensive electrochemical property, including long cycling stability and large C-rate performance.

## 2. Experimental

### 2.1. One-pot synthesis of large-scale sulfur–polypyrrole composite

The composite was prepared as follows: First, 0.50 g of $Na_2S$ and 0.2 g of S powder were grinded in agate mortar and then dissolved in a three flask with 100 mL of DDI water containing 10 mL of 1 wt % Triton X-100 ($C_{34}H_{62}O_{11}$, TX-100). And then 40 mL of 1 M HCl was slowly added into the yellow mixing solution and sealed the flask. Then 20 mL of 1 M $FeCl_3$ (more than three times the amount of pyrrole) was dropped into the three flask slowly with violent stirring and ice bath. After that 100 mg pyrrole (Shanghai Chemical Corp, 98%) in 20 mL ethanol was dropped into the yellow suspension and kept stirring for 24 h at ice-water bath. Then the gray composite was centrifuged, and then washed with de-ionized water and ethanol for several times until $Fe^{3+}$ is not detected by $SCN^-$, followed immersing in 1 M $H_3PO_4$ for several hours in vacuum. The suspension was refluxed at 80 °C for 24 h to dope $PO_4^{3-}$ into the PPy as much as possible and then was separated by centrifugation. Finally, the resulting composite was obtained after keeping in a vacuum oven at 60 °C for 12 h. Meanwhile, we also synthesized S@PPy without $PO_4^{3-}$ doping with the same synthesis method.

For comparison, without adding pyrrole monomer, the S@acetylene black (S@AB) composite was prepared with the similar synthesis route.

### 2.2. Materials characterization

SEM images were observed with JEOL JSM-6700F. TEM observation was carried out with JEM-200XC. The structure of the product was detected by powder X-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 1.54056$ Å). Fourier-transformed infrared (FTIR) spectrum was obtained by an infrared spectrometer (Shimadzu, UV-2501PC, Japan) to evaluate the existance of PPy in composite.

### 2.3. Electrochemical characterization

The electrode slurry was prepared by mixing active material, acetylene black, and PVDF (8:1:1 wt%) in N-methyl-2-pyrrolidine (NMP) as the solvent. The uniform slurry was pasted on an aluminum foil and then dried at 50 °C for 12 h in vacuum. The dried cathode material had the high sulfur loading of 2.6 mg $cm^{-2}$. The CR2016 coin batteries were assembled inside an Ar-filled glove box with lithium metal as anode and Celgard 2400 membrane as separator. The electrolyte consists of 1.0 M lithium bis-trifluoromethanesulfonylimide (LiTFSI) and 0.1 M $LiNO_3$ in a mixed solvent of DOL-DME (1:1 v/v). The coin cells were galvanostatically charged and discharged between 1.5 and 3.0 V (vs. $Li/Li^+$) with the Land CT-2001A Battery Test System. Cyclic voltammetry (CV) was set at 0.1 mV $s^{-1}$ with an electrochemical workstation (CHI660D USA). The electrochemical impedance spectroscopy (EIS, 0.01 Hz–100 kHz, 5 mV) was also measured. All electrochemical measurements were conducted at 25 °C.

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