Electronic Supplementary Information

Decoration of Sulfur with Porous Metal nanostructure: An Alternative Strategy to Improve the Cyclability of Sulfur Cathode Materials for Advanced Lithium-sulfur Batteries

Xinyong Tao, Feng Chen, Yang Xia, Hui Huang, Yongping Gan, Xiaorong Chen, Wenkui Zhang*

College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, China. fax: +86 571 88320394;
Tel.: +86 571 88320394. E-mail:msechem@zjut.edu.cn

Experiment

The pristine S microparticles were prepared by facile reactions of metal ion precipitation of polysulfides and H_2O_2 oxidation of ZnS (Scheme 1). 3.6g $Na_2S{\cdot}9H_2O$, 1.4g sublimed S and 0.208g NaOH were solved into 40ml de-ionized water to achieve sodium polysulfide (Na_2S_x) solution.2.2g $ZnCl_2$ was solved into 40 ml de-ionized water to obtain $ZnCl_2$ solution. Subsequently, the sodium polysulfide solution was added to the $ZnCl_2$ solution slowly with magnetic stirring. Then H_2O_2 solution was added to oxidize ZnS. After 12 h reaction, the product was separated centrifugally, washed with de-ionized water and absolute ethanol. Then the product was dried in oven at 80 ^oC for 12 h.

The as-synthesized pristine S microparticles (0.7 g) were dispersed into 40 ml H_2PtCl_6 solution (0.038 mol/L) by ultrasonic treatment for 10 min. Subsequently, excess $NaBH_4$ solution was added to the mixture slowly with rapid magnetic stirring. The products were separated centrifugally, washed with de-ionized water and absolute ethanol. After wash, the product was dried in oven at 80 ^oC for 12 h.

To obtain the Ni decorated S microparticles, the as-synthesized pristine S microparticles (1.0 g) were dispersed into 40 ml $NiSO_4$ solution (0.129 mol/L) by ultrasonic treatment for 10 min. Subsequently, excess $NaBH_4$ solution was added to the mixture slowly with rapid magnetic stirring. The products were separated centrifugally, washed with de-ionized water and absolute ethanol. After wash, the product was dried in oven at 80 ^oC for 12 h.

The phase purity and crystalline structure of the samples were characterized by the X-ray diffraction (XRD) using X'Pert Pro diffractometer for Cu Kα radiation (λ = 1.5418Å). The particle size and morphology were observed by scanning electron microscope (SEM, Hitachi

S-4800) and TEM (FEI Tecnai G2 F30) equipped with energy dispersive X-Ray spectroscopy (EDX). Thermogravimetric analysis (TGA) was evaluated under a nitrogen flow rate of 20 mL/min by using a thermogravimetric analyzer (Mettler Toledo) operated at a heating rate of 20 ^{o}C /min from room temperature to 700 ^{o}C.

Electrochemical performances were investigated using CR2025 coin-type cells assembled in an argon-filled glove box. To prepare the cathode, active material, acetylene black and polyvinylidene fluoride (PVDF) binder were mixed according to the ratio of 70:15:15 by weight. The mixture was dispersed in N-methylpyrrolidone (NMP), and the resultant viscous slurry was cast on nickel foil and dried at 60 ^{o}C under vacuum for 12 h. After that, the cells were assembled with lithium foil as the anode. The electrolyte was 1 mol/L bis (trifluoromethane) sulfonimide lithium salt dissolved in a mixture of 1, 3-dioxolane (DOL) and dimethoxymethane (DME) (1: 1 by volume).

Electrochemical capacity measurements were conducted on a Neware Battery Test System with galvanostatic charge and discharge in the voltage range of 1.5-3.0 V at room temperature. Cyclic voltammograms (CV) were performed with a CHI 650b electro-chemical work station in the voltage range of 1.5-3.0 V at a scan rate of 0.1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) tests were carried out with the frequency ranging from 0.1 Hz to 100 kHz.

Supporting figure

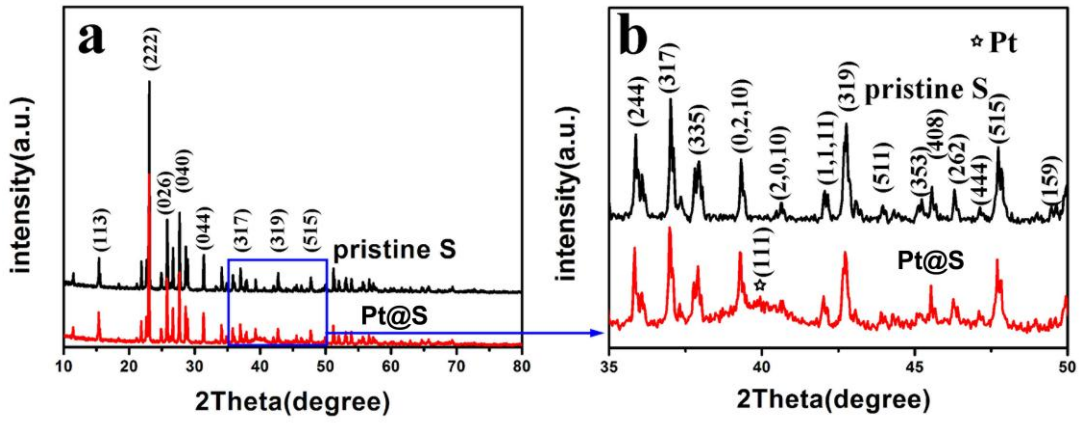

Fig. S1. (a) XRD patterns of the Pt@S and the pristine S samples. (b) The partial enlargement of the XRD pattern with 2 theta ranging from 35 to 50 degree.

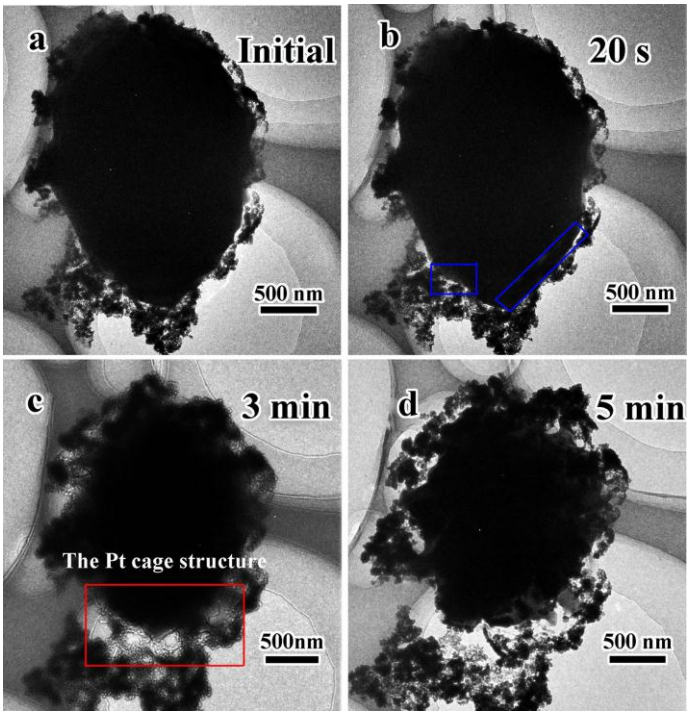

Fig. S2. TEM images of the Pt@S under the electron beam radiation (300KeV)

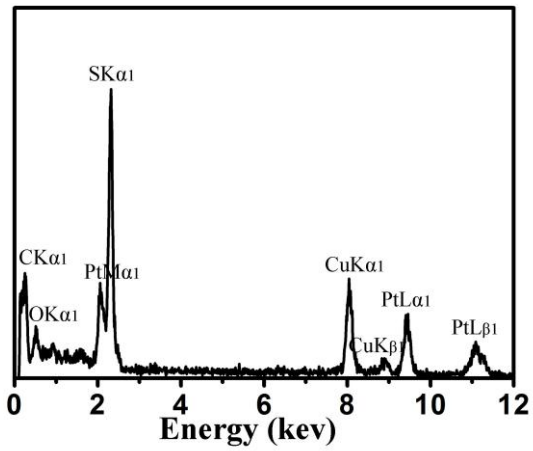

Fig. S3. EDX of Pt@S particle

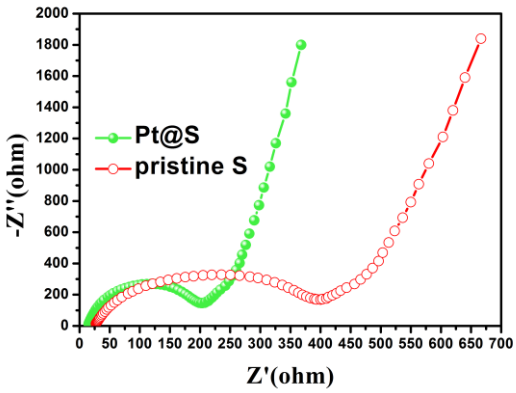

Fig. S4. EIS spectra of pristine S electrodes and Pt@S electrodes

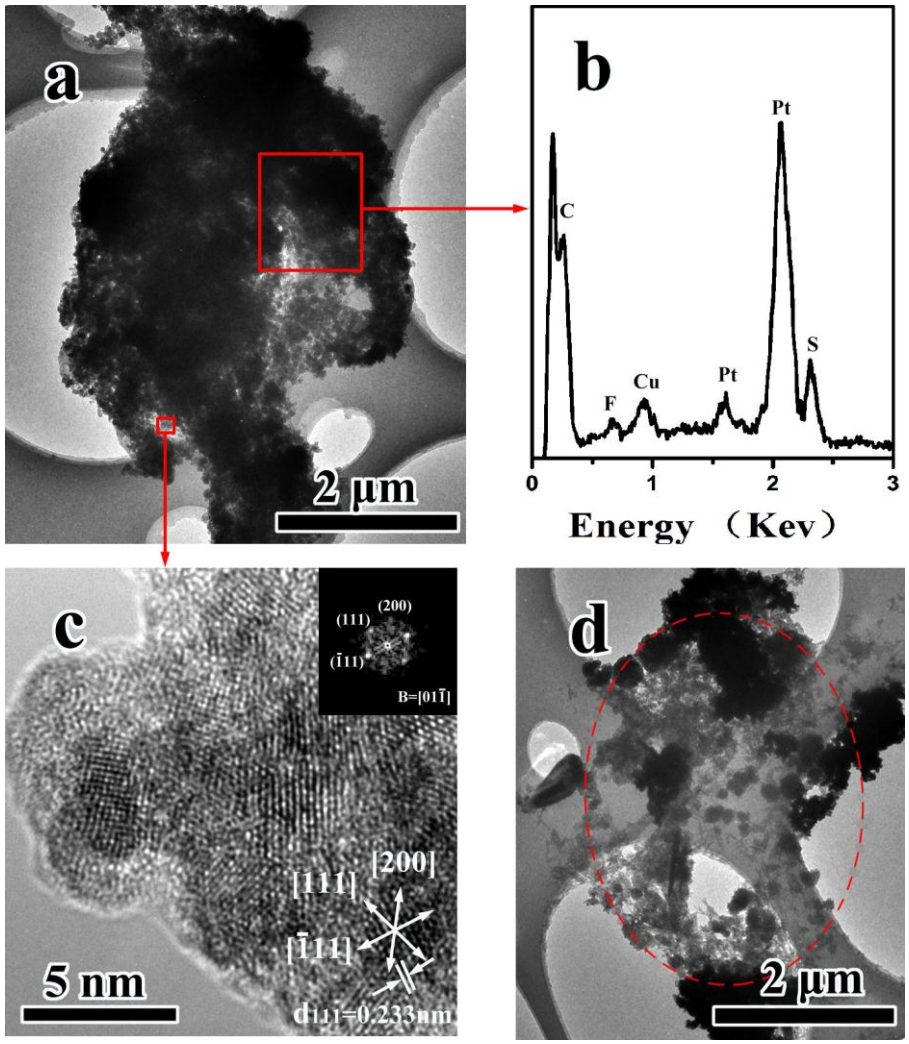

Fig. S5. (a) TEM image of Pt@S particle after 50 cycling. (b) EDX of (a). (c) HRTEM image of Pt nanostructures. (d) TEM image of Pt@S particle after 3h heat treatment at 300 ^{o}C.

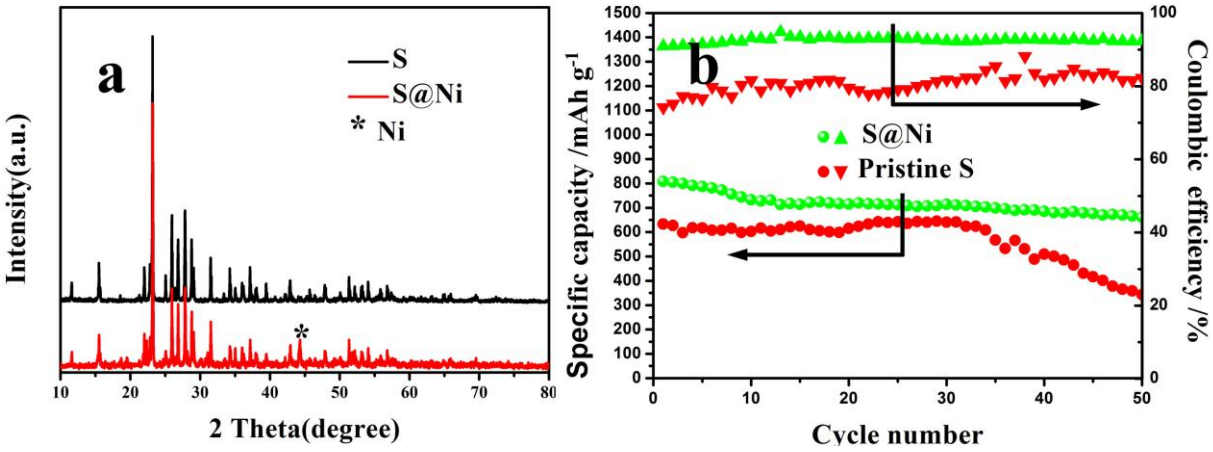

Fig. S6. (a) XRD pattern of Ni@S and pristine S. (b) Cycling performance of S and Ni@S at a current density of 0.1 C.