Supplementary Material (ESI) for Journal of Materials Chemistry

A Novel Pyrolyzed Polyacrylonitrile-Sulfur@MWCNT Composite Cathode Material for High-rate Rechargeable Lithium/Sulfur Batteries

Lichao Yin, Jiulin Wang*, Jun Yang* and Yanna Nuli [a]

[a.] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, P. R. China. Fax: (+86)-21-54747667; Tel: (+86)-21-54747667; E-mail: wangjiulin@sjtu.edu.cn, yangj723@sjtu.edu.cn*

Experimental Section

1. Materials

MWCNT with diameters of 40-60 nm and lengths of 5-50 μm was obtained from Shenzhen Billtechnologies (China). AN, IA, Nitric acid, Sulfuric acid, DMSO and AIBN were obtained from Aladdin-reagent and used as received. Commercial PAN, the best one selected in our reachable range, was from Sigma-Aldrich.

2. Acidization of MWCNT with Aqua Regia

In a 100 mL glass flask, 1 g of MWCNT, 10 mL of nitric acid, and 30 mL of sulfuric acid were added. The flask was transferred into an ultrasonic water bath for 2.5 h, and then diluted with distilled water (300 mL), filtered, and washed with distilled water until the pH was more than 5.0. The acidified MWCNT (ca. 0.95 g) was obtained by drying under vacuum at 60 ºC.

3. *In situ* polymerization

A typical procedure was as follows: in a 200 mL glass flask, 0.5 g of acidified MWCNT, 25 mL of DMSO and 25 mL of distilled water were added. The flask was transferred into an ultrasonic water bath for 10 min. Then, 10mL (8 g) of AN and 0.3 g of IA were added under ultrasonic condition for 5 min, and 75 mg of AIBN was added. The flask was bubbled with nitrogen gas for 20 min, sealed with a rubber septum and transferred into a water bath (65 ºC) to polymerize under vigorous stirring. Over predetermined times, samples were taken out from the flask under nitrogen gas. The PAN@MWCNT composite was obtained by filtration, washing with ethanol three times and drying under vacuum at 60 ºC.

4. Preparations of the pPAN-S@MWCNT composite and pPAN-S composite

The pPAN-S@MWCNT composite was prepared by heating the mixture of PAN@MWCNT powder and sulfur (7 : 1 in wt.) at 300 ºC in nitrogen atmosphere for certain time. The pPAN-S@MWCNT composite with sulfur content around 63%, 48% and 30% were obtained by controlling heating time for 2 h, 3 h and 7 h, respectively.

The pPAN-S composite was prepared by heating the mixture of commercial PAN powder and sulfur (7 : 1 in wt.) at 300 ºC in nitrogen atmosphere for 3 h.

5. Structural and morphological characterization

The monomer conversion was determined gravimetrically. X-Ray diffraction (XRD) patterns were recorded using Cu-Ka radiation at 40 kV with an X-ray diffractometer (D/max-2200 / PC, Rigaku). The morphologies of the composites were investigated using a scanning electron microscope (SEM, JEOL JSM-7401F). A thin layer of gold was sputter-coated on the sample for charge dissipation during SEM imaging. The microstructure of the composites was characterized using a transmission electron microscope (TEM, JOEL JEM-100CX). Elemental composition of the pPAN-S@MWCNT composite was measured by elemental analysis (EA, PE 2400 II, Perkin Elmer).

6. Electrochemical characterization

The electrochemical performances of composites were evaluated by using coin-type cells with lithium metal anode. The cathodes were prepared by pasting a mixture of active material, Super P conductive carbon black (40 nm, Timical) and PTFE as binder at a weight ratio of 80 : 10 : 10. After rolling the mixture to sheet, it was cut to Φ 12 mm sheets, dried and pressed onto foamed nickel current collector. Finally, the sample electrodes were dried at 80 ºC in vacuum for 4 h. The CR2016 coin cells were assembled in an argon-filled glove box (MB-10 compact, MBRAUN) using 1M $LiPF_6$/EC + DMC (1 : 1 by volume, ethylene carbonate (EC), dimethyl carbonate (DMC)) as electrolyte and ENTEK ET20-26 as separator. The charge and discharge tests were conducted on a LAND battery test system (Wuhan Kingnuo Electronics Co., Ltd., China) at 25 ºC with certain current density. The cut-off voltage was 1 V versus Li/Li^+ for discharge and 3V for charge.

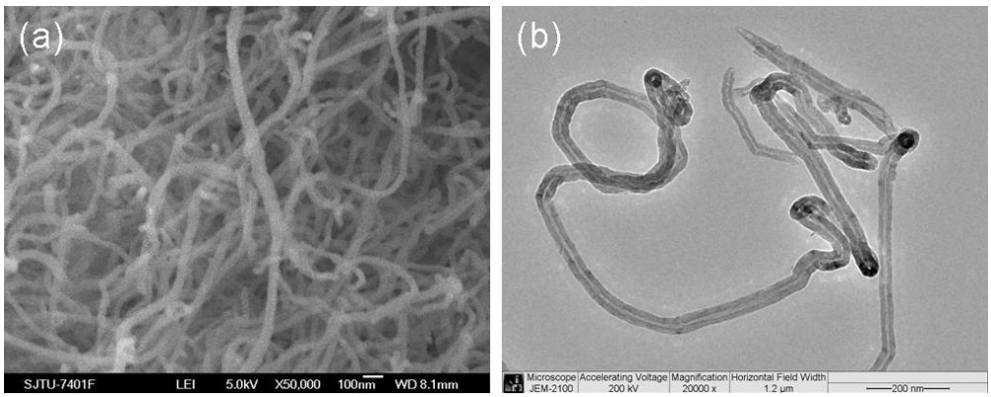

Figure S1.SEM (a) and TEM (b) images of MWCNT.

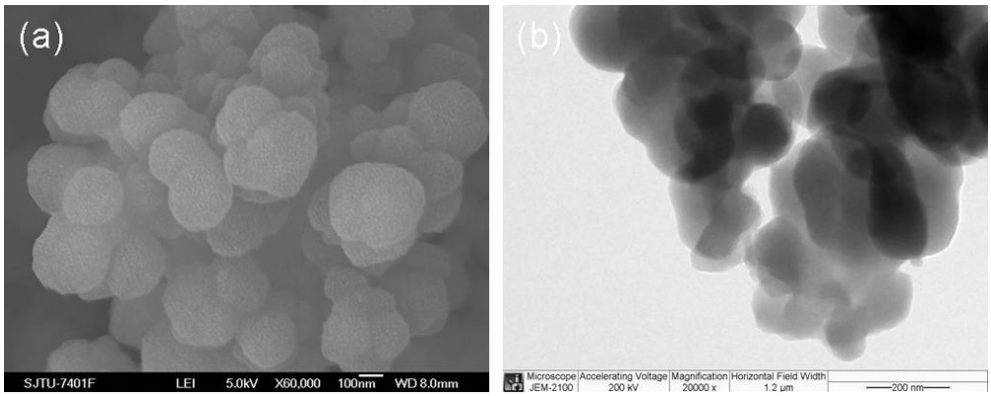

Figure S2. SEM (a) and TEM (b) images of commercial PAN.

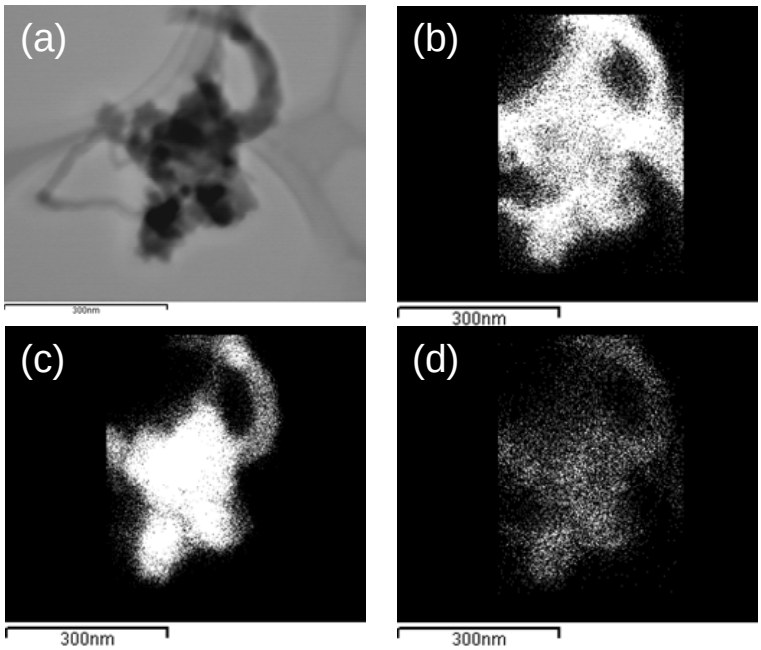

Figure S3. TEM image and elemental mapping of pPAN-S@MWCNT composite. (a) TEM image of pPAN-S@MWCNT composite particle. Elemental mapping of (b) carbon, (c) sulfur and (d) nitrogen by energy-dispersive X-ray spectroscopy (EDS).

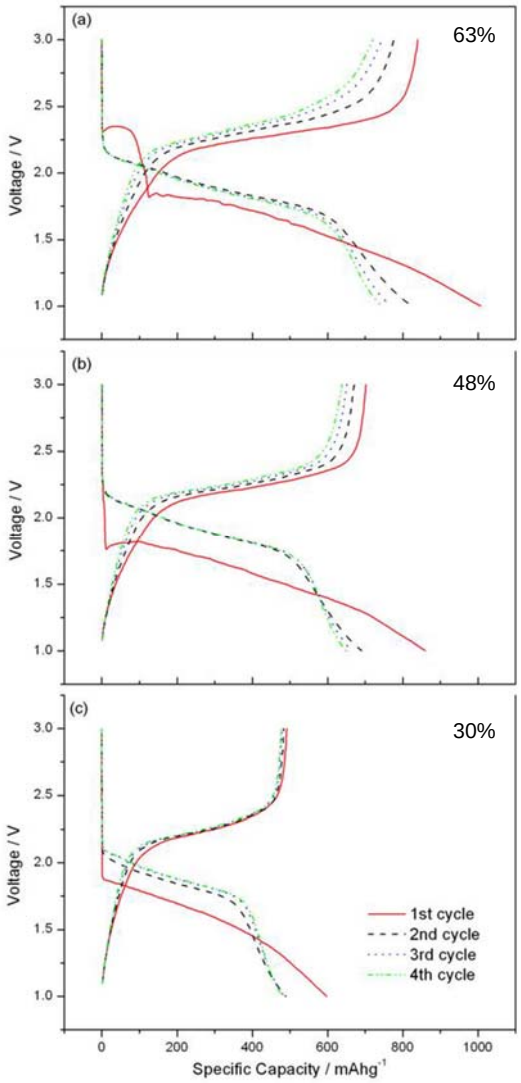

Figure S4: Charge/discharge curves of Li/S cells with the pPAN-S@MWCNT composites containing different sulfur content at 0.1C rate. (a) 63%, (b) 48%, (c) 30%.

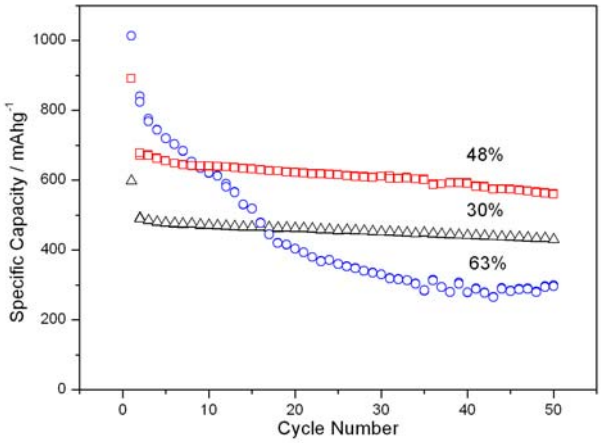

Figure S5. Cycling performance of Li/S cells with the pPAN-S@MWCNT composites containing different sulfur content at 0.1C rate.