Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

# Electronic Supplementary Information

## Biomineralization-induced self-assembly to porous hollow carbon nanocapsule monolith and application for Li-S Battery

Wen Hu,[*ab] Huamin Zhang,[*a] Yining Zhang,[a] Meiri Wang,[a] Chao Qu[a] and Jianhong Yi[b]

[a]Division of Energy Storage, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

[b]Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, P. R. China

*To whom correspondence should be addressed. Tel: +86-411-84379072; Fax: +86-411-84665057; E-mail: huwen756@126.com; zhanghm@dicp.ac.cn

Experimental Section

Porous hollow carbon nanocapsule monoliths were prepared by a biosilicification-induced self-assembly method. In a typical synthesis, TEOS (0.58 mL, Sinopharm Chemical Reagent Co., Ltd.) was added dropwise into a mixed solution containing absolute ethanol (3 mL), water (0.2 mL) and one drop of 0.5 M HCl with stirring over 1.5 h at room temperature to complete the hydrolysis of TEOS into orthosilicic acid and its oligomers. Then choline chloride (0.3 g, Sinopharm Chemical Reagent Co., Ltd.) was introduced and stirred for 1 h. Afterward 20 wt % resols' ethanolic solution (1.25 g), synthesized by the method reported by Zhao et al.,[1] was gradually added to the mixture and stirred for 1 h. Water addition (5.3 mL) and immediate pH adjustment to 5.0~5.5 with 0.1 M NaOH under vigorous stirring finally gave a 10 g homogeneous water/ethanol (v/v 1:1) sol solution containing 0.2 M choline stabilized-silicic acid (1.5 wt %) and 2.5 wt % resols. Collagen sponges (1.5 × 1.5 × 0.2 cm) were cut from reconstituted type Ⅰ collagen tapes (Beijing Jiade Sunshine Technology Co., Ltd). They were pre-expanded with water, treated with $6.67\times10^{-4}$ M PAH (average Mw 15000, Sigma-Aldrich) for 4 h, rinsed briefly with water, and immersed in 1 mL of the sol solution mentioned above at room temperature for 4 days with daily change of the impregnating medium. The infused collagen sponges were air dehydrated in a fume hood overnight, and thermopolymerized in an oven at 100 ℃ for 24 h. The as-made samples, orange-yellow in color, were carbonized in a tubular furnace under $N_2$ flow at 800 ℃ for 6 h, suspended in 10 wt % HF solution for 24 h to remove silica, washed with water and vacuumdried at 60 ℃ for 24 h to get the porous hollow carbon

nanocapsule monoliths. The synthesis of the porous hollow carbon nanocapsules-sulfur nanocomposite was performed using a melt-diffusion strategy. Microsized powders of porous hollow carbon nanocapsule monoliths and sublimed sulfur (Sigma-Aldrich) with a weight ratio of 1:1 were mixed and ground together, then heated at 155 ℃ for 12 h under flowing $N_2$ atmosphere in a tubular furnace.

XRD patterns were measured on a PANalytical X'Pert Pro diffractometer with Cu Kα radiation. FE-SEM and TEM measurements were carried out with FEI Quanta 200F and FEI Tecnai $G^2$ Spirit instruments, respectively. The $N_2$ adsorption/desorption isotherm was collected using Micromeritics ASAP2020 surface area analyzer.

The carbon-sulfur cathode was fabricated by mixing 80 wt % active materials, 10 wt % acetylene black, and 10 wt % polyvinylidene difluoride (PVDF) in N-methyl-2-pyrrolidinone (NMP) as dispersant. Then the resulting slurry was cast onto aluminum foil. After solvent evaporation in vacuum oven at 60 ℃ for 12 h, the electrode sheet was pressed and cut into disks (sulfur surface density of ≈ 0.7 mg $cm^{-2}$). CR2016-type coin cells were assembled in an Ar-filled glovebox using lithium metal as the counter/reference electrode, Celgard 2400 as a separator, and 1.0 M bis-(trifluoromethanesulfonyl)imide lithium (LiTFSI) in 1:1 v/v 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) as the electrolyte (Zhangjiagang Guotai Huarong Chemical New Material Co., Ltd.). CV experiment was carried out with a CHI611C potentiostat in a voltage range of 1.5-3 V vs. $Li/Li^+$ at a scan rate of 0.1 mV $s^{-1}$. Galvanostatic charge-discharge test was conducted on a LAND-CT2001A instrument

at current density of 0.1 C (168 mA $g^{-1}$) on the basis of active sulfur in a voltage range of 1.5-2.8 V.

References

1 Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, H. F. Yang, Z. Li, C. Z. Yu, B. Tu and D. Y. Zhao, *Angew. Chem. Int. Ed.*, 2005, **44**, 70539.