

Electronic Supplementary Information (ESI)

Immobilization of sulfur in microgels for lithium-sulfur battery

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SII. Experimental procedures

1.1. Materials

All chemicals were purchased from Aldrich. Poly(ethylene glycol) dimethacrylate (PEGDMA, $M_n \approx 550$ g/mol) was purified with neutral Al_2O_3 . Tetrahydrofuran (THF), chloroform ($CHCl_3$), and other organic solvents were purified by distillation. Sulfur, 1-naphthylamine, 3-bromo-1-propanol, 3-thiophenemethanol, 5-dimethylamino-2-nitroso-phenol, *N*-bromosuccinimide (NBS), *i*-PrMgCl (2.0 M solution in THF), allyl-MgBr (2.0 M solution in THF), Ni(dppp)Cl₂, *o*-dichlorobenzene (DCB), 2,2'-azobis(2-methylpropionamide) dihydrochloride (AAPH),

polyethylene binder, conductive carbon black, polypropylene separator, lithium foil, lithium bis(trifluoromethane)sulfonimide (LiTFSI), lithium nitrate (LiNO₃), 1,3-dioxolane, and 1,2-dimethoxyethane were used as received. The water used in all experiments was of Millipore Milli-Q grade.

1.2. Synthesis of allyl-terminated P3OET

The monomer 2-bromo-5-iodo-3-oligo(ethylene oxide)₄-thiophene was prepared following the methods reported in literature.^[1,2] 2-bromo-5-iodo-3-oligo(ethylene oxide)₄-thiophene (1.8 mmol) was added into a three-necked flask equipped with N₂ purge system. Then the atmosphere in the flask was replaced with N₂. Freshly distilled THF (5.0 mL) was added into the flask via a syringe and the mixture was stirred at 60 °C. *i*-PrMgCl (1.8 mmol) was added via a syringe. After stirring at room temperature for 20h, the mixture was diluted with THF (10.0 mL), and Ni(dppp)Cl₂ (0.05 mmol) was added into the mixture with N₂ protection. Allyl-MgBr (1.8 mmol) was added after ca. 10 min, and the mixture was stirred for another 5 min. Toluene was added to the mixture, and the organic layer was washed with water, dried over anhydrous MgSO₄. After concentration under the reduced pressure, the polymer solution was participated into excess hexanes for at least five times, and collected by suction filtration to give purified polymers ($M_n = 5500$, and PDI = 1.10; see Fig. S2 below for GPC trace with THF as an eluent). ¹H NMR is given in Fig. S3 below. The yield was around 45%.

1.3. Synthesis of S-P3OET

Allyl-terminated P3OET was dissolved in DCB and added to an excess of sulfur, with the weight ratio S:P3OET = 9:1. The reaction mixture was stirred for 1 h at 165 °C. After complete conversion, the reaction mixture was quenched in methanol. After centrifugation, the product

was dried under reduced pressure ($M_n = 7500$, and PDI = 1.19; see Fig. S1 below for GPC trace with THF as an eluent). ^1H NMR is given in Fig. S3 below.

1.4. Synthesis of the SM

The S-P3OET (1.0 mmol) was added into water (100.0 mL) in a round-bottom flask equipped with a stirrer, a N_2 gas inlet, and a condenser. After 30 min N_2 purge, PEGDMA (1.0×10^{-2} mmol) was added, and the temperature was raised to 70.0 °C and the polymerization was initiated by adding AAPH (0.5 mmol). The polymerization was allowed to proceed for 7h. The SM microgels were obtained by centrifugation, redispersed in water, and purified by 3 days' dialysis (Spectra/Por[®] molecularporous membrane tubing, cutoff 12000-14000) against water.

1.5. Battery fabrication and testing

The SM (in the control experiments, the S-P3OET assemblies was used) as an active materials was used to formulate the composite cathode, and conductive carbon black was used to ensure the electronic percolation into the electrode volume. A mixture of the SM, carbon black, and the polyethylene binder with CHCl_3 enabled the production of an ink that was blade casted onto a surface-treated aluminium foil (carbon-coated; as the current collector). After evaporation of the solvent CHCl_3 in air at room temperature, a composite electrode was obtained. Further drying in a vacuum oven at 60 °C for 72 h was done before the cathode was stored for two weeks in the glove box. A composition of 85/10/5 (mass ratio) of SM/carbon black/polyethylene binder was used. The sulfur loading was approximately 1 mg/cm². Li-S batteries (2032 type coin cells, with the separator, cathode, and counter electrode diameter of ca. 19, 14, and 16 mm, respectively) were assembled in an argon filled glove box, by using a polypropylene separator, lithium foil as the reference/counter electrode, and LiTFSI (1.0 M in a 1:1 v/v mixture of 1,3-dioxolane and 1,2-dimethoxy ethane) containing LiNO_3 (1 wt%) as the electrolyte. Batteries were tested using a

Solartron 1470 cell test system. The cyclic voltammetry (CV) curves were recorded on a CH Instruments 660E potentiostat. Battery cycling was done on an Arbin BT2000 battery tester. The testes were carried out at a cut-off potential of 1.0-3.0 V.

1.6. Other characterizations

¹H NMR spectra were recorded in the solvent CDCl₃ on a Bruker AVIII 500MHz solution-state NMR spectrometer. TEM images were taken on a JEOL JEM-1400 transmission electron microscope and operated at an accelerating voltage of 100 kV. The samples were prepared by drop-casting 10 μL of a deep violet solution onto copper grids and dried overnight.

The relative molecular weights and the molecular weight distribution were determined by gel permeation chromatography (GPC) on a set of three μ-styragel columns with packing particles having pore diameters of 500, 10⁴, and 10⁵ Å. The columns show a linear separation in the range of 5.0×10² g/mol to 1.0×10⁶ g/mol, and are placed in a thermostatted compartment at 25 °C. A Wyatt Dawn Hellos-II multi-angle light scattering detector and a Wyatt Optilab refractive index detector were used to measure light scattering and refractive index, respectively. The laser sources of both of these detectors operated at 690 nm. Each polymer solution was filtered through a 0.80 μm filter before injection. GPC measurements were performed on THF solutions at 25 °C (conc. 5 mg/mL) with their eluent rates set to 1 mL/min.

Dynamic light scattering (DLS) was performed on a 90Plus multi angle particle sizing analyzer equipped with a BI-9000AT digital autocorrelator (Brookhaven Instruments, Inc.). A He-Ne laser (35 mW, 659 nm) was used as the light source. In dynamic LLS (DLS), the Laplace inversion (here the CONTIN method was used) of each measured intensity-intensity time correlation function in a dilute dispersion can lead to a line-width distribution $G(\Gamma)$. For a purely diffusive relaxation, Γ is related to the translational diffusion coefficient D by $(\Gamma/q^2)_{C \rightarrow 0, q \rightarrow 0} = D$,

so that $G(\Gamma)$ can be converted to a transitional diffusion coefficient distribution and hydrodynamic diameter ($\langle D_h \rangle$) distribution by using the Stokes-Einstein equation, $\langle D_h \rangle = 2(k_B T / 6\pi\eta) / D$, where k_B , T , and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.^[3] All samples were passed through Millipore Millex-HV filters with a pore size of 0.80 μm to remove dust before the DLS measurements.

References

- [1] A. Kiriya, V. Senkovskyy and M. Sommer, *Macromol. Rapid Commun.*, 2011, **32**, 1503.
- [2] Y.-Z. Ma, R.W. Shaw, X. Yu, H.M. O'Neill and K.L. Hong, *J. Phys. Chem. B*, 2012, **116**, 14451.
- [3] B. Chu, *Laser Light Scattering*. 2nd ed. New York: Academic Press; 1991.

SI2. Figures

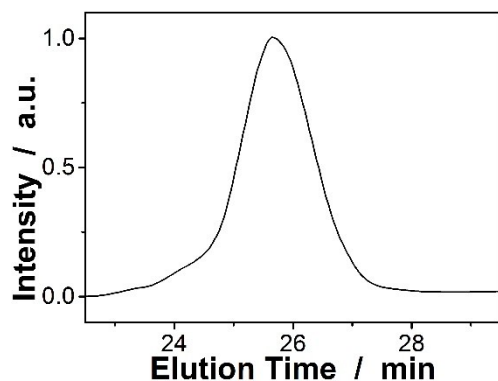


Fig. S1. GPC trace of S-P3OET in THF.

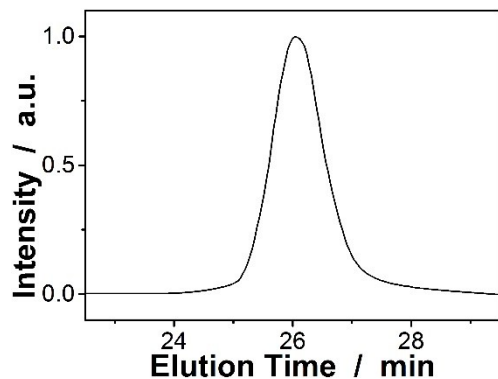


Fig. S2. GPC trace of allyl-terminated P3OET in THF.

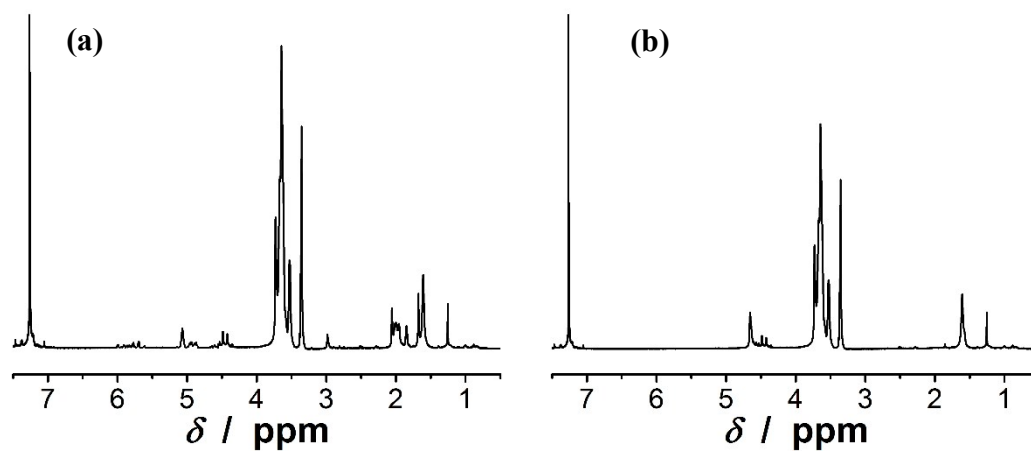


Fig. S3. ¹H NMR spectra of (a) the allyl-terminated P3OET and (b) S-P3OET in CDCl₃.

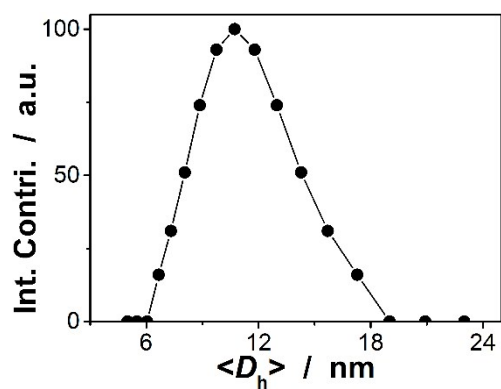


Fig. S4. DLS size distribution of the S-P3OET assemblies.

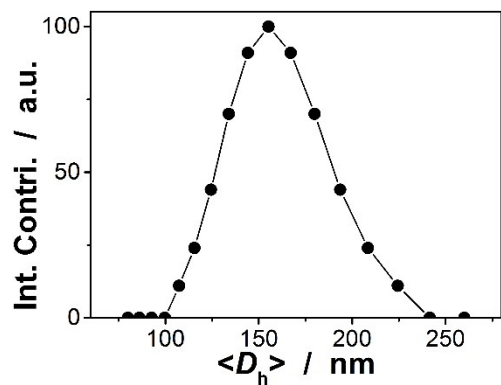


Fig. S5. DLS size distribution of the SM.

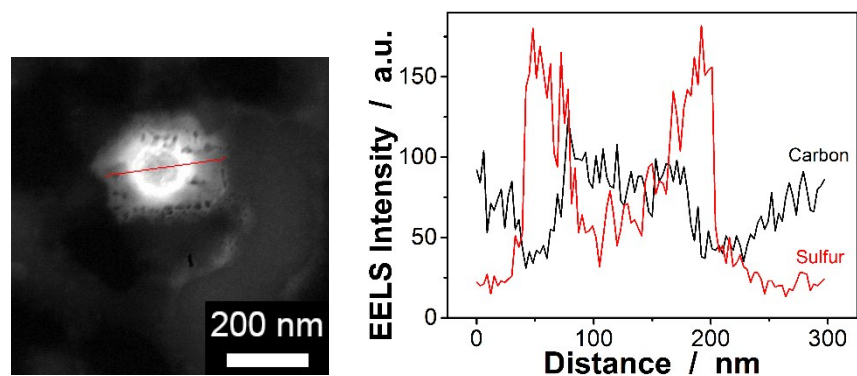


Fig. S6. EELS recorded on an individual particle of the SM.

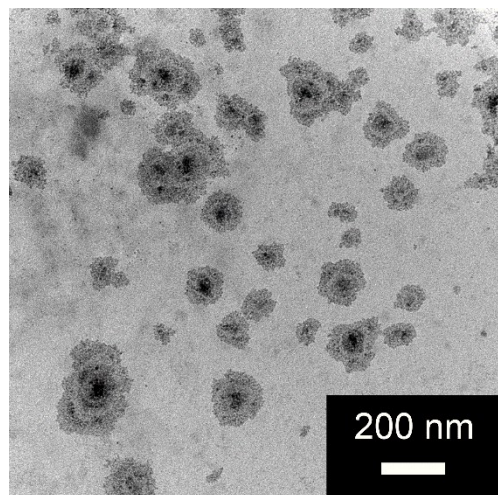


Fig. S7. Typical TEM image of the SM treated with the organic solvents of chloroform, 1,3-dioxolane and 1,2-dimethoxyethane.

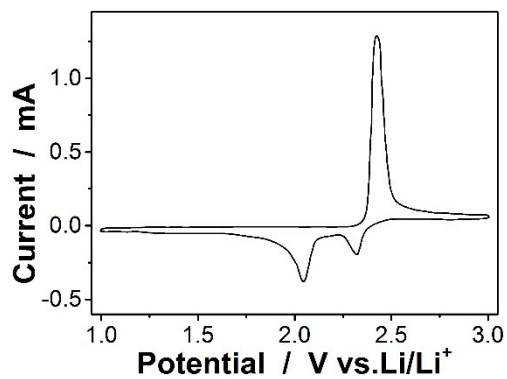


Fig. S8. Cyclic voltammogram measured on the coin Li-S battery with the S-P3OET electrode.

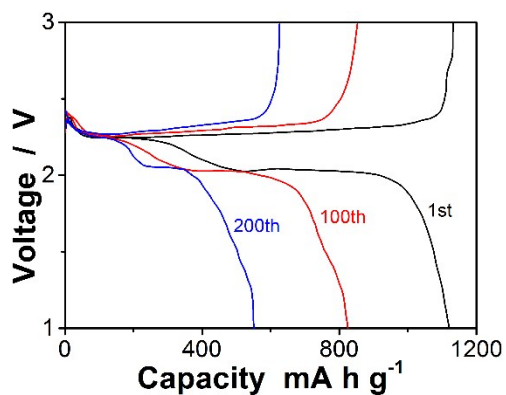


Fig. S9. Charge/discharge profiles measured at a rate of $0.1C$ on the coin Li-S battery with the S-P3OET electrode.

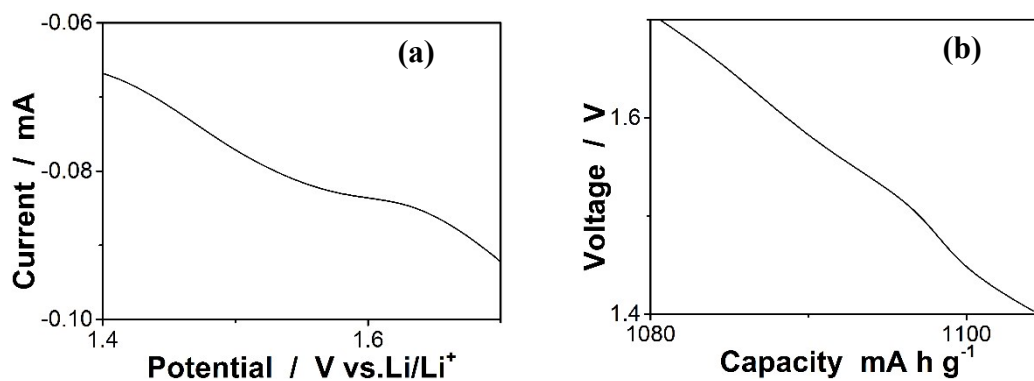


Fig. S10. The partial enlarged details of (a) cyclic voltammogram and (b) discharge curves for the coin Li-S battery with the SM electrode.

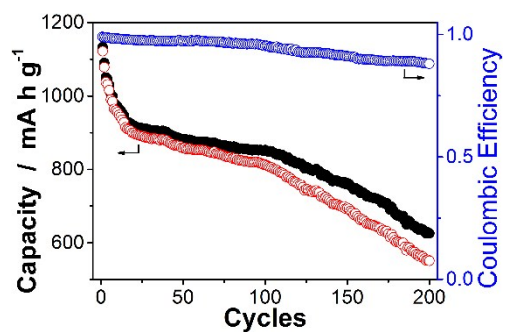


Fig. S11. Cycle life of the charge capacity (solid symbols), the discharge capacity (open symbols), and the Coulombic efficiency, measured at a rate of $0.1C$ on the coin Li-S battery with the S-P3OET electrode.

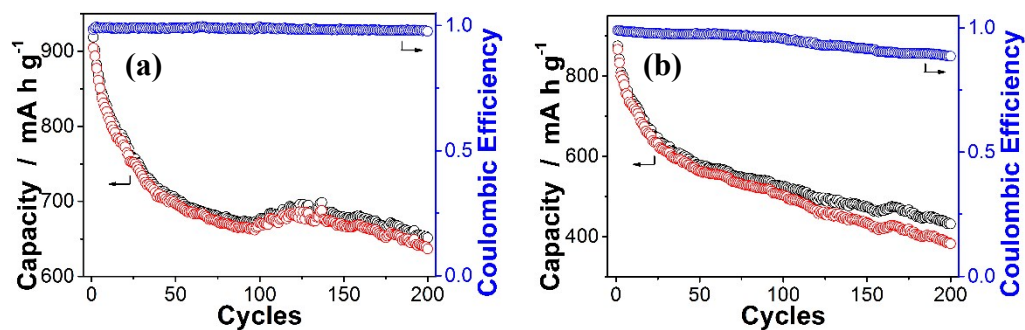


Fig. S12. Cycle life of the charge capacity (solid symbols), the discharge capacity (open symbols), and the Coulombic efficiency, measured at a rate of 0.25C on the coin Li-S battery with (a) the SM electrode and (b) the S-P3OET electrode.

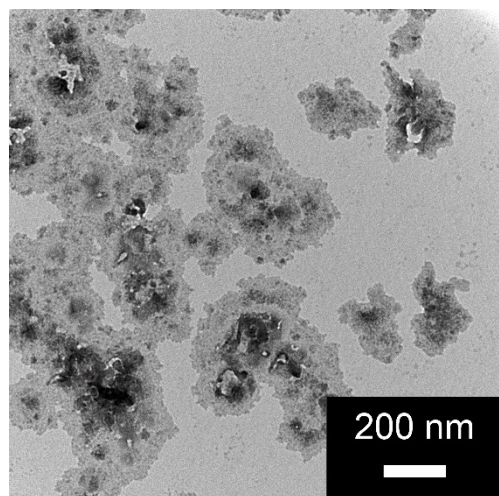


Fig. S13. Typical TEM image of the regained composite microgels, which were obtained from a disassembled coin cell after running 200 cycles.

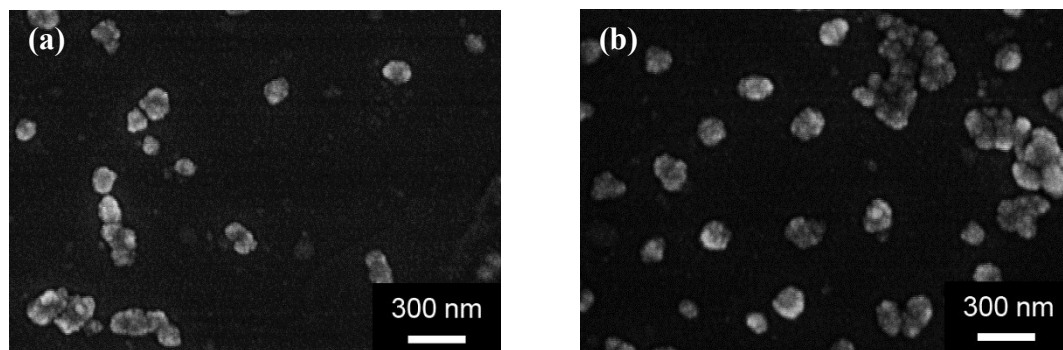


Fig. S14. Typical SEM images of (a) the SM, and (b) the regained composite microgels which were obtained from a disassembled coin cell after running 200 cycles.

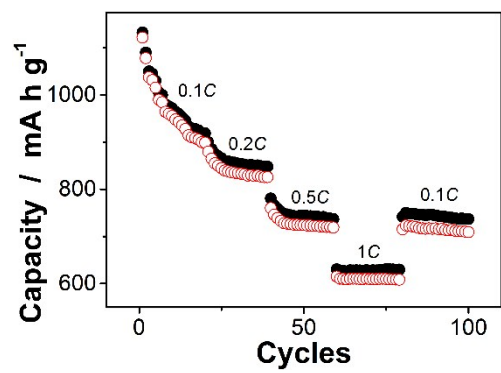


Fig. S15. The charge/discharge capacities at various current densities, measured on the coin Li-S battery with the S-P3OET electrode.