# Support Information

## A Liquid Metal-Based Self-Adaptive Sulfur-Gallium Composite for Long-Cycle Lithium-Sulfur Batteries

*Mengqi Zhu, Songmei Li*, Bin Li*, Shubin Yang*

Key Laboratory of Aerospace Advanced Materials and Performance of Ministry of Education, School of Materials Science & Engineering, Beihang University, Beijing, 100191, China.

E-mail: songmei_li@buaa.edu.cn; li_bin@buaa.edu.cn.

## Experimental Section

*Preparation of sulfur nanoparticles (nanoS) and the core-shell sulfur@gallium composite (S@Ga):* 5.04 g sodium thiosulfate was added into 500 mL deionized water to obtain settled solution (regard as A), 24.2g polyvinyl pyrrolidone (PVP) was added into 500 mL deionized water (regard as B). After the PVP was dissolved completely, solution A were added in B under mechanical stirring. Then, hydrochloric acid (40 mL, 1.2 M) were slowly added into the mix solution with a speed of 200 $\mu$L min$^{-1}$. After continuous stirring for 4h, the precipitate was centrifuged and washed for several times with deionized water, followed by drying under 60 $^{o}$C for 12h. Gallium and prepared sulfur nanoparticles were mixed in a plastic vessel with mass ratios of 2:8 and 4:6. Then the mixture were heated to ~35 $^{o}$C to melt the added gallium. After gallium was molten, the mixture was stirred for several hours under ~ 35 $^{o}$C to gain a uniform S@Ga nanocomposite with care-shell structure.

*Electrochemical measurement*: Firstly, as-synthesized active materials (sulfur and S@Ga nanoparticles), carbon black and polyvinylidene fluoride (PVDF) (7:2:1, wt%) were directly mixed with 300μL N-methyl-2-pyrrolidinone (NMP) to fabricated uniform slurry. Then the resulting slurry was smeared on stainless steel sheets and dried under vacuum condition at 60 $^{o}$C for more than 12 h. Test cells were assembled in 2032 type coin cells with metal lithium as anodes and the prepared electrodes as cathodes. The commercial polypropylene (PP) membrane was applied as separator and electrolyte was obtained by dissolving 1M LiTFSI in a mixture of dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 by volume). The electrolyte used in each cell was about 40 μL. The sulfur content was ~56 wt.% of the electrode with a mass loading of ~ 0.45 mg cm$^{-2}$ and 1.5 mg cm$^{-2}$. Cyclic voltammetry tests were conducted between the voltage range from 1.5 to 3 V (vs. Li/Li$^{+}$) with a ARBIN instrument at a scanning rate of 0.1 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) tests were conducted to evaluate the reaction kinetics of different cathodes in the range of frequency from 0.1Hz to 100 kHz with a voltage amplitude of 10 mV.

*Preparation of Ga shell, S@Ga nanoparticles at different cycling states and separators after cycling:* Before the observation of gallium shell, the S@Ga powder was completely frozen to ensure the solidification of gallium, then the powder was washed by $CS_2$ for several times to remove the sulfur. Resultant powder was dried under vacuum at room temperature. To observe the morphologies of S@Ga nanoparticles at different cycling states, the batteries with S@Ga cathodes were disassembled after different cycling stages and the obtained S@Ga cathodes were washed by DME for several times. Then the cathodes were dried under vacuum for over 24 h. To observe the separators of batteries with S@Ga and nanoS cathodes, batteries were disassembled after 50 cycles.

*Materials characterization* : Morphologies and composition of as-synthesized sulfur and S@Ga nanoparticles were measured by scanning electron microscopy (SEM, Hitachi S-4800), the attached Energy Dispersive Spectrometer (EDS) and transmission electron microscope (TEM). The phase composition was carried out at room temperature using a X-ray diffraction (XRD, D/max 2200-PC). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) tests were proceed to analyze the element composition and valence on the surface of S@Ga nanoparticles.

*Diameter quantification :* To quantify the diameter distribution of S@Ga nanoparticles at different state, related SEM morphologies of S@Ga cathodes were divided into sixteen regions with same areas (Figure S7), then in each region, five nanoparticles were randomly chosen and quantified to achieve 80 values, regarding as the diameter distribution of S@Ga nanoparticles.

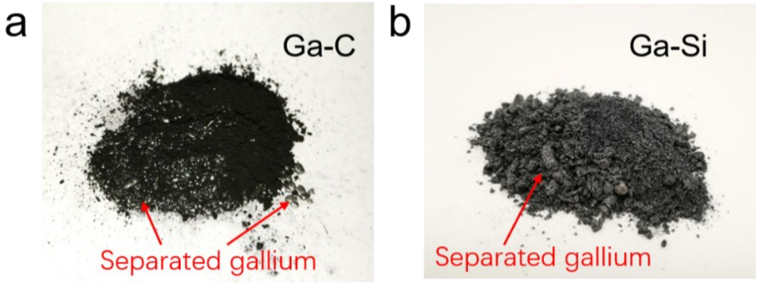

**Figure S1.** Mixtures of gallium-carbon spheres and gallium-silicon nanoparticles after stirring for several hours, showing many separated liquid gallium drops.

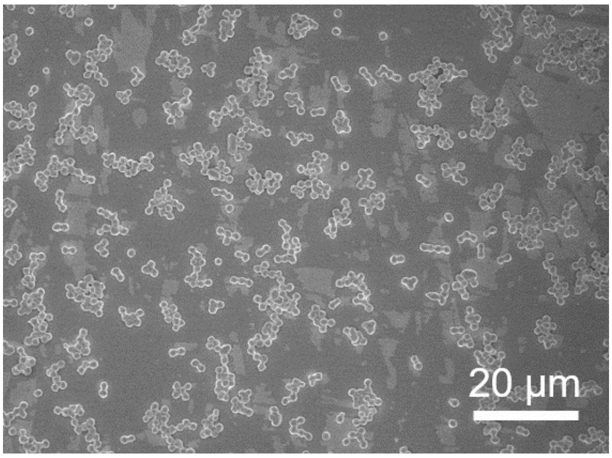

**Figure S2.** SEM image of as-prepared sulfur nanoparticles.

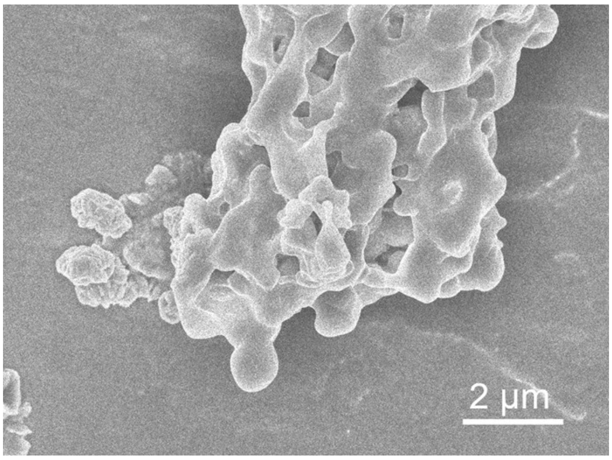

**Figure S3.** SEM image of the S@Ga composite with 40 wt.% gallium.

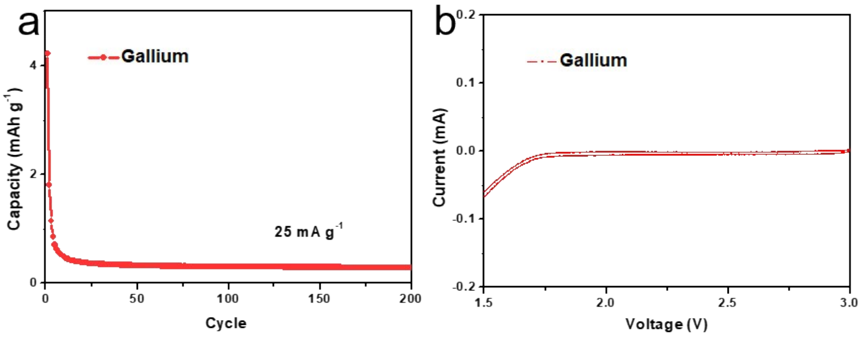

**Figure S4.** The (a) CV curve and (b) long-term cycling of the gallium electrode.

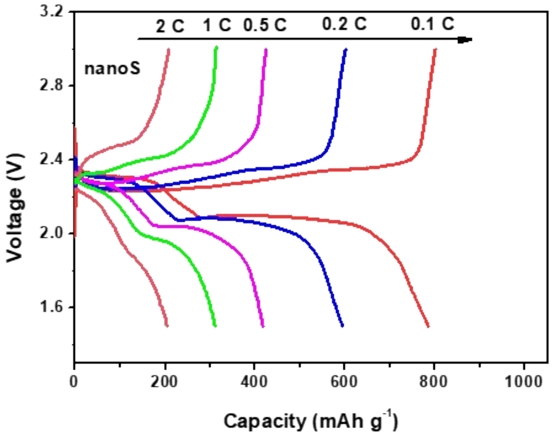

**Figure S5.** Voltage-capacity profiles at different rates of naonoS electrode.

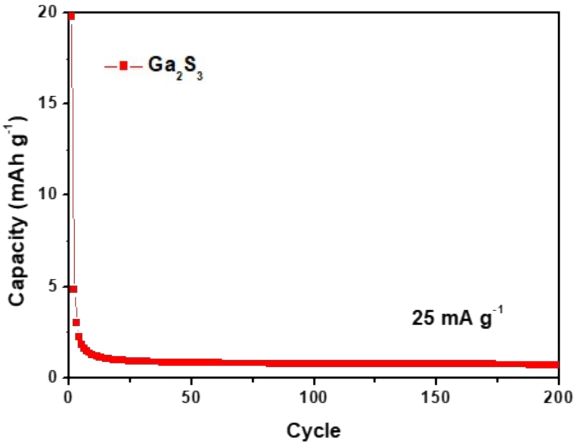

**Figure S6.** Long-term cycling of the $Ga_2S_3$ electrode.

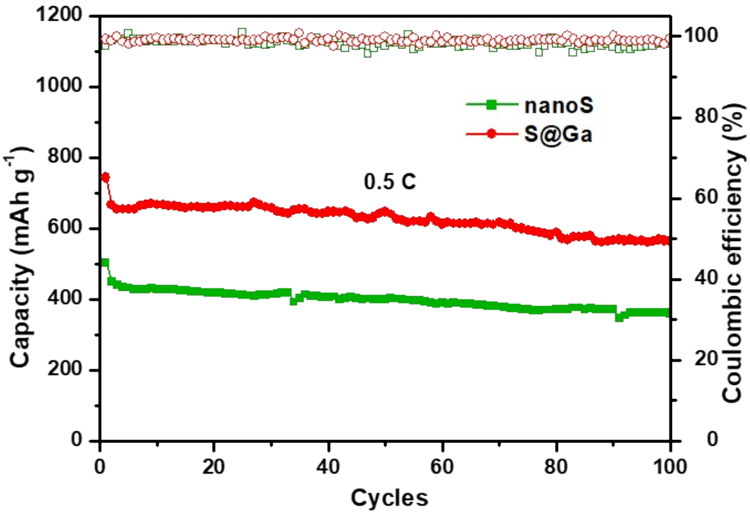

**Figure S7.** Cycling performances of nanoS and S@Ga cathodes at 0.5 C.

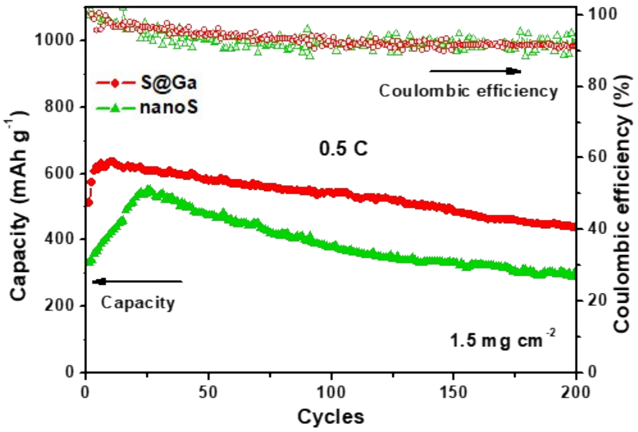

**Figure S8.** Cycling performances of S@Ga and nanoS cathodes at 0.5 C with the sulfur laoding of about 1.5 mg cm$^{-2}$.

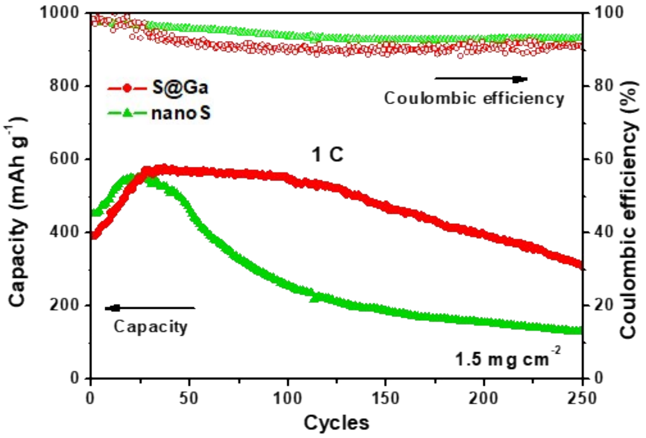

**Figure S9.** Cycling performances of S@Ga and nanoS cathodes at 1 C with the sulfur laoding of about 1.5 mg cm$^{-2}$.

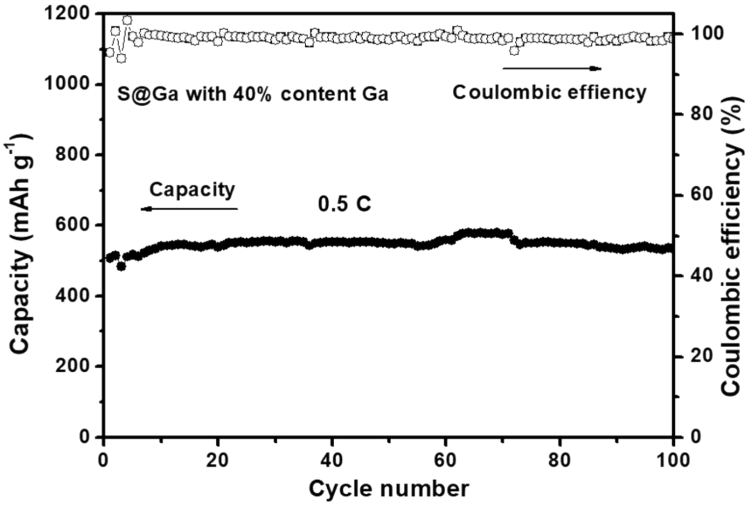

**Figure S10.** Cycling performance of the S@Ga composite with 40% content Ga at 0.5 C.

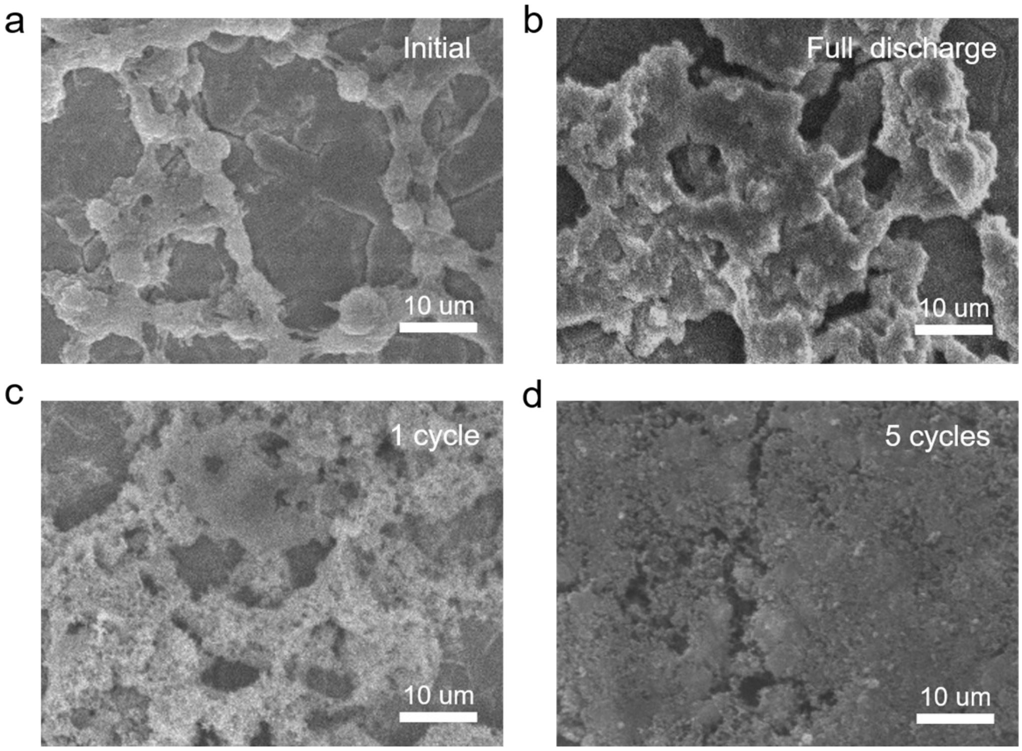

**Figure S11.** SEM morphologies of nanoS cathodes at different cycling states.

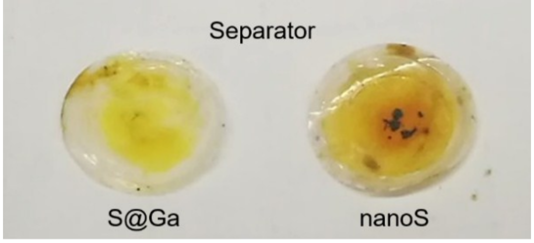

**Figure S12.** The separator photographs of batterries with S@Ga and S cathodes after 50 cycles at 1C.

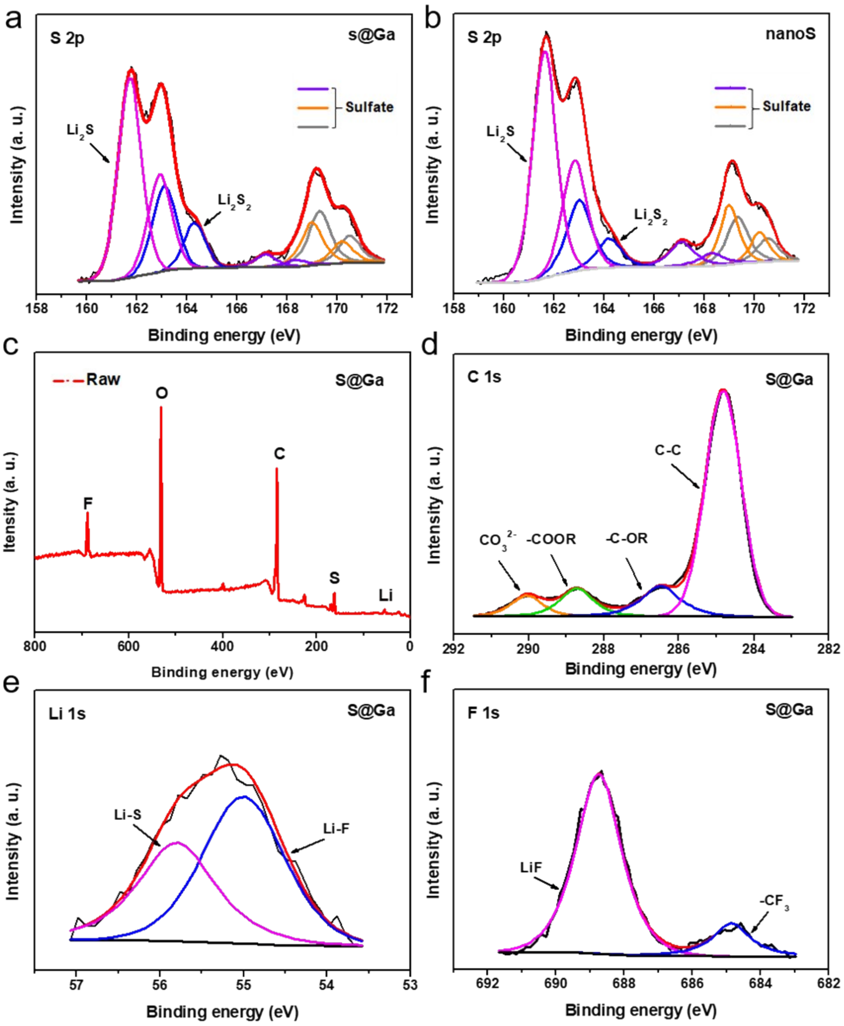

**Figure S13.** High-resolution spectra of S 2s of lithium anodes of batteries with (a) S@Ga and (b) nanoS cathodes. (c) Wide spectral scan, and high-resolution spectra of (d) C 1s, (e) Li 1s and (f) F 1s of lithium anode coupled with S@Ga cathode.

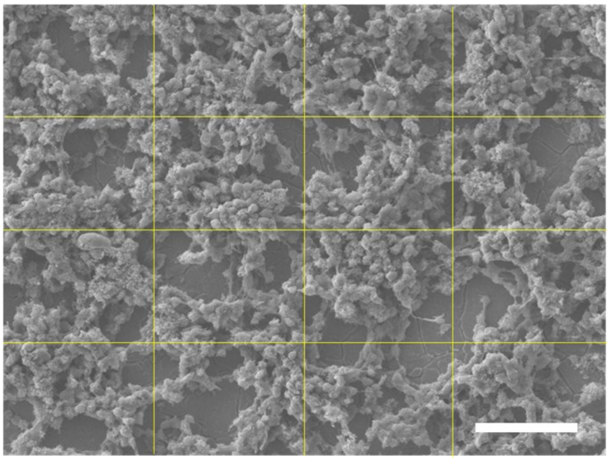

**Figure S14.** Statistical method to evaluate the diameter distribution of S@Ga nanoparticles as illustrated in the experimental section. Scar bar: 20 μm