# Supporting Information

# One-step Synthesis of Sulphur-impregnated Graphene Cathode for Lithium-Sulphur Batteries

Min-Sik Park[a], Ji-Sang Yu[a], Ki Jae Kim[a], Goojin Jeong[a], Jae-Hun Kim[a], Yong-Nam Jo[a], Uk Hwang[a], Shin Kang[b], Taewoo Woo[b], and Young-Jun Kim*[a]

[a]*Advanced Batteries Research Center, Korea Electronics Technology Institute, 68 Yatap-dong, Bundang-gu, Seongnam 463-816, Republic of Korea.*

[b]*Technology Innovation Center, SK Holdings, 99 Seorin-dong, Jongro-gu, Seoul 110-110, Republic of Korea.*

Fig. S1 shows the morphology and microstructure of elemental S powder and conventional S-C composite prepared by mechanical milling at different magnifications. To prepare S-C composite, a mixture of 74 wt% of elemental S and 26 wt% of ketchen black as a conducting agent was milled for 5 h at room temperature in an Ar atmosphere and then sieved with 325-mesh. As shown in Fig. S1b, elemental S powder was uniformly covered with ketchen black.

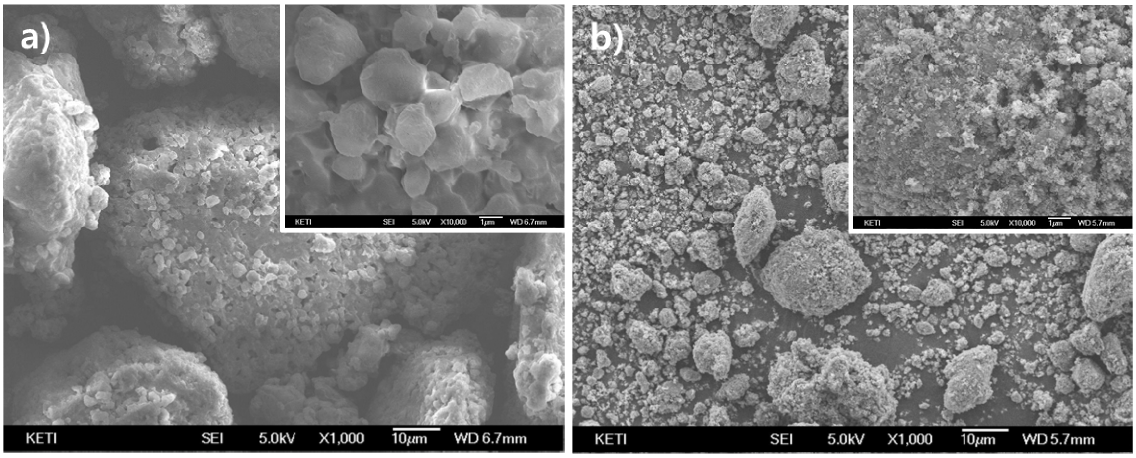

Fig. S1 FESEM image of (a) elemental S powder and (b) conventional S-C composite prepared by mechanical milling.

The morphology and microstructure of graphene sheets are given in Fig. S2. The graphene sheets are randomly stacked, forming sufficient free space for S storage between each graphene sheet. We found that the graphene sheet has less than ten single graphene layers and an average size of a few tens of microns.

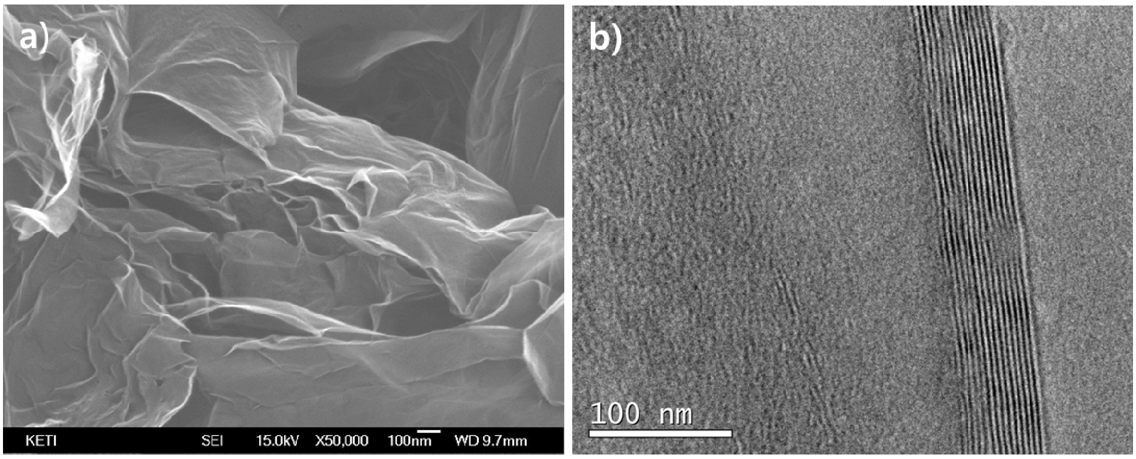

Fig. S2 (a) FESEM image and (b) HRTEM image of graphene sheets.

Fig. S3a and b show a comparison of the surface area and pore volume of graphene sheets and S-impregnated graphene composite prepared by a precipitation method using 0.3M $Na_2S_2O_3$ solution. The surface area variation was obtained by a Brunauer-Emmett-Teller (BET) method in which the surface area of graphene was significantly decreased from 305.4 to 5.9 $m^2$ $g^{-1}$ after the growth of S particles in the interior space of graphene sheets. According to Barret-Joyner-Halenda (BJH) results, the total pore volume is also decreased from 1.08 to 0.05 $cm^3$ $g^{-1}$ at $P/P_0$=0.98. It reveals that most of the free space between graphene sheets is occupied by S particles in our synthetic process. In addition, we found that a small increase in averaged particle size in the S-impregnated graphene composite and the distribution is narrow as presented in Fig. S3c.

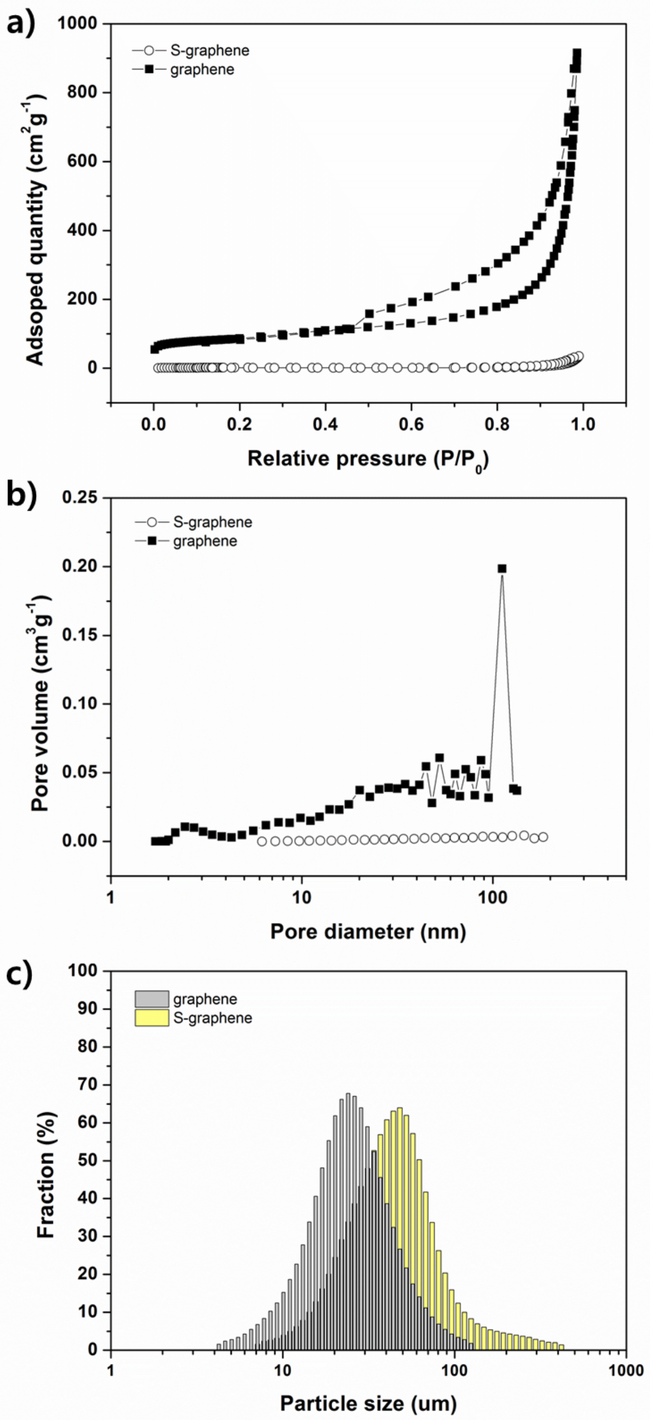

Fig. S3 (a) Surface area, (b) pore volume, and (c) particle size distribution of graphene and S-impregnated graphene composite prepared by precipitation method using 0.3M $Na_2S_2O_3$ solution.

Fig.S4 shows the morphological changes in S-impregnated graphene composite synthesized with different $Na_2S_2O_3$ concentrations. Reaction temperature and S precipitation time were fixed at room temperature and 24 h, respectively. Along with increasing $Na_2S_2O_3$ concentration, the morphology of S-impregnated graphene changed, as shown in Fig. S4. At low concentrations of $Na_2S_2O_3$, we could not observe the formation of S particles. A few microns of S particles were grown in the interior space of randomly dispersed graphene sheets using 0.3M $Na_2S_2O_3$. It appears that the S particles are well wrapped with graphene sheets. When the concentration of $Na_2S_2O_3$was increased to 0.5M, larger S particles were observed and some S particles escaped out of the graphene.

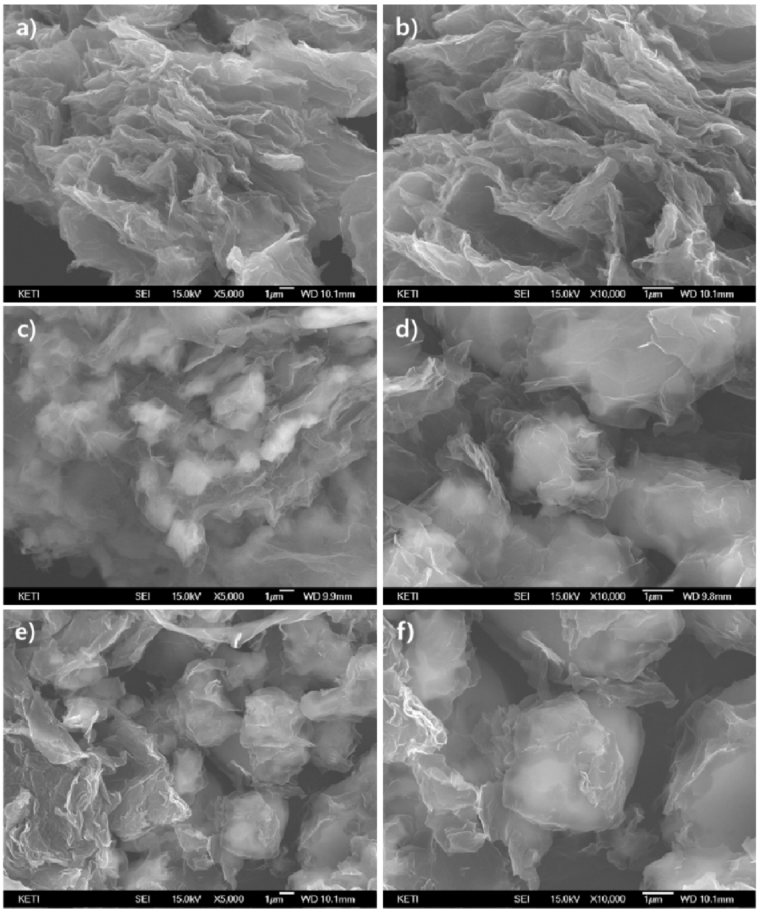

Fig. S4 Morphologies of S-impregnated graphene composite prepared by precipitation with different concentrations of $Na_2S_2O_3$; (a-b) 0.1M $Na_2S_2O_3$, (c-d) 0.3M $Na_2S_2O_3$, and (e-f) 0.5M $Na_2S_2O_3$.

Fig. S5 shows chemical compositions of S-impregnated graphene composite prepared by precipitation with different concentrations. The results were obtained by combustion of each prepared powder. Along with increasing $Na_2S_2O_3$ concentration, the content of S in the composite is proportionally increased. At optimized synthetic condition of 0.3M $Na_2S_2O_3$, the composite has 83.8 wt% of S.

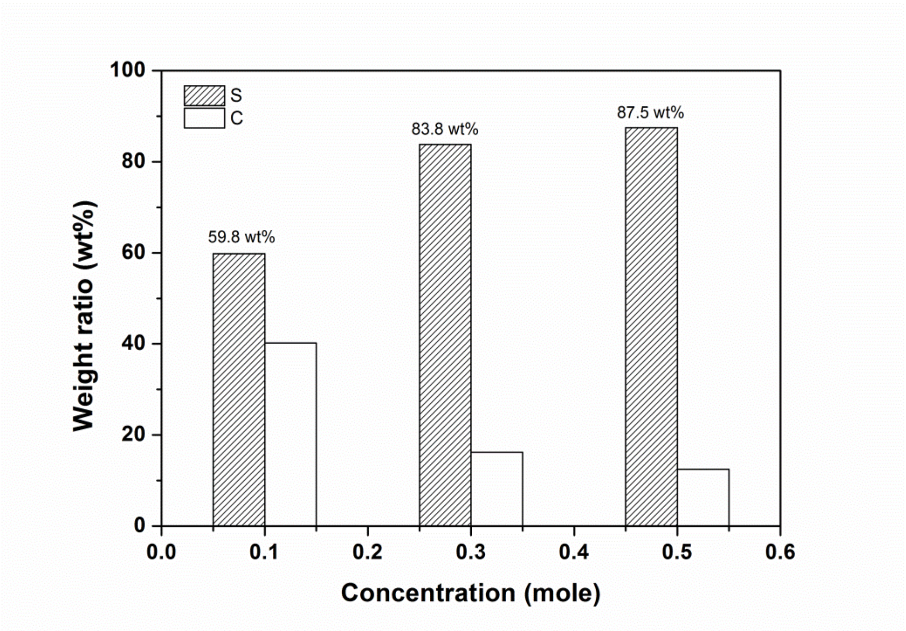

Fig. S5 Chemical composition of S-impregnated graphene composite prepared by precipitation with different concentrations of $Na_2S_2O_3$; 0.1, 0.3, and 0.5M.

Fig. S6 shows cyclic voltammograms of conventional S-Carbon composite and S-impregnated graphene composite prepared by precipitation method using 0.3M $Na_2S_2O_3$ solution. There are two oxidation peaks, observed at 2.4 and 1.9 V *vs.* $Li/Li^+$, corresponding to reduction peaks at 2.4 and 2.5 V *vs.* $Li/Li^+$, respectively. We found that the S-impregnated graphene composite exhibit a better reversibility in the second cycle, which supports that undesirable capacity loss due to side reactions of polysulphides is effectively reduced.

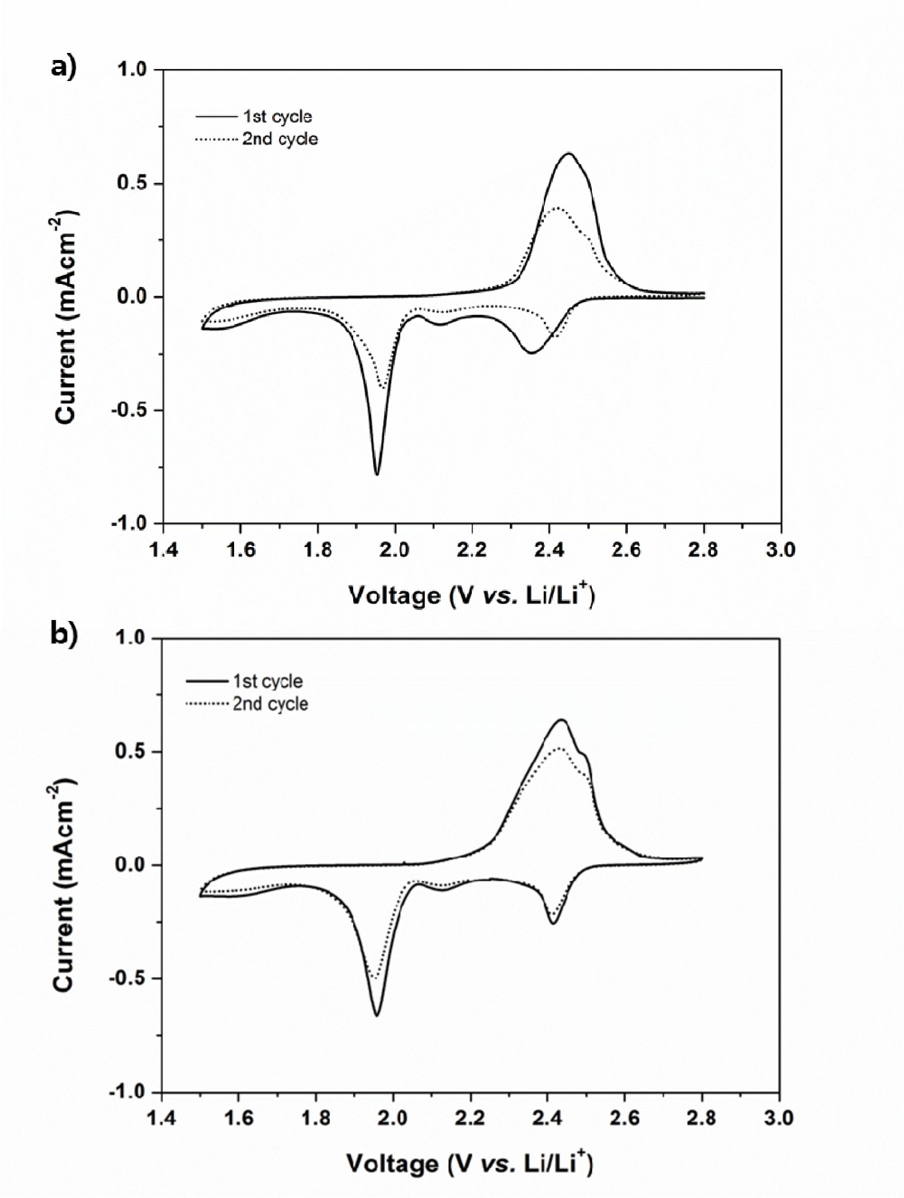

Fig. S6 Cyclic voltammograms of (a) conventional S-C composite and (b) S-impregnated graphene composite; both electrodes containing 66.6 wt% active S were tested in a voltage range of 1.8 - 2.6 V *vs.* Li/Li$^{+}$ with a scan rate of 0.1 mV s$^{-1}$.

Fig. S7 shows cyclic efficiencies of conventional S-Carbon composite and S-impregnated graphene composite prepared by precipitation method using 0.3M $Na_2S_2O_3$ solution during 50 cycles. It can be seen clearly that conventional S-C composite shows a notable overcharging at the first cycle and it continuously occurred during cycles, which is regarded as a major reason for facilitating capacity loss. Considering reaction mechanism of S, dissolved polysulfides from the electrode could not contribute to the subsequent formation of low-order polysulphides anymore. They might be passing through the separator and chemically deposit on the surface of metallic lithium.

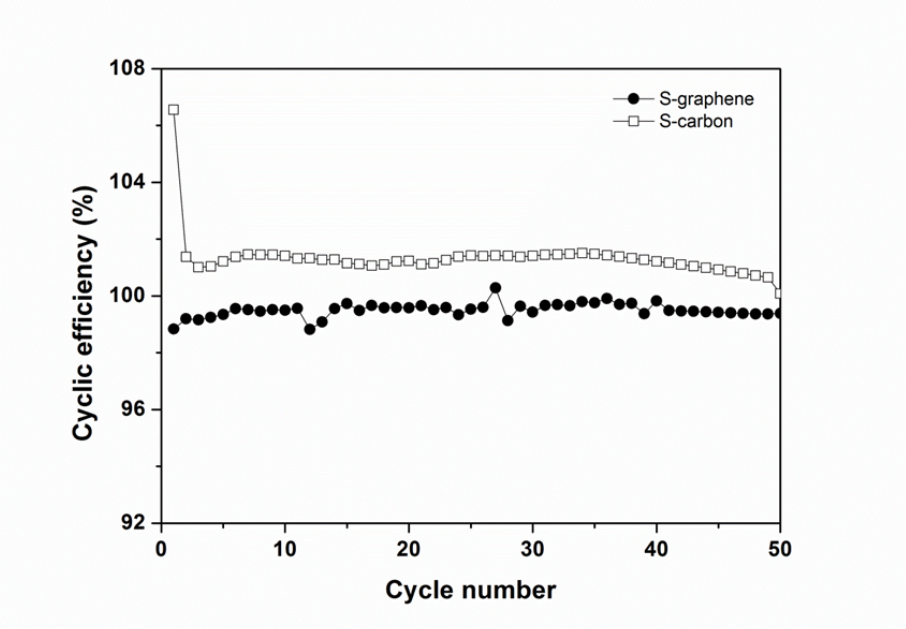

Fig. S7 Cyclic efficienciesof (a) conventional S-C composite and (b) S-impregnated graphene composite during 50 cycles.

The cyclic efficiency was estimated based on the ratio of achieved charge capacity to discharge capacity at each cycle. The abnormal cyclic efficiency of S-C composite is a general characteristic of S cathode originated from the shuttle reaction of polysulphides. Upon discharging, S initiates phase transformation into $Li_2S_8$, $Li_2S_6$, $Li_2S_4$, $Li_2S_2$, and $Li_2S$ in order. During a subsequent charging, the final discharge products, $L_2S_2$ or $Li_2S$, should be reversibly recovered to S. However, some soluble polysulphides do not fully recovered into S and participate in charge transfer reactions between soluble polusulphides ($Li_xS_2$, $4 \leq _x \leq 8$), which results in an additional charge capacity. In this reason, the estimated cyclic efficiency of S-C composite is higher than 100%. In this regard, the morphology and microstructure of S-impregnated graphene are advantageous to reduce the undesirable polysulphides dissolution during cycle.