In-situ sulfur loading in graphene-like nano-cell by template-free method for Li-S batteries

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Supporting Information



Fig. S1 SEM images of composites from GLC@ZnS to S@GLC by oxidation of Fe(NO₃)₃ solutions (a) as deposited, (b) after 48 h, (c) after 96 h. (d) EDS of S@GLC composite after 96 h. The results showed that Zn was completely cleared away and S was remained after 96 h.



Fig. S2 The full XPS spectra of S@GLC050



Fig. S3 (a) SAED patterns and diameter of ring of carbon materials. The SAED pattern of carbon materials in which sulfur was eliminated by thermal treatment (at 300 °C for 30min) is bright concentric rings, indicating the polycrystalline structure. By measuring the radius of diffraction ring, the lattice constant is about 0.236 nm.



Fig. S4 Theoretical estimate of sulfur content in S@GLC by *in-situ* sulfur loading based on the size of

ZnS nanoparticles



Fig. S5 SEM image of (a) GLC@ZnS nanoparticles with size of 150 nm, (b) S@GLC150 composite.



Fig. S6 XRD patterns of In-situ S@GLC and sulfur.



Fig. S7 SEM image of (a) GLC-wrapped ZnO nanoparticles (GLC@ZnO), (b) GLC after HCl etching,(c) S@GLC by melting-diffusion sulfur loading method. (d) Schematic illustration of synthetic process for S@GLC composite by melting-diffusion sulfur loading.

Synthesis of S@GLC by melting-diffusion sulfur loading method: 3.0 g of ZnO nanoparticles were transferred in a quartz tube and heat treated at a rate of 15 °C min⁻¹ under Ar ambient. When the temperature reached 760 °C, 200 sccm of H₂ was led into tube. And then 2.4 mL pyridine was led into tube at rate of 0.08 mL min⁻¹. After depositing and cooling down to room temperature, dark grey GLC@ZnO composite were obtained. The obtained black composite was etching by HCl solution for 24 h. GLC was collected by filtration and washed by deionized water several times. The water in the wet composite was finally removed *via* freeze-drying. The dry powders of GLC was mixed with sulfur at ration of GLC:S= 20:80 and 23:77, respectively. The mixtures were sealed in a glass vessel under argon protection, and heated at 150 °C for 12 h and followed 300 °C for 4 h in a quartz tube furnace.



Fig. S8 (a) Amplified SEM image and (b) TGA curve of S@GLC by melting-diffusion sulfur loading.



Fig. S9 TGA curve of S@GLC by mixing S and GLC at weight ratio of sulfur : GLC = 23 : 77 and

treated in melting-diffusion process.



Fig. S10 Cycling performance of in-situ S@GLC050, in-situ S@GLC150 and S@GLC by meltingdiffusion sulfur loading composites as cathode over 100 cycles at charge/discharge rate of 0.2 C

Cathode material	Synthesis method	Initial capacity (mA h g ⁻¹)	Retention (mA h g ⁻¹)	Cycle number	Rate	Sulfur content
Go/S ¹	MD		954	50	0.1 C	46.2 wt.%
rGo/S ²	MD	927	685	100	1 C	67 wt.%
G/S ³	MD	1210	958	50	0.17 C	60 wt.%
G/S ⁴	MD	1068	450	80	0.1 C	66 wt.%
G/S	$S_2O_3^{2-} + H^+$	900	615	100	0.1 C	73 wt.%
N-G/S ⁵	$S^{2-} + S_2O_3^{2-}$	1167	978	150	0.2 C	65 wt.%
N-G/S ⁶	$S_2O_3^{2-} + H^+$	1356	847	100	0.1 C	80 wt.%
			578	500	1 C	80 wt.%
rGo/S ⁷	Sonicate	1317	1125	200	0.3 A g ⁻¹	63 wt.%
N-G/S ⁸	MD	1150	880	100	0.3 A g ⁻¹	68.6 wt.%
N-G/S ⁹	MD	1138	821	100	0.3 A g ⁻¹	52 wt.%
N/P-G/CNT/S ¹⁰	MD	1446	912	100	0.1 C	56.7 wt.%
		921	795	400	1 C	56.7 wt.%
G/S ¹¹	MD	1430	700	300	1 C	78.9 wt.%
This work		1253	648	100	0.2 C	77 wt.%
		850	502	400	1 C	77 wt,.%

.Table S1 Cell performance based on Graphene-sulfur composite cathodes

Go: graphene oxide; rGo: reduced graphene oxide; N-G: nitrogen-doped graphene

N/P-G: N/P co-doped graphene; CNT: carbon nanotube; MD: melting-diffusion sulfur loading

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