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Electronic Supplementary Information

Manganese dioxide nanosheet functionalized reduced graphene oxide as compacted cathode matrix for lithium-sulphur batteries with low electrolyte/sulphur ratio

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Calculation method for areal capacity and volumetric capacity

The areal capacity (C_A-cathode) and volumetric capacity (C_V-cathode) based on the volume of the cathode were obtained from formula (1) and (2), respectively. The volumetric capacity (C_V-cell) based on the volume of the entire cell was obtained from formula (3). $C_{sulphur}$ is the specific capacity based on the mass of sulphur, mA h g^{-1}; $\rho_{A\text{-}sulphur}$ is the areal sulphur loading of the cathode, mg cm^{-2}; $L_{cathode}$ is the thickness of the cathode, cm; $V_{cathode}$ is the volume of the cathode, cm^{-3}; V_{cell} represents the total volume of the cathode, anode, separator and electrolyte, cm^{-3}.

$C_{A\text{-cathode}} = C_{sulphur} * \rho_{A\text{-sulphur}}$ (1)

$C_{V\text{-cathode}} = C_{A\text{-cathode}}/L_{cathode}$ (2)

$C_{V\text{-cell}} = C_{V\text{-cathode}} * (V_{cathode}/ V_{cell})$ (3)

For example, for the MnO_2@rGO/S cathode with sulphur content of 70 wt%, areal sulphur loading of 4 mg cm^{-2} and thickness of 29 μm, it delivers the discharge capacity of 711 mA h g^{-1} at 1.34 mA cm^{-2}, the areal capacity and volumetric capacity could be calculated as follows.

$C_{A\text{-cathode}}$ = 711 mA h g^{-1} * (4*10^{-3} g cm^{-2}) ≈ 2.84 mA h cm^{-2}.

$C_{V\text{-cathode}}$ = 2.84 mA h cm^{-2}/ (29*10^{-4} cm) ≈ 979 mA h cm^{-3}.

For the cell, the diameters of the cathode and Li anode are 14 mm, the thicknesses of the MnO_2@rGO/S cathode and Li anode are 29 μm and 65 μm, respectively. The diameter and thickness of the separator are 1.8 cm and 25 μm, respectively. The volume occupied by the electrolyte is about 25 μL including the electrolyte adsorbed in the separator and cathode.

$V_{cell} = V_{cathode} + V_{anode} + V_{separator} + V_{electrolyte} = 3.14 * 0.7 * 0.7 * 29 * 10^{-4}\ cm^{-3} + 3.14 * 0.7 * 0.7 * 65 * 10^{-4}\ cm^{-3} + 3.14 * 0.9 * 0.9 * 25 * 10^{-4}\ cm^{-3} + 0.025\ cm^{-3} \approx 0.0458\ cm^{-3}$.

Thus, $C_{V\text{-cell}} = C_{V\text{-cathode}} * (V_{cathode}/ V_{cell}) \approx$ 979 mA h cm^{-3} * (0.0044cm^3 / 0.0458 cm^3) ≈ 94.1 mAh cm^{-3}.

The voltage of the discharge plateau is ~2.0 V. Thus, the volumetric energy density of the cell: $E_{V\text{-cell}} = C_{V\text{-cell}}$ * 2.0 V = 94.1 A h L^{-1}* 2.0 V ≈ 188 W h L^{-1}.

Notably, if considering that the electrolyte could be adsorbed into cathodes and separator, the actual volumetric capacity and volumetric energy density based on the entire cell will be higher than the calculated values.

The average decay rate per cycle v is obtained from formula (1), where C_{in}, C_{re} and N_{cyc} represent the initial capacity, the retention capacity after cycling and the cycling numbers, respectively.

$$v = [(C_{in} - C_{re}) / C_{in}] / N_{cyc} * 100 \text{ wt\%} \quad (1)$$

For example, when the electrode delivers an initial capacity of 771 mA h g^{-1} at 3 C, and the capacity is maintained at 640 mA h g^{-1} after 500 cycles, the following average decay rate can be obtained:

$v = [(771 \text{ mA h g}^{-1} - 640 \text{ mA h g}^{-1}) / 771 \text{ mA h g}^{-1}] / 500 * 100 \text{ wt\%} \approx 0.034 \text{ wt\%}$."

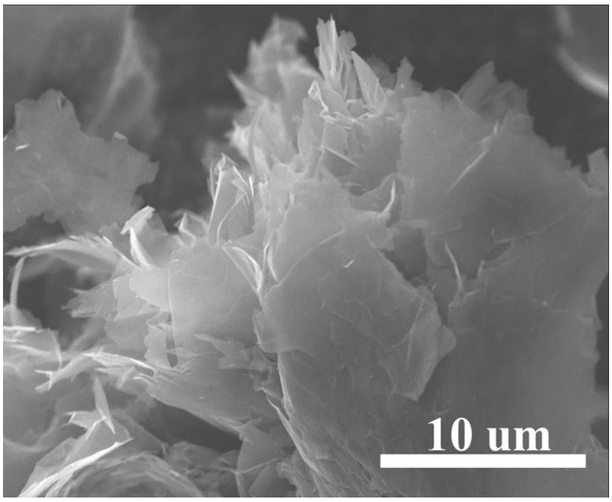

Figure S1 SEM image of GO.

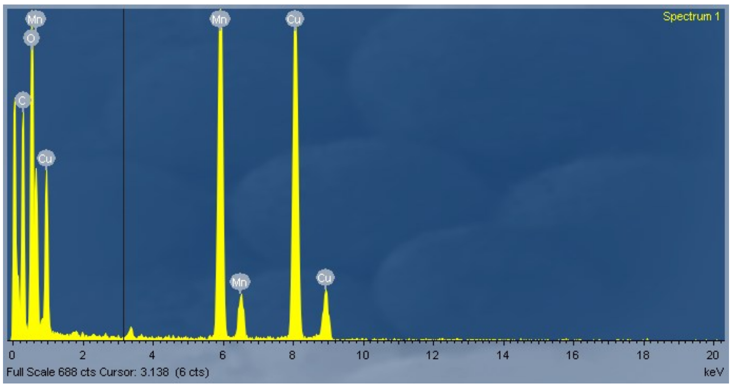

Figure S2 EDS of MnO_2@GO nanosheets.

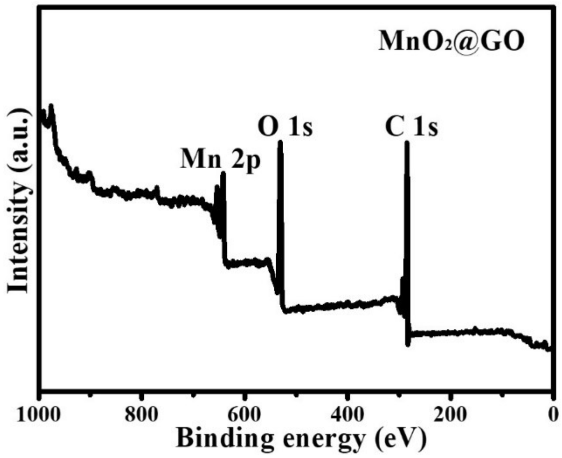

Figure S3 XPS survey spectra of the MnO_2@GO nanosheets.

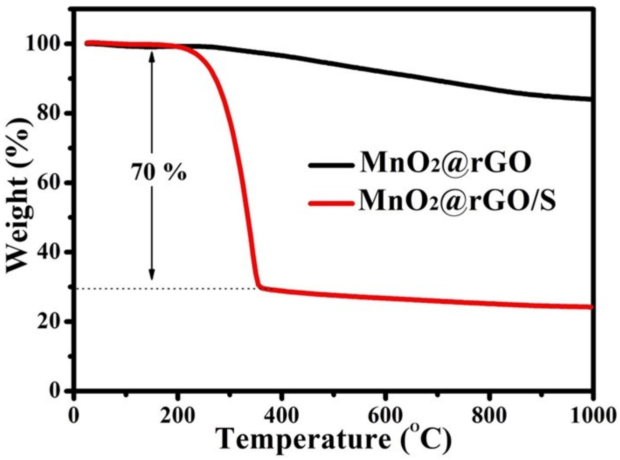

Figure S4 TGA curves for MnO_2@rGO/S and MnO_2@rGO composites.

The weight loss of MnO_2@rGO in as-prepared MnO_2@rGO/S can be neglected until the sulphur has completely evaporated. Elemental analysis was performed to reconfirm the sulphur content of the sample, sulphur loading in rGO/S was 70.39 wt%, which is consistent with the TGA result.

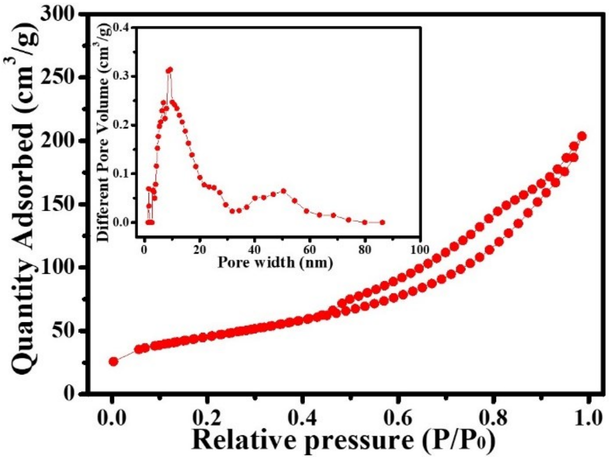

Figure S5 N_2 adorption and desorption isotherms of MnO_2@rGO nanosheets, and inset is the corresponding pore size distributions.

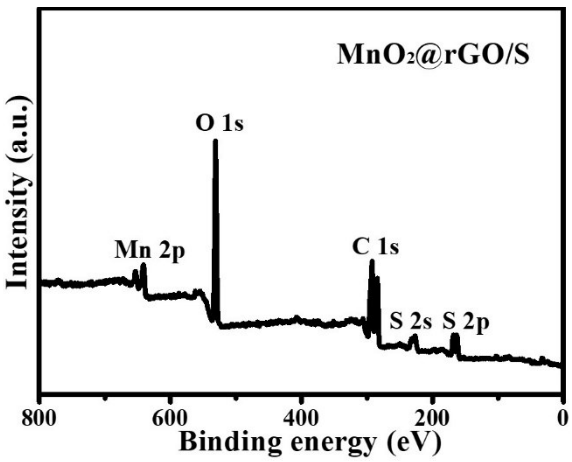

Fig. S6 XPS survey spectra of the MnO_2@rGO/S composite.

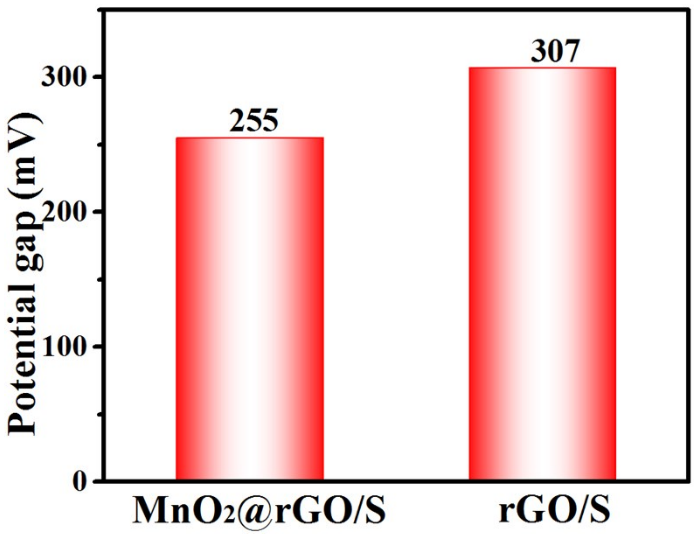

Figure S7 Potential gaps between redox peaks obtained from CV results.

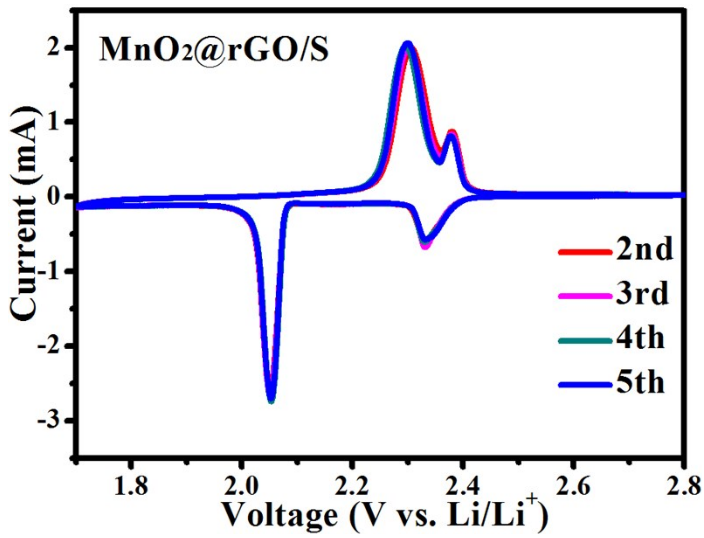

Figure S8 CV profiles for MnO_2@rGO/S composite.

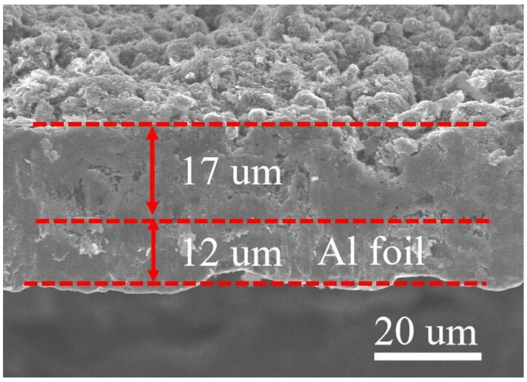

Figure S9. Cross-sectional SEM image of the MnO_2@rGO/S cathode piece.

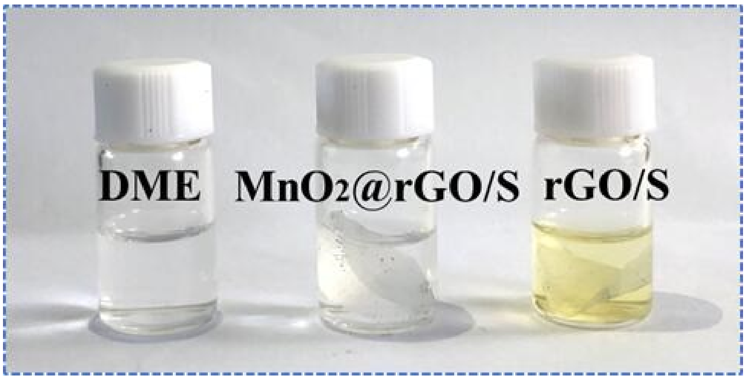

Figure S10. Photographs for DME before and after the separators were soaked.

Table S1. Comparison of electrochemical performance of the cathodes between this work and reported.

Cathode materials	E/S ratio ($\mu L\ mg^{-1}$)	S loading ($mg\ cm^{-2}$)	Electrochemical performance at high sulphur loading, capacity fading rate	Reference
TiN-TiO_2/G/LPS[1]	10.3	4.3	1.42 mAh cm^{-2} after 2000 cycles, 0.017% per cycle	1
Ti_4O_7/S[2]	28-32	1.5-1.8	~1.8 mAh cm^{-2} after 100 cycles, 0.12 % per cycle	2
TiO/C/S[3]	25	4	~2.5 mAh cm^{-2} after 50 cycles, /	3
VN/graphene/LPS[4]	~30	3	~2.7 mAh cm^{-2} after 200 cycles, 0.1 % per cycle	4
CMK-3/S[5]	~5	2	~1.4 mAh cm^{-2} after 100 cycles, 0.45 % per cycle	5
MOF/CNT/S[6]	/	4.57	~3.5 mAh cm^{-2} after 200 cycles, /	6

VO_2-VN/G/S[7]	~7.5	4.2	~4.1 mAh cm^{-2} after 50 cycles, 0.85 % per cycle	7
G/hollow carbon/S[8]	~15	5	~5.7 mAh cm^{-2} after 50 cycles, ~0.58 % per cycle	8
MnO_2@rGO/S	**4**	**4**	**~2.31 mAh cm^{-2} after 100 cycles, 0.19 % per cycle**	**This work**

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