

Supporting Information

The Facile Synthesis and Enhanced Lithium-Sulfur Batteries Performance of Amorphous Cobalt Boride (Co₂B)@Graphene Composite Cathode

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Experimental Section

Synthesis of Co₂B@rGO: In a typical synthesis procedure, 1 mmol cobaltous chloride (CoCl₂) was added into 50 ml deionized water under a vigorous stirring to complete dissolution. And then, the GO dispersion solution with different volume of 5 ml, 10 ml, and 15 ml were dropped into above solution and stirred for another 40 min. After fully electrostatic attraction between Co²⁺ and GO nanosheets, 5 ml sodium borohydride (NaBH₄) solution (0.5 mol/L) was added and maintained at room temperature for 60 min under vigorous stirring. The resulting products were collected by centrifuging and washing with DI and ethanol for three times. The Co₂B@rGO samples were finally dried in a vacuum overnight for further characterizations. Besides, a commonly accepted reaction mechanism for the CoCl₂ with NaBH₄ was expressed as:



References:

[1]: S. A. Lindley, J. K. Cooper, M. D. Rojas-Andrade, V. Fung, C. J. Leahy, S. Chen and J. Z. Zhang, ACS applied materials & interfaces, 2018, 10, 12992-13001.

Synthesis of $\text{Co}_3\text{O}_4@\text{rGO}$: 10 ml GO (3mg/ml) was dispersed in ethanol (300mL) and pretreated with stirring for 0.5 h. Subsequently, 1mmol of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ was added to the above solution at room temperature. The reaction mixture was kept at room temperature with stirring for 2 h. Then, it was transferred to a 50 mL autoclave with a Teflon inner layer for hydrothermal reaction at 180 °C for 2 h. The resulting products were collected by centrifuging and washing with DI and ethanol for three times.

Synthesis of $\text{Co}_2\text{B}@\text{rGO}/\text{S}$ ($\text{Co}_3\text{O}_4@\text{rGO}/\text{S}$): The $\text{Co}_2\text{B}@\text{rGO}/\text{S}$ composite material was obtained from a melt-diffusion method. The $\text{Co}_2\text{B}@\text{rGO}$ and pure sulfur were mixed with a mass ratio of 3:7, and add into a certain amount of CS_2 stirred under magnetic stirrers. The collected powder was transferred into a sealed vessel and heated at 155 °C for 12 h. The synthesis procedure of $\text{Co}_3\text{O}_4@\text{rGO}/\text{S}$ was the same as $\text{Co}_2\text{B}@\text{rGO}/\text{S}$

Material Characterization: The morphology and microstructure characterization for $\text{Co}_2\text{B}@\text{rGO}$ were conducted using a SEM (Hitachi, SU8010) and HRTEM (G2 F20FEI Tecnai G2 F20 microscope at 200 kV) respectively. The crystal structure was characterized by X-ray diffraction (PANalytical X'Pert PRO, monochromated Cu $K\alpha$ radiation 40 mA, 40 kV). Elemental analysis was performed using inductively-coupled plasma atomic emission spectroscopy (ICP-AES PerkinElmer Optima 8300). The sulfur content in the composite was tested with a TG thermogravimetric analyzer

system. XPS (ThermoFisher ESCALAB 250Xi) analysis was performed to analyze the compositions and contents of element.

Electrochemical Measurements: The cathodes were prepared by mixing active materials, Ketjen Black and PVDF, with a weight ratio of 8:1:1 in NMP to form a uniform slurry, and then directly coated onto a cleaned aluminum foil by a doctor-balding. Then the electrode was dried at 60 °C for 12 h. The diameter of the round disk electrodes is 10 mm. The 2025 coin cells were assembled with Li metal disc as anode in a glovebox filled with Ar. The electrolyte was composed of 1 mol/L lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in a solvent of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 ratio by volume) with 2% LiNO₃ addition. CV test was recorded on a CHI660D electrochemical workstation between 1.5 and 3.0 V. A Neware battery test system was used to perform charge/discharge measurements; the voltage window is 1.7-2.8 V for various current rates (1 C is equivalent to 1675 mA/g). Besides, the sulfur areal density and electrolyte to sulfur ratio of the Co₂B@rGO is about 1.0 mg cm⁻² and 20 μL mg⁻¹ respectively.

Supplementary Figures

Table S1: The ICP analysis of Co₂B@rGO

material	Composition		Atomic ratio
	Co	B	Co:B
Co ₂ B/rGO	1.163 mg/L	0.933 mg/L	2.1:1

Table S2: The BET analysis of Co₂B@rGO , Co₃O₄@ rGO and rGO

Sample	BET Surface Area
Co ₂ B@rGO	91.7 m ² /g
Co ₃ O ₄ @rGO	94.7 m ² /g
rGO	232.4 m ² /g

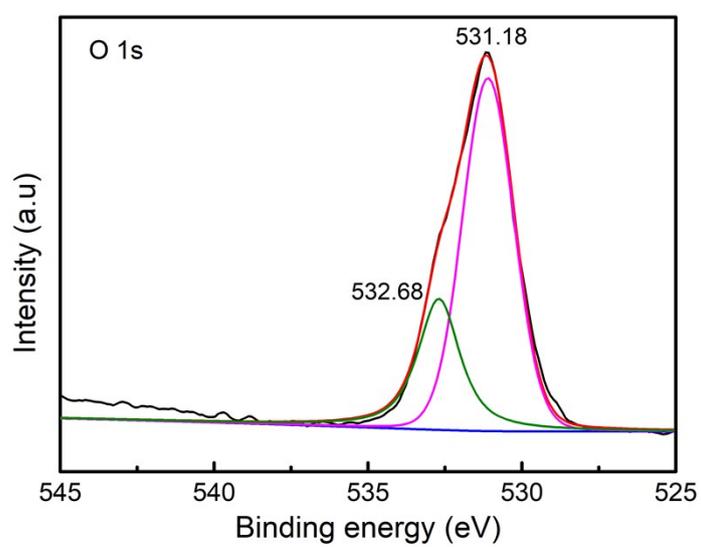


Figure S1. O 1s and core levels spectra of Co₂B@rGO product

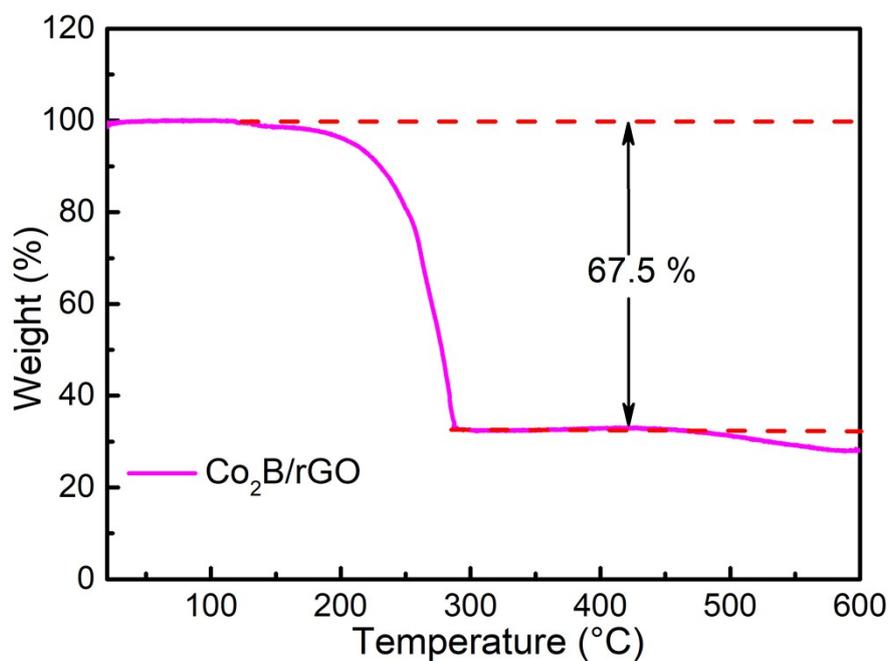


Figure S2. TG curve of Co₂B@rGO/S

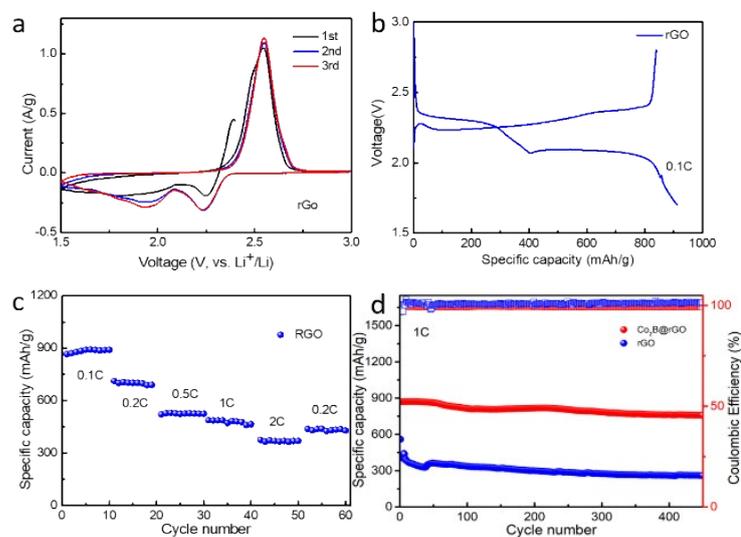


Figure S3. a) CV curves of rGO composites recorded at 0.1 mV s⁻¹. b) Discharge and charge voltage profiles at 0.1 C. c) Rate performances of the rGO electrodes at different current densities. d) Cycling performance of Co₂B@rGO and rGO electrodes at 1C over 450 cycles.

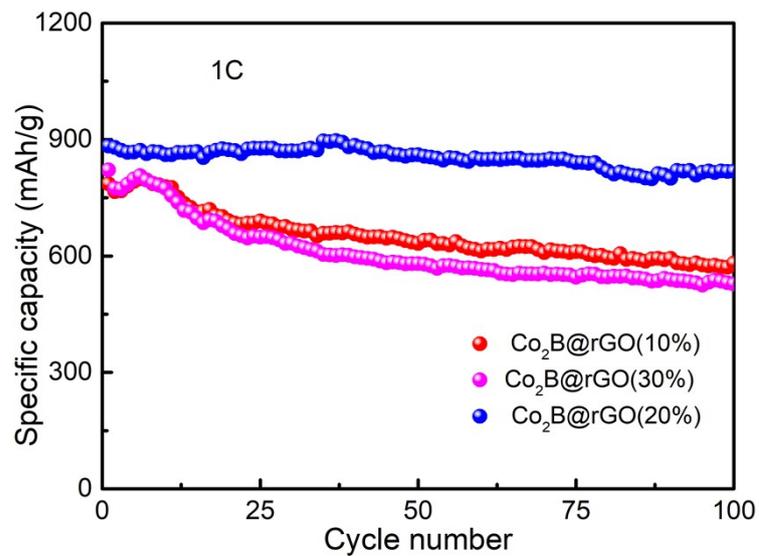


Figure S4. The cycling performance of Co₂B@rGO electrodes with different Co₂B contents at 1C

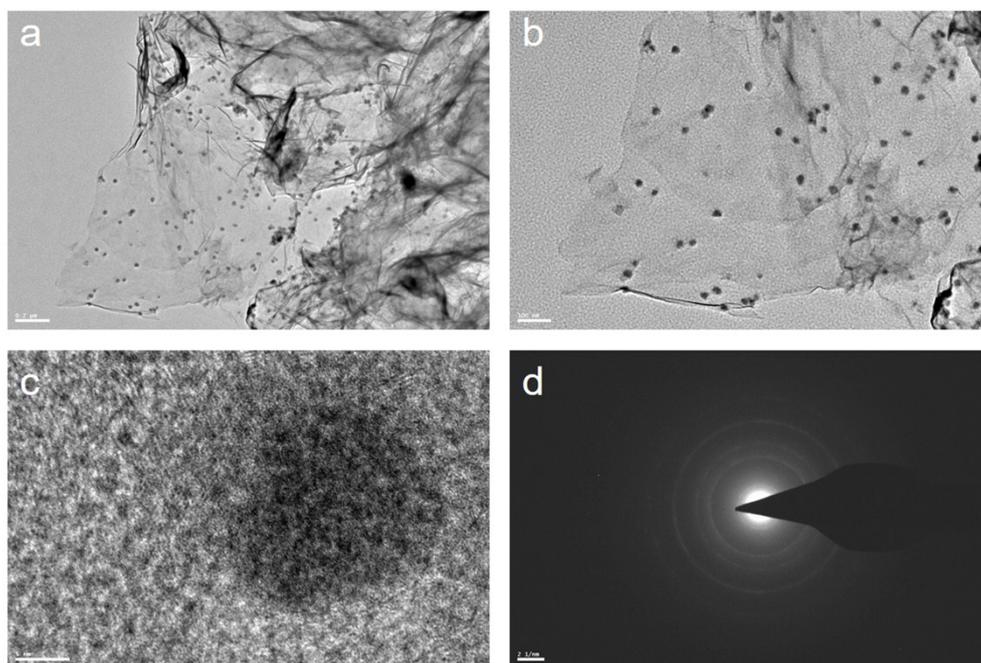


Figure S5. a, b) TEM images of Co₂B@rGO. c) HRTEM image of Co₂B@rGO. d) the lattice structure and the Fast Fourier Transform of the Co₂B@rGO.

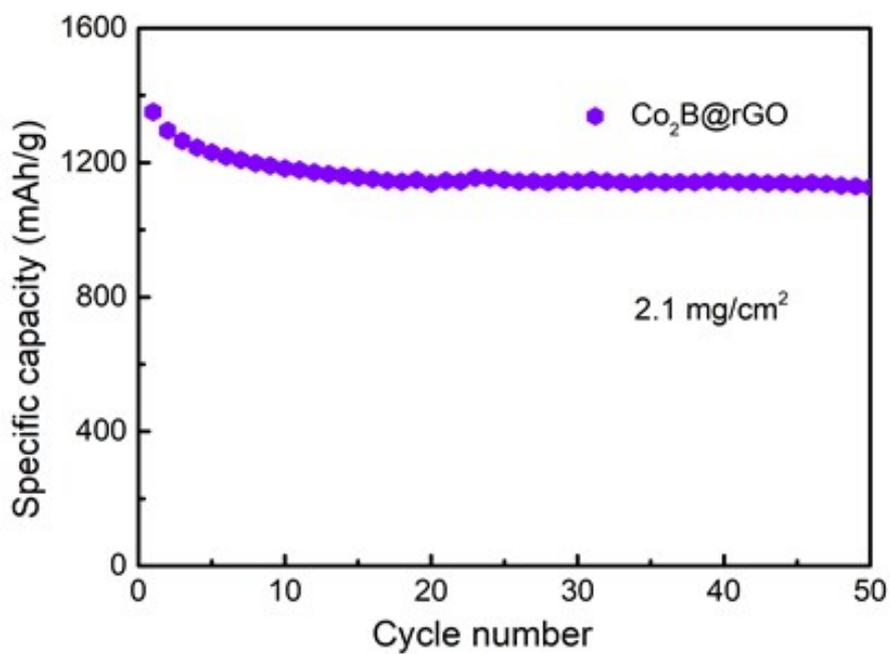


Figure S6. Cycling performance of $\text{Co}_2\text{B}@r\text{GO}/\text{S}$ at 0.2C

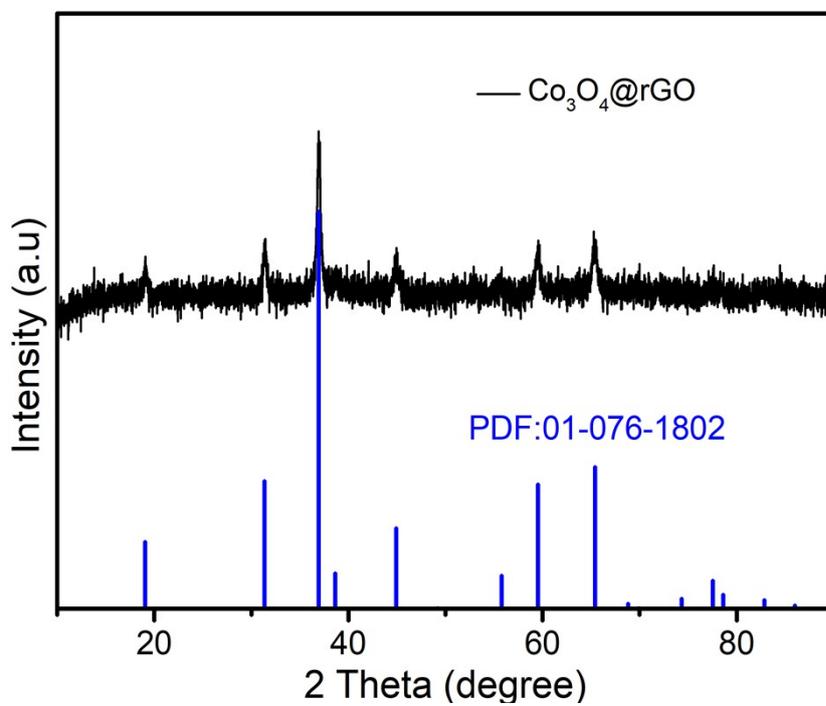


Figure S7. XRD pattern of $\text{Co}_3\text{O}_4@r\text{GO}$ product

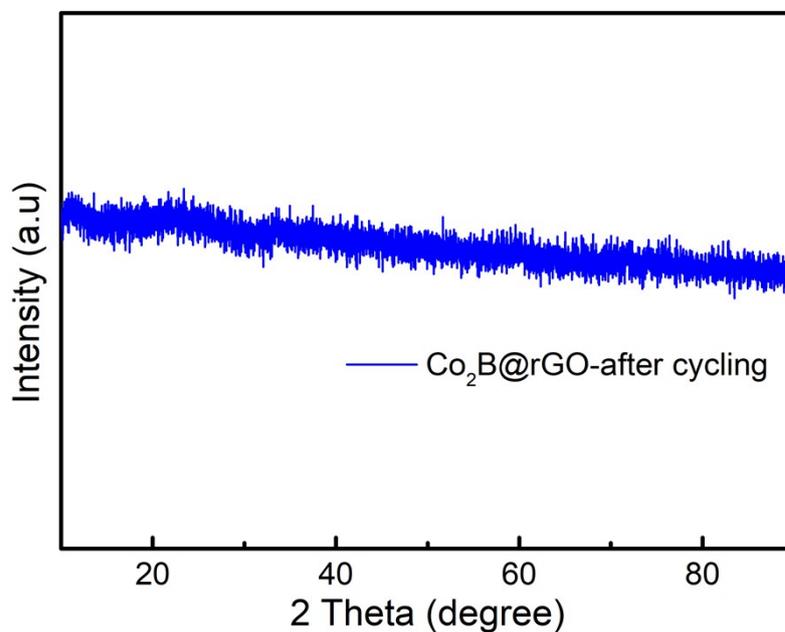


Figure S8. XRD pattern of $\text{Co}_2\text{B}@\text{rGO}$ after cycling test

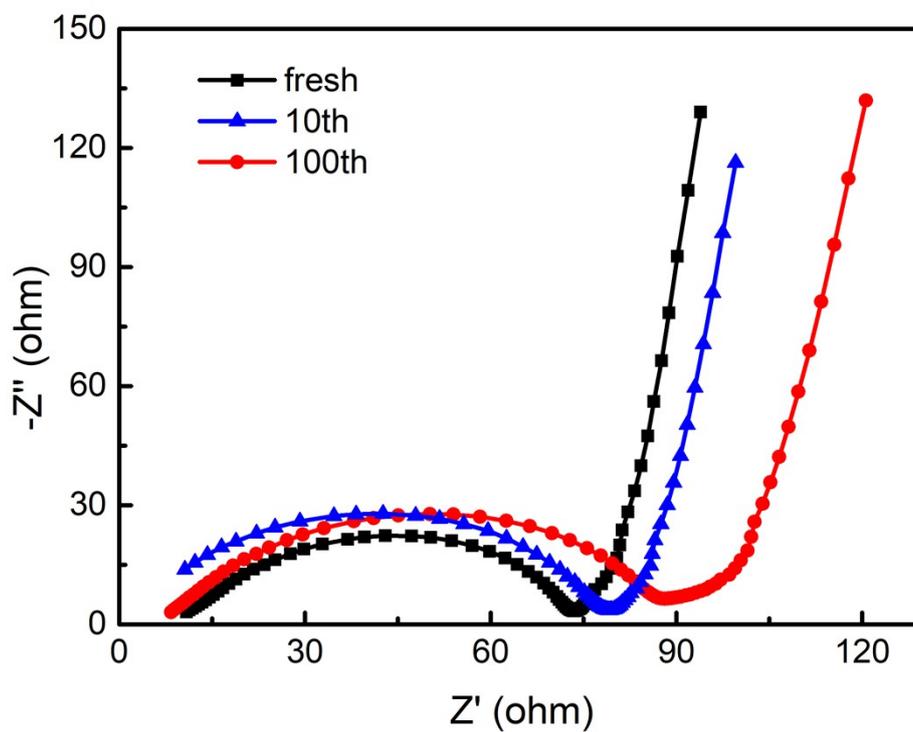


Figure S9. EIS results of $\text{Co}_2\text{B}@\text{rGO}$ after different cycles.

Table S3. The performance of Co₂B@rGO/S with other reported metallic compound@rGO/S composites.

Metallic compound@rGO	Initial capacity (mAh/g)	Current rate(C)	Cycle number	Degradation rate per cycle (%)	reference
Co ₂ B@rGO	1543	0.1	100	0.09	our work
	870	1	450	0.029	
Mo ₄ O ₁₁ -graphene	1190	0.1	80	0.323	Nano Energy, 2017,33, 306–312
MXene/rGO	1210	0.1	100	0.173	Chem. Eur. J. 2017,23,12613– 12619
MoO ₂ /G	1468	0.1	10	0.182	J.Mater.Chem. A,2017,5, 25187-25192
TiO ₂ /graphene	871	1	400	0.04	Angew. Chem., Int. Ed., 2015, 54,12886-12890
MoO ₂ /G	806	1	500	0.035	J.Mater.Chem. A,2017,5, 25187-25192
NPC/G	786	1	300	0.043	Adv. Funct. Mater. 2018, 28, 1707592
MoS ₂ /rGO	877	1	500	0.116	ACS Appl. Mater. Interfaces 2018,10,4, 3707-3713
VN/G	1128	1	200	0.093	NATURE COMMUNICATIONS DOI:10.1038/ncomms14627

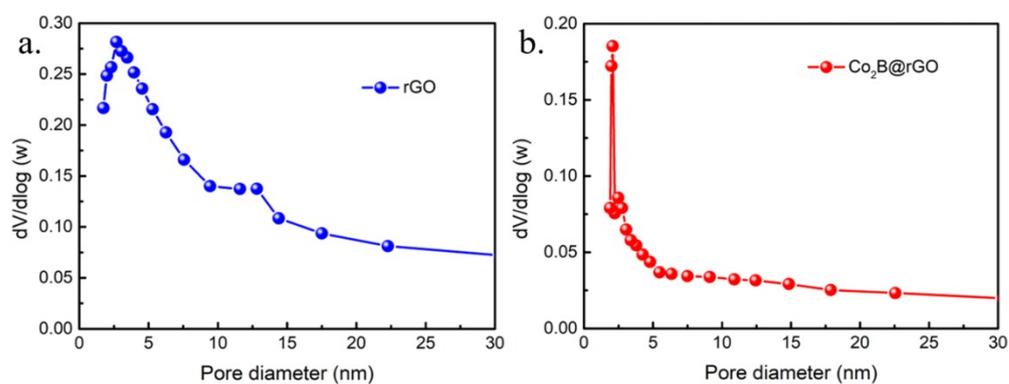


Figure S10. The pore size distributions of rGO (a) and Co₂B@rGO, respectively.