

Electronic Supplementary Information

Spray-drying Assembly of 3D N, P-Co-doped Graphene Microspheres Entrenched with Core-Shell CoP/MoP@C Nanoparticles for Enhanced Lithium-Ion Storage

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Table S1. Summary of synthesis routes for metal phosphides.

Direct agents	Phosphorus (P) Precursors	Metal Precursors	Methods	Ref.
Pure Phosphorus (P)	White Phosphorus	Metal particles	Ball milling	1, 2
	Red Phosphorus		Calcination	3
	Black Phosphorus		Hydrothermal (red P)	4
			Solvothermal (red P)	5
Metallo-organic compounds	Trioctylphosphine (TOP)	Organometallic Particle	Calcination	6, 7
	Tricyclophosphine oxide (TOPO)			8
	Trimethylsilylphosphine (TMSP)		Solvothermal reaction	9
	Tributylphosphine (TBP)			10
	Triphenylphosphine (TPP)			11
PH₃ gas	P ₄	Metal oxides	Hydrothermal reaction	12, 13
	H ₂ PO ₂ ⁻	Metal halides	Temperature program reduction	14, 15
	PO ₃ ³⁻	Metal phosphates		16
	PO ₄ ³⁻	Metal phosphites	Decomposition of H ₂ PO ₂ ⁻	17
P³⁻ and others	Na ₃ P	Metallic compounds	Calcination	18
	Ca ₃ P ₂		Electrolysis	19, 20
	Etc.		Solvothermal reaction	21

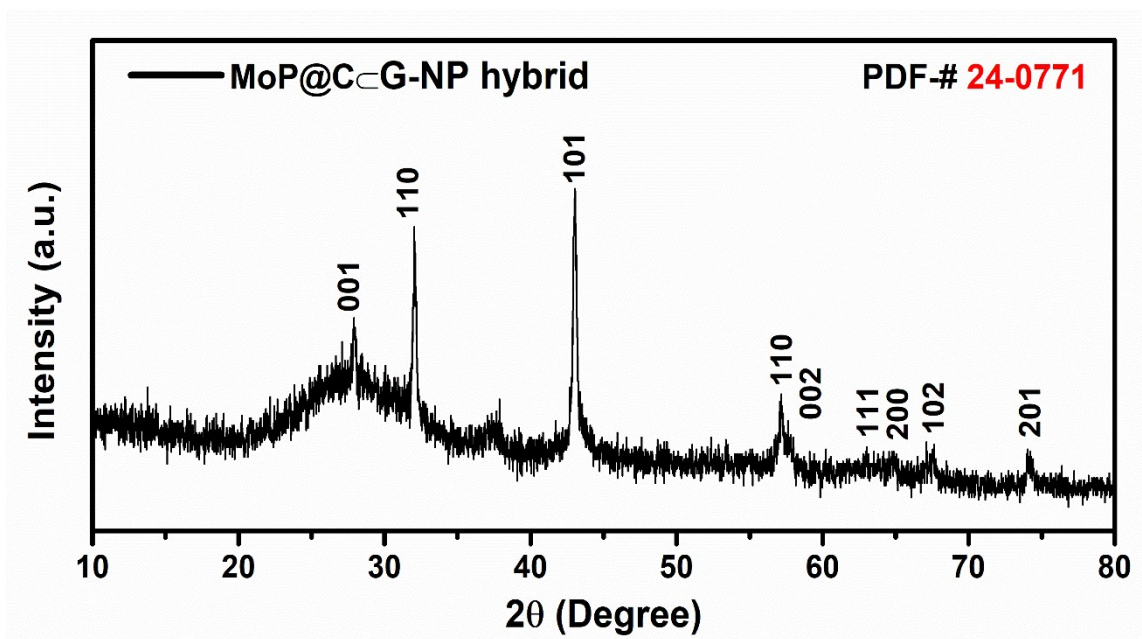


Figure S1. X-ray diffraction pattern of the as-fabricated MoP@C-G-NP composite.

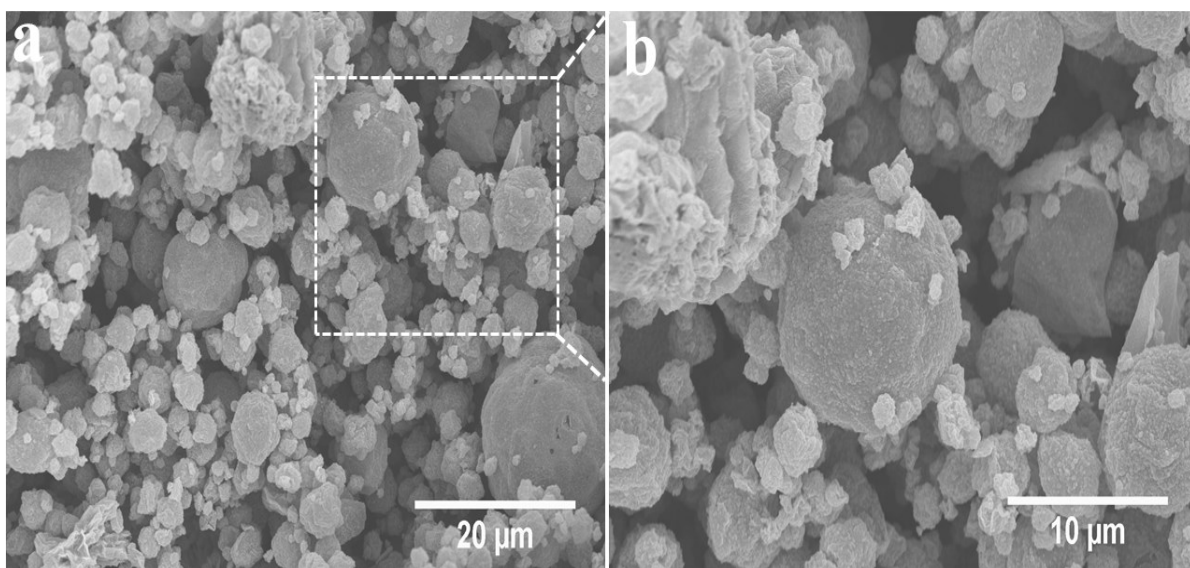


Figure S2. (a-b) SEM images of CoP@C≡G-NP composit.

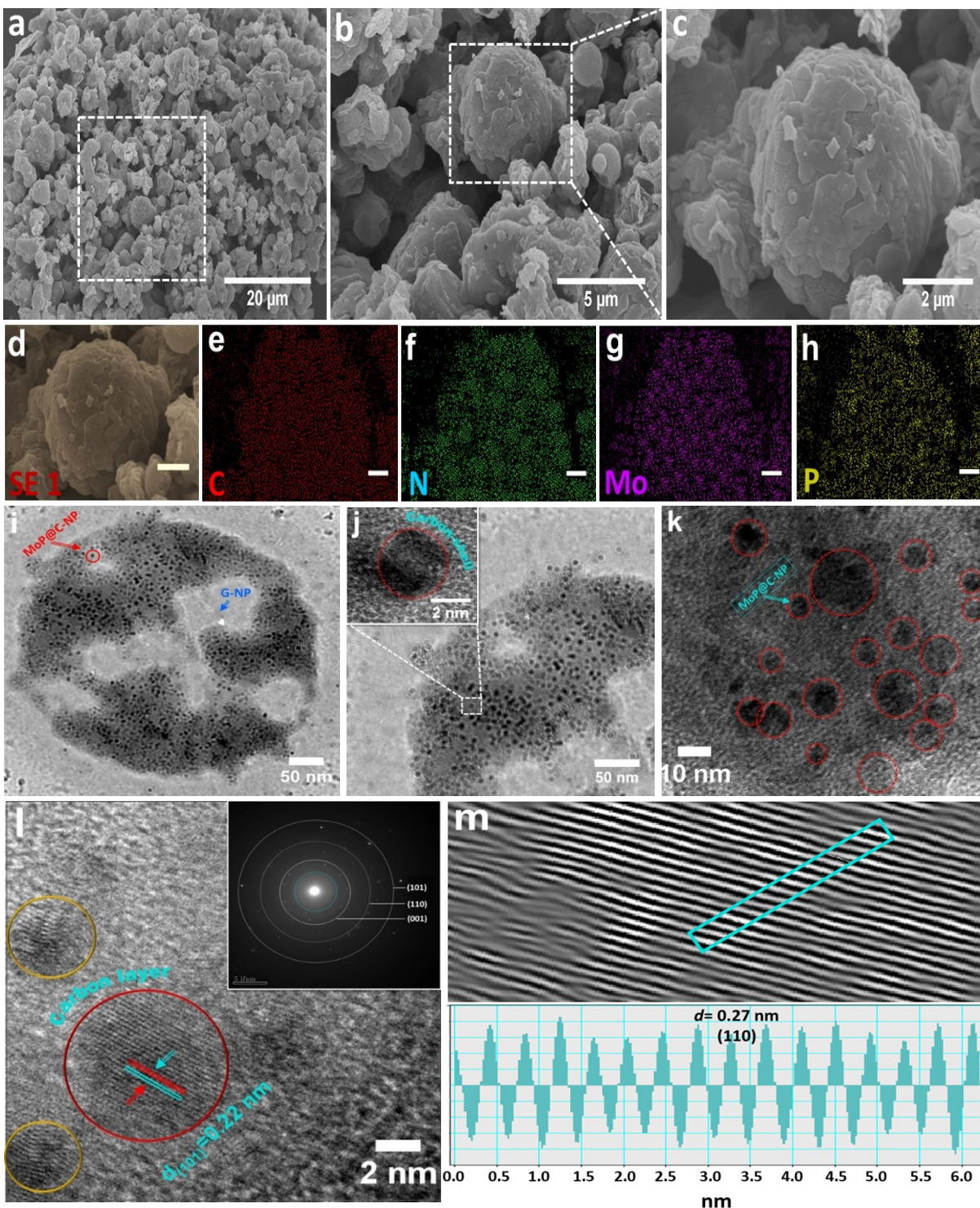


Figure S3. Structure analysis of MoP@C-NP@G-NP. (a-c) Low- and high-resolution SEM images of MoP@C@G-NP hybrid; (d-h) corresponding SEM EDS elemental mapping. Scale bar: 0.5 μm . (i-k) Low-resolution TEM images and (l) high-resolution TEM lattice images show the marked d-spacing of 0.27 nm corresponding to the (110) plane of MoP@C@G-NP hybrid (Inset show selected area electron diffraction patterns), (m) and the corresponding lattices masked by Gatan Software 2.11.

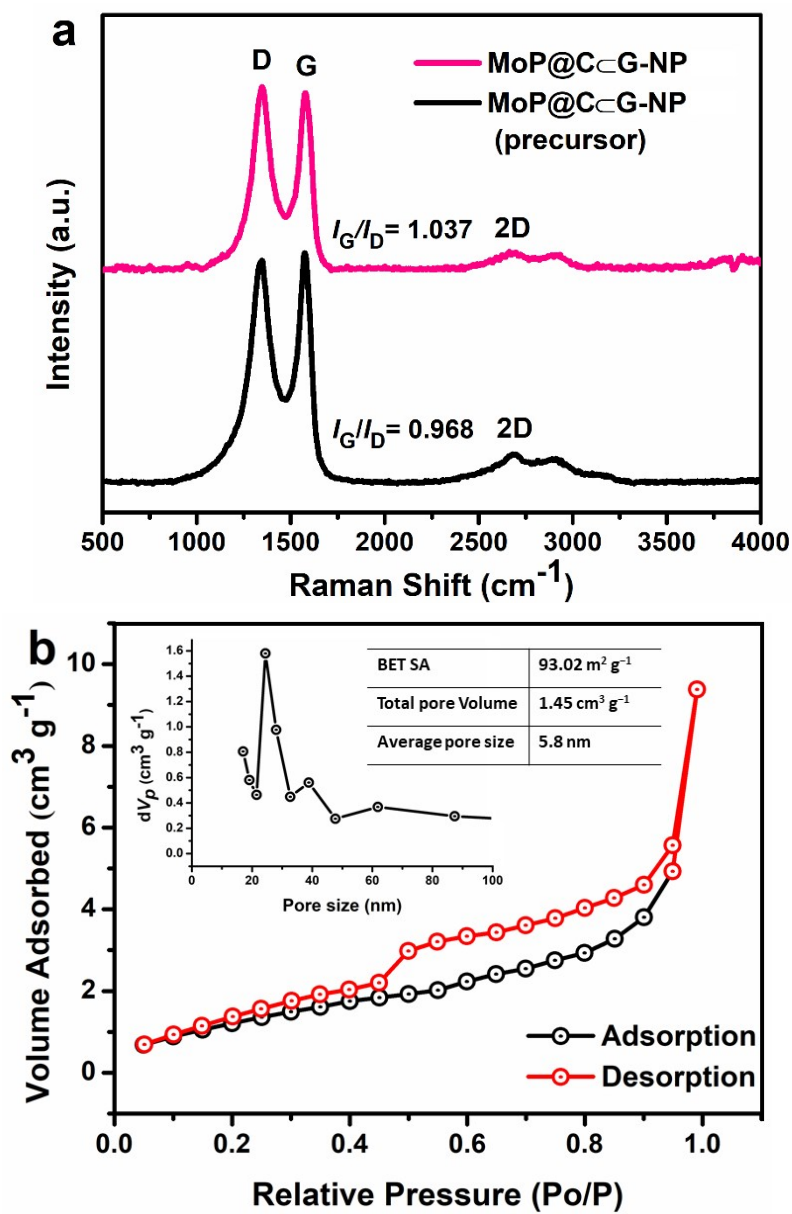


Figure S4 Chemical composition characterization of MoP@C-G-NP composite. (a) Raman spectrum (b) N_2 adsorption/desorption isotherm. The inset in (b) is the corresponding pore size distribution.

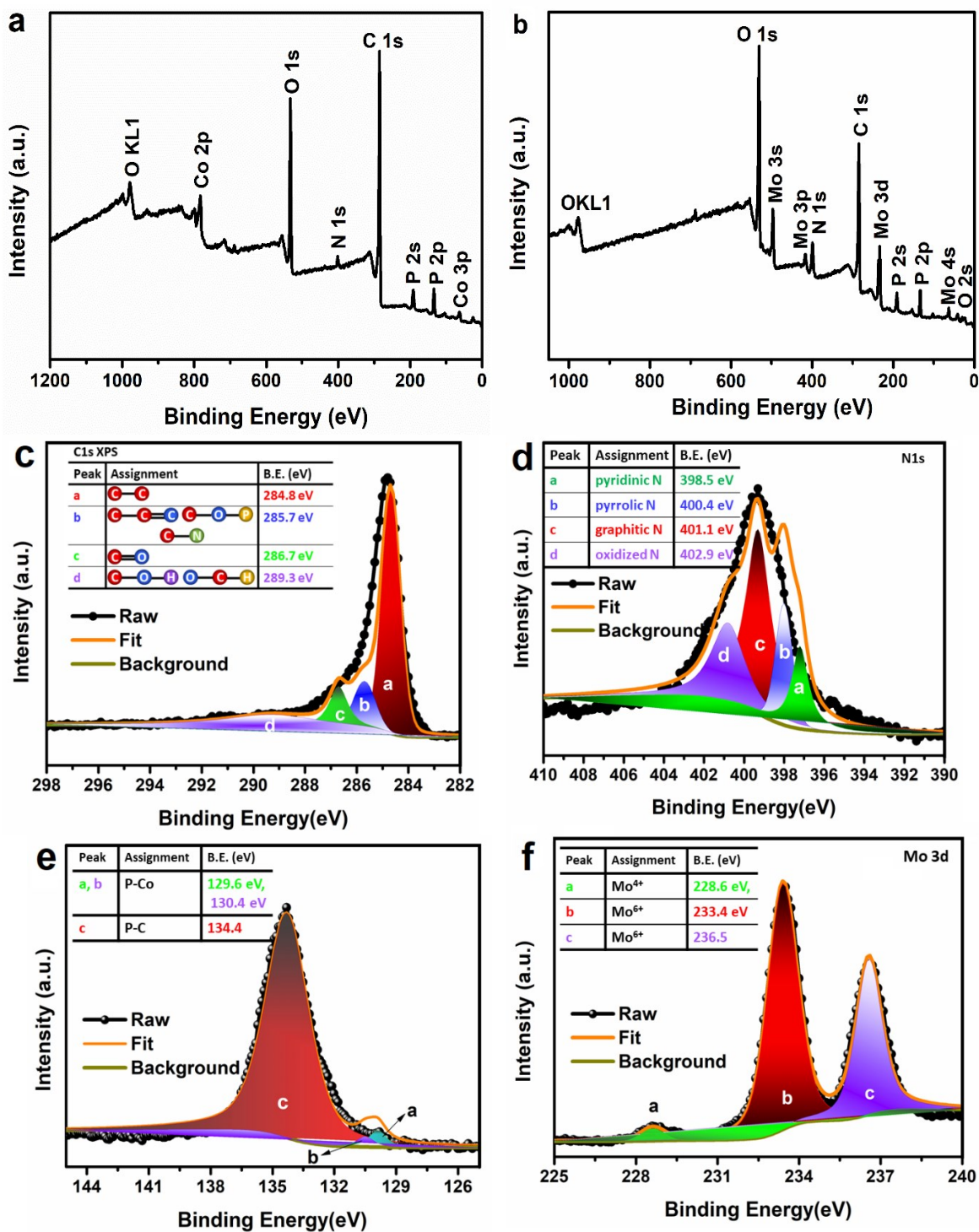


Figure S5. (a) XPS survey spectrum of CoP@C≡G-NP composite. (b-f) XPS characterization of MoP@C≡G-NP hybrid. (b) survey spectrum (c) high-resolution C 1s, (d) N 1s (e) P 2p, and (f) Mo 3d, respectively.

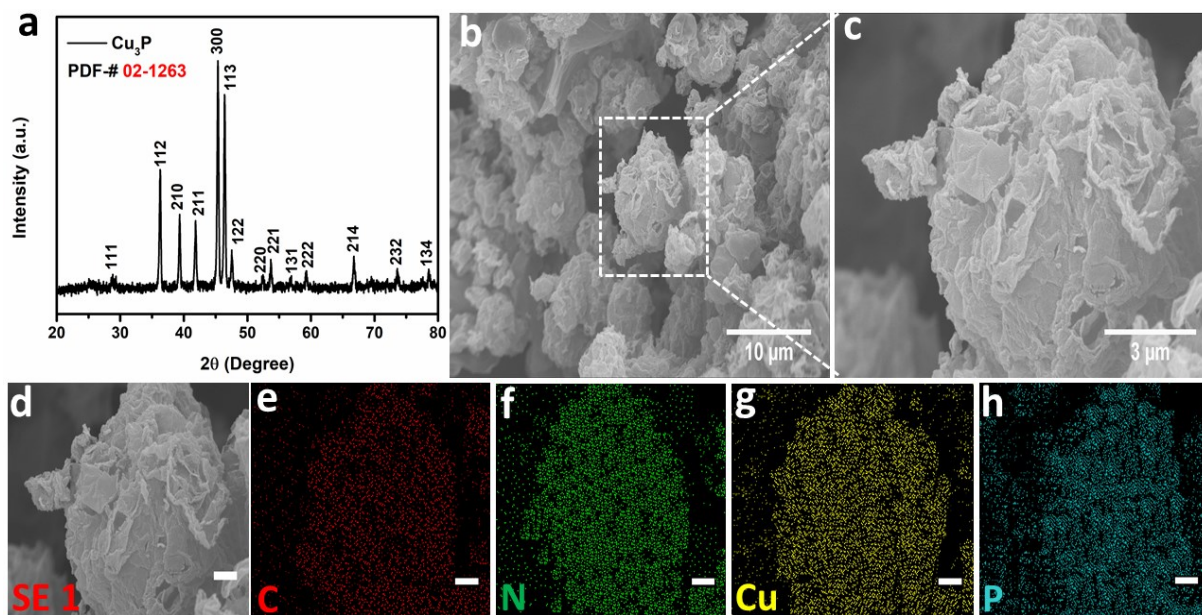


Figure S6. Structure analysis of CuP@C≡G-NP. (a) XRD patterns of the CuP@C≡G-NP hybrid; (b-c) Low- and high-resolution SEM images of CuP@C≡G-NP hybrid; (d-h) SEM images and the corresponding elemental mapping images.

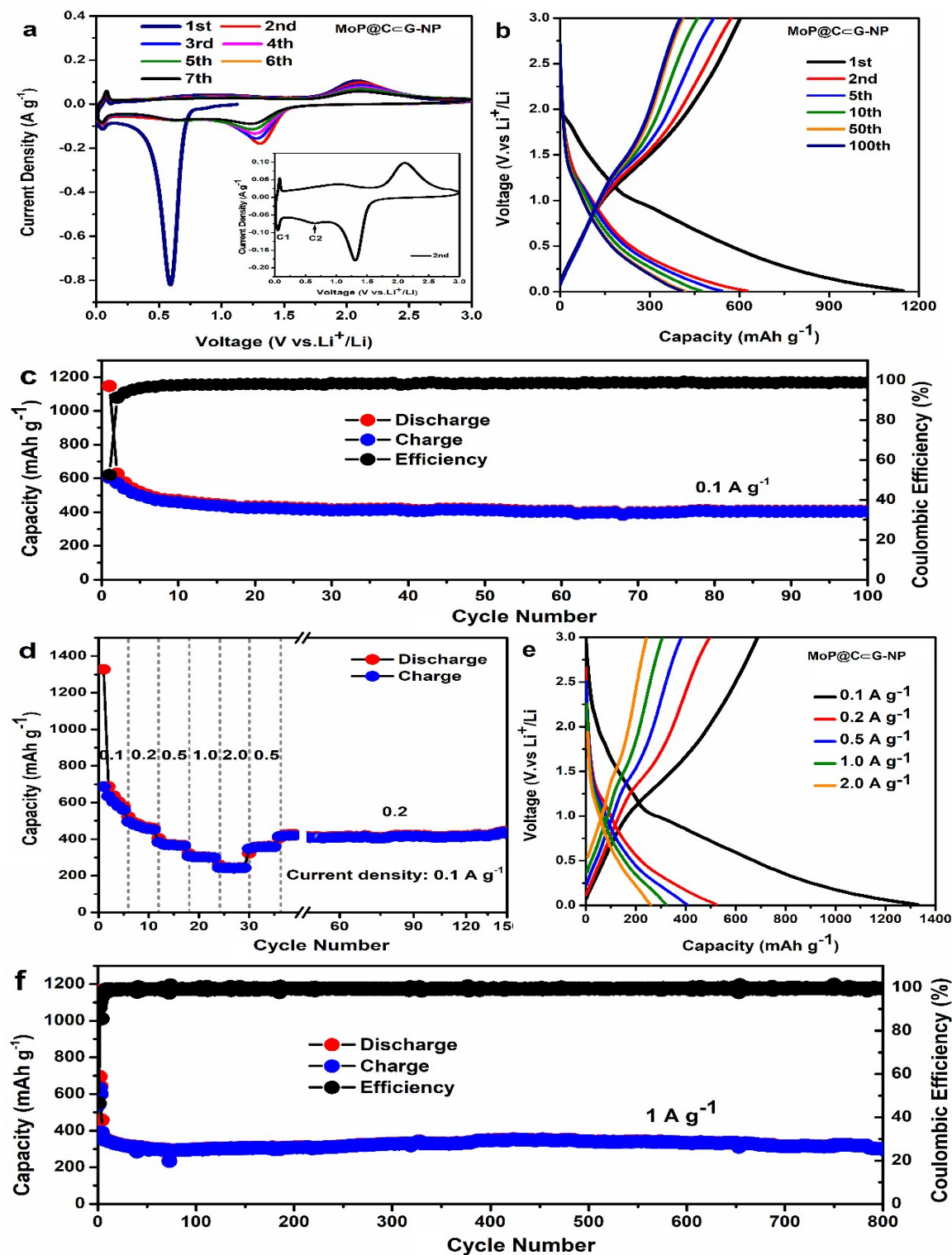


Figure S7. Electrochemical performance of the MoP@C≡G-NP composite for lithium storage. (a) Cyclic voltammograms of the first seven cycles at scan rate of 0.1 mV s⁻¹. (b) Galvanostatic discharge-charge profiles. Voltage range: 0.01-3V versus Li⁺/Li; current density 0.1 A g⁻¹. (c) Cycling performance and the corresponding CE at 0.1 A g⁻¹. (d) Rate performance and (e) corresponding discharge-charge profiles with rates ranging from 0.1 to 2.0 A g⁻¹. (f) Long cycling performance at 1.0 A g⁻¹ after 800 cycles.

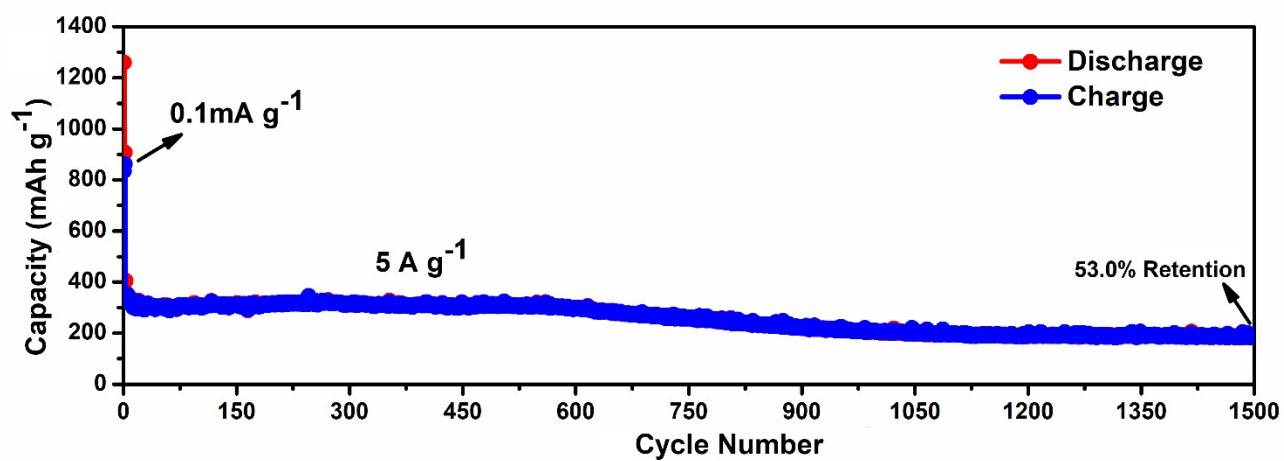


Figure S8. Long-term cycling performance of CoP@C/G-NP electrode at a current density of 5 A g⁻¹ after 1500 cycles.

Table S2. Comparison of Li-ion storage performance of CoP@C≡G-NP and MoP@C≡G-NP composites with other Co/Mo phosphide composites.

Name of Electrode	Synthesis route	Capacity after cycling	Capacity retention	Ref.
CoP@C≡PCF/NCNTs	vapor-phase phosphorization strategy	577 mAh g ⁻¹ after 140 cycles at 0.2 A g ⁻¹	98% after 140 cycles	22
CoP@RGO	hydrothermal method	967 mAh g ⁻¹ after 200 cycles at 0.2 A g ⁻¹	83% after 200 cycles	23
Co _x P@NC hybrid	template directing method	526 mAh g ⁻¹ after 600 cycles at 1.0 A g ⁻¹	78% after 600 cycles	24
CoP≡NPPCS	self-template and self-assembly strategy	437 mAh g ⁻¹ after 800 cycles at 1 A g ⁻¹	51% after 800 cycles	25
Co-P/graphene nanocomposites	one-pot solution approach	929 mAh g ⁻¹ after 1000 cycles at 0.1 A g ⁻¹	83% after 100 cycles	26
CoP/C nano boxes	Pyrolysis strategy	523 mAh g ⁻¹ after 1000 cycles at 5 A g ⁻¹	60.2 % after 1000 cycles	27
Fe-CoP/CC	Hydrothermal process	1320 mAh g ⁻¹ after 140 cycles at 0.2 A g ⁻¹	76.5% after 200 cycles	28
CoP@C-CNTs	Pyrolysis of MOFs	692 mAh g ⁻¹ after 100 cycles at 0.1 A g ⁻¹	81% after 100 cycles	29
CoP@CNCs	Pyrolysis-phosphorization method	714.1 mAh g ⁻¹ after 500 cycles at 2 A g ⁻¹	77 % after 500 cycles	30
CoP@NC/rGO	In situ growth of Co-MOFs	733 mAh g ⁻¹ after 300 cycles at 0.25 A g ⁻¹	91 % after 300 cycles	31
CoP@C/BC	Hydrothermal method	351 mAh g ⁻¹ after 1000 cycles at 1 A g ⁻¹	82.9 % after 1000 cycles	32
CoP@N/P-(C/CNTs)	Pyrolysis-phosphorization strategy	600 mAh g ⁻¹ after 200 cycles at 0.5 A g ⁻¹	81.6 % after 200 cycles	33
CoP nanorod arrays		390 mAh g ⁻¹ after 900 cycles at 0.4 A g ⁻¹	53% after 900 cycles	34
CoP HR@rGO	Hydrothermal and phosphorization method	714.7 mAh g ⁻¹ after 100 cycles at 0.1 A g ⁻¹	78% after 100 cycles	35
CoP/C nanosheets	Carbonization-phosphorization strategy	612 mAh g ⁻¹ after 500 cycles at 0.4 A g ⁻¹	77.2 % after 500 cycles	36
CoP3@PPy microcubes	Template method	650 mAh g ⁻¹ after 220 cycles at 0.5 A g ⁻¹	81.2 % after 220 cycles	37
3D porous MoP@C hybrid	Template sol-gel method	1028 mAh g ⁻¹ after 100 cycles at 0.1 A g ⁻¹	83.4 % after 100 cycles	38
MoP-C microspheres	Carbonization and phosphorization	1152 mAh g ⁻¹ after 1200 cycles at 0.2 A g ⁻¹	79.2 % after 100 cycles	39
H-MoP@rGO	Hydrothermal-phosphorization method	353.8 mAh g ⁻¹ after 600 cycles at 1 A g ⁻¹	74.3 % after 100 cycles	40
MoP@C	Self-polymerization-phosphidation	496 mAh g ⁻¹ after 400 cycles at 1 A g ⁻¹	93 % after 400 cycles	41

	strategy			
MoP@NCNFs	electrospinning method	840 mAh g ⁻¹ after 200 cycles at 0.1 A g ⁻¹	77.3 % after 200 cycles	⁴²
CoP@C $\subset$ G-NP	Spray-drying	494 mAh g ⁻¹ after 500 cycles at 0.5 A g ⁻¹	86.7 % after 500 cycles	This work
CoP@C $\subset$ G-NP	Spray-drying	438 mAh g ⁻¹ after 500 cycles at 1 A g ⁻¹	74.7 % after 500 cycles	This work
MoP@C $\subset$ G-NP	Spray-drying	301 mAh g ⁻¹ after 800 cycles at 1 A g ⁻¹	87.4 % after 800 cycles	This work

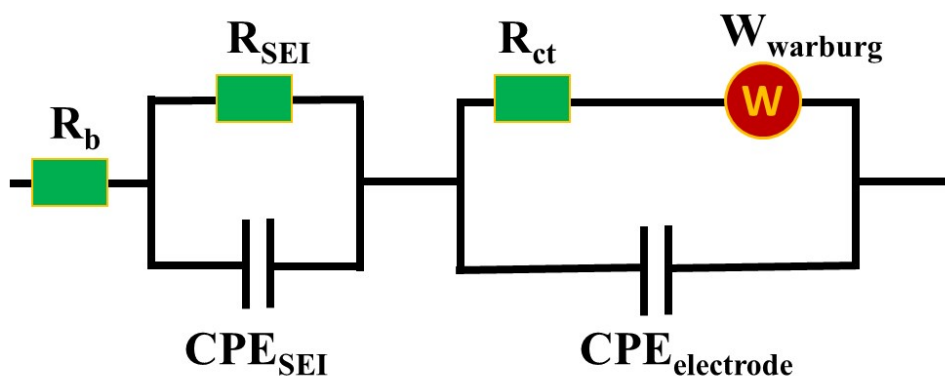


Figure S9. Equivalent circuit model used for fitting the CoP@C≡G-NP and MoP@C≡G-NP electrodes Nyquist plots in half-cell system. Where R_b : bulk resistance of cell (electrolyte, separator, and electrodes). R_{SEI} , CPE_{SEI} : resistance and capacitance of the interfacial layer. R_{ct} , $CPE_{electrode}$: charge-transfer resistance and double layer capacitance. W : Warburg impedance (diffusional effects of Li ion on the host material).

Table S3. EIS Fitting parameters.

CoP@C≡G-NP	R_b/Ohm	R_{SEI}/Ohm	R_{ct}/Ohm	W/Ohm
Before cycles	6.5	9.5	357.7	84.6
After 25 th cycles	17.8	11.6	77.1	46.7
After 50 th cycles	4.7	10.4	165.6	48.2
MoP@C≡G-NP				
Before cycles	9.8	10.4	334.1	83.4
After 25 th cycles	19.7	12.8	66.1	51.7
After 50 th cycles	2.8	11.4	121.4	45.1

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