Supporting Information

Uniform Nitrogen-rich Interphase Optimizes Interfacial Kinetics for Stable Graphite Anodes

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Experimental Section

Preparation of CPAN

The CPAN was obtained by heating polyacrylonitrile (PAN, Mw=150000) at 400 °C for 6 h under an Ar atmosphere with a ramping rate of 5 °C min^{-1}.

Preparation of Gr@CPAN

The Gr@CPAN was synthesised by initially dissolving 0.25 g of polyacrylonitrile (PAN) in dimethylformamide (DMF). Subsequently, 10 g of graphite (Gr) was introduced into the solution, followed by vigorous stirring for 5 h. The homogeneous mixture was then immersed in deionized water, inducing the phase inversion method which precipitated the DMF-dissolved PAN, thereby coating the graphite surface. Finally, the obtained composite was subjected to heat treatment at 400 °C for 6 h under a N_2 atmosphere, employing a heating rate of 5 °C min^{-1}, to yield the final Gr@CPAN. Gr@$CPAN_{0.5}$ and Gr@$CPAN_1$ were obtained through an identical process, differing solely in PAN addition (0.5 g and 1 g, respectively).

Material Characterization

Surface architecture of Gr, CPAN, and Gr@CPAN was visualised through field-emission SEM (ZEISS Sigma 300) and aberration-corrected TEM (FEI Talos F200X G2), resolving hierarchical porosity down to sub-5 nm. Powder XRD (Haoyuan DX-2700BH, Cu Kα) traced phase evolution across 10–90° at 5° min^{-1}. Determination of the specific surface area of the samples was carried out employing a fully automated specific surface analyzer (BET, iPore400, PhysiChem Instruments). TGA (Hengjiu HCT-1) quantified CPAN content of Gr@CPAN by mass loss between 25 °C and 800 °C. XPS (Thermo Scientific K-Alpha) was used to identify the components of the solid electrolyte interphase of Gr and Gr@CPAN after cycling.

Electrochemical Measurements

All electrode (Gr, Gr@CPAN, Gr@$CPAN_{0.5}$, Gr@$CPAN_1$, and NCM811) slurries were prepared in a Thinky ARE-310 planetary mixer, keeping active material, acetylene black, and PVDF at a mass ratio of 90:5:5. The slurry containing graphite and graphite-based materials were coated onto copper foil current collector, whereas the NCM811 slurry was uniformly

applied onto aluminum foil. All electrodes were pre-dried at 40 °C for 2 h, then vacuum-dried at 50 °C for 12 h. Half-cell discs (diameter: 10 mm, mass loading: ~1.5 mg cm^{-2}) were punched from Gr, Gr@CPAN, Gr@$CPAN_{0.5}$, and Gr@$CPAN_1$ electrodes, full-cell cathode (NCM811, diameter: 10 mm, mass loading: ~10 mg cm^{-2}) were paired with anodes (Gr and Gr@CPAN, diameter: 12 mm, mass loading: ~6.7 mg cm^{-2}). Coin-type half-cells and full-cells were assembled using CR2032 and CR2025 hardware (purchased from Canrd), respectively. Celgard 2500 was used as the separator and the electrolyte was 1.0 M $LiPF_6$ in EC: DMC: EMC = 1:1:1 Vol%.

Galvanostatic testing was performed within voltage range of 0.01 to 3 V for half-cells and 0.5 to 4.3 V for NCM811 full-cell. All cells initially underwent one formation cycle at 0.1 C, followed by long-term cycling at 1 C (1 C= 370 for half cells and 1 C=200 mAh g^{-1} for full-cells). The tests was conducted on a NEWARE battery test system (Shenzhen, China) at 27 °C. To assess lithiophilicity, both Gr and Gr@CPAN anodes were first discharged to 0 V. Subsequently, lithium deposition was conducted by applying a constant current density of 0.5 mA cm^{-2} for 2 h. Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were recorded on an electrochemical workstation (DongHua Analytical DH7006B). For half-cells, CV scans ranged from 0.01–3 V at a sweep rate of 0.05 mV s^{-1}. Multi-rate CV tests utilized the same voltage window with sweep rates of 0.05, 0.1, 0.2, and 0.3 mV s^{-1}. EIS spectra were acquired over a frequency range from 0.1 Hz–10 kHz with a 10 mV amplitude. In-situ EIS characterization involved sequential discharge and charge processes between 0.01 and 3 V, with impedance collected at 0.1 V intervals using identical frequency parameters. Subsequent distribution of relaxation times (DRT) analysis was performed using the DRT-TOOLS toolbox (https://sites.google.com/site/drttools/) with MATLAB R2021.

Note S1. The detailed CPAN content calculation process.

The mass fraction of carbonized polyacrylonitrile (CPAN) in the Gr@CPAN composite was determined from thermogravimetric analysis (TGA) data. Let a and b represent the mass fractions of CPAN and graphite in the composite, respectively, where a + b = 1.

Upon heating to 800 °C under nitrogen atmosphere, the measured mass retentions are:

Gr@CPAN composite: 98.65%

Pure CPAN: 73.46%

Pristine graphite: 99.95%

The overall mass loss of Gr@CPAN (1.35%) arises from the combined contributions of CPAN decomposition (26.54% loss) and graphite residual mass loss (0.05% loss). This relationship is expressed as:

$0.2654a + 0.0005b = 0.0135$

Substituting $b = 1 - a$ and solving:

$0.2654a + 0.0005(1 - a) = 0.0135$

$a = (0.0135 - 0.0005) / (0.2654 - 0.0005) = 0.0491$ or 4.91 wt%

Thus, the CPAN content in Gr@CPAN is determined to be 4.91 wt%.

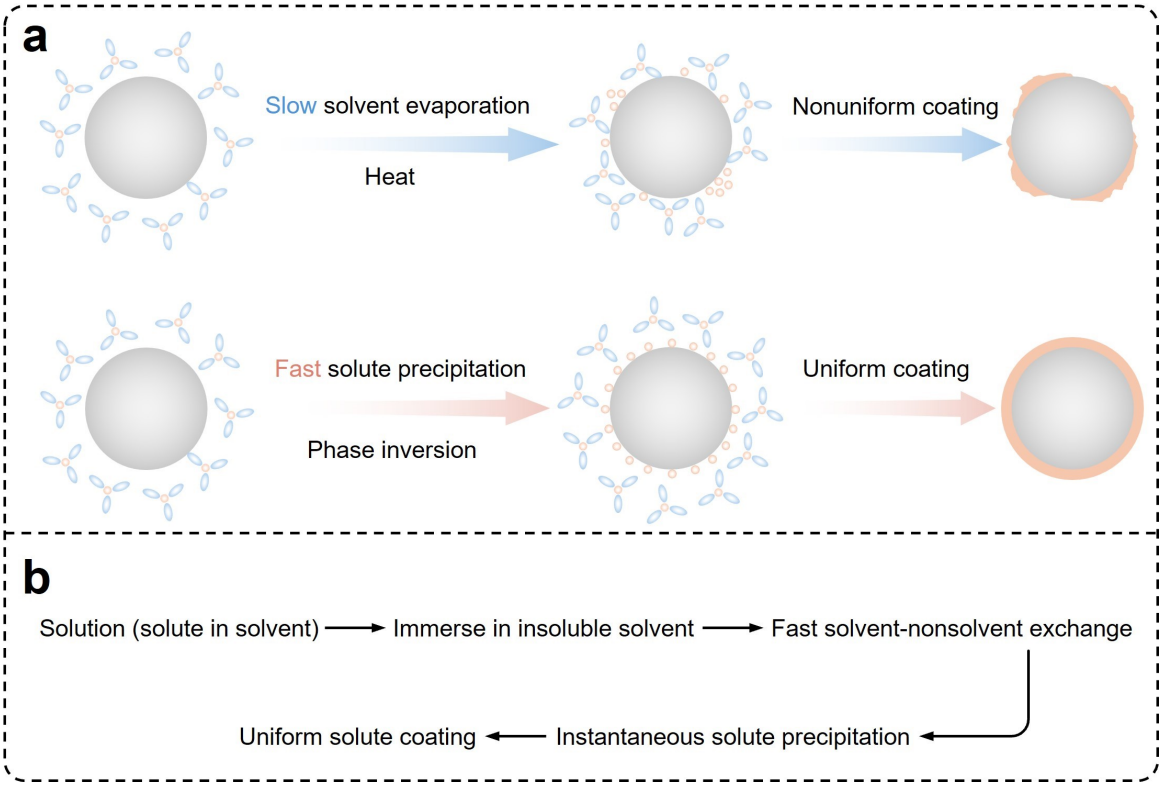

Fig. S1. (a) Comparison between conventional wet coating and phase inversion coating. (b) Flow chart of phase inversion coating process.

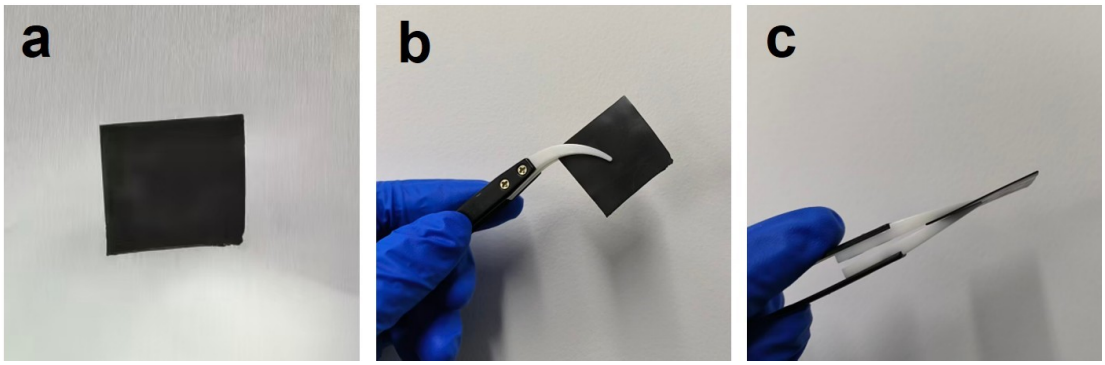

Fig. S2. (a-c) Optical photos of precursors obtained after phase inversion method.

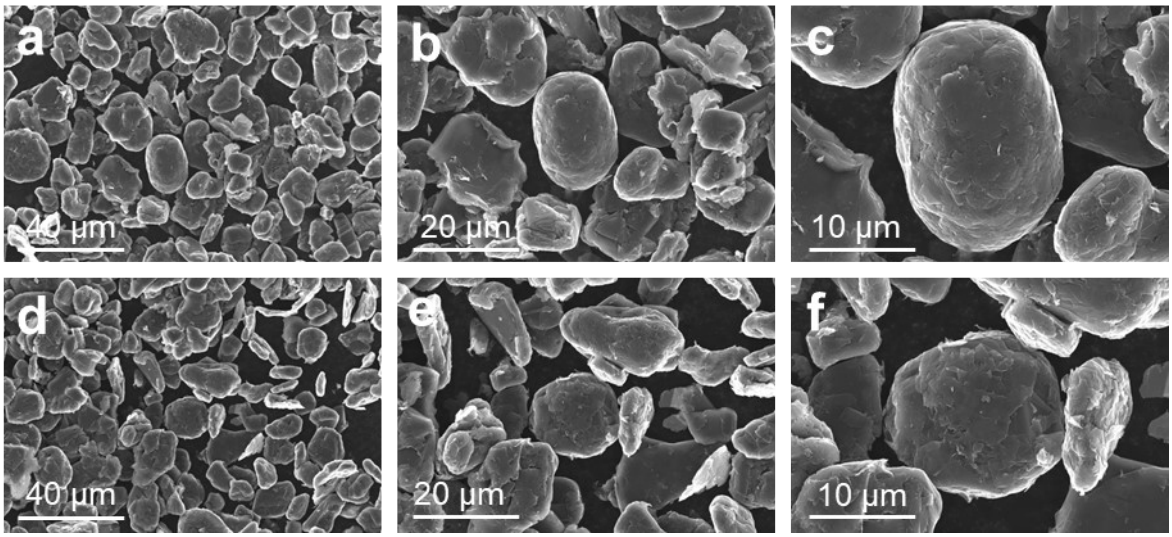

Fig. S3. (a-f) SEM images of Gr@CPAN.

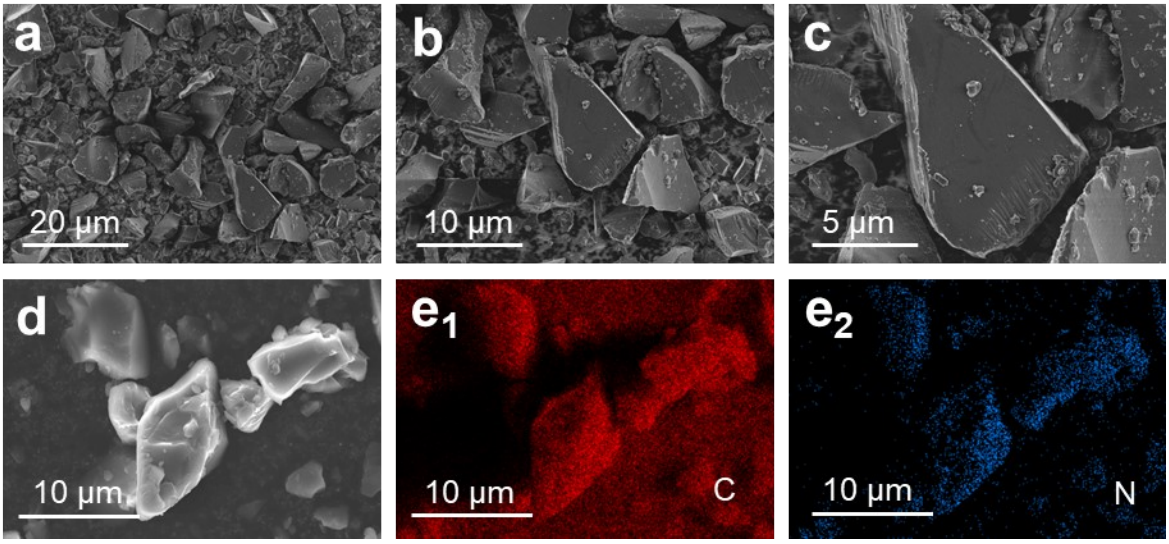

Fig. S4. (a-d) SEM images of CPAN. (e_1, e_2) Corresponding EDS mappings of C and N.

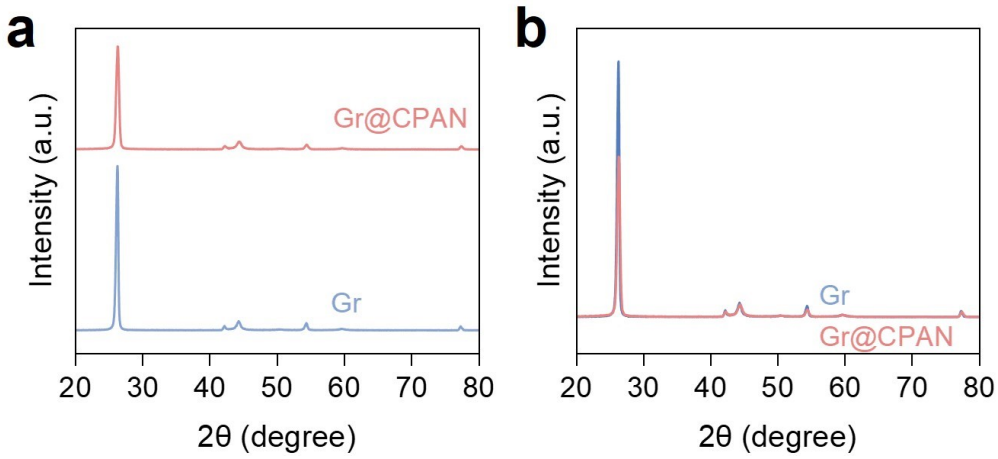

Fig. S5. (a) XRD patterns of Gr and Gr@CPAN. (b) XRD stack diagram of Gr and Gr@CPAN.

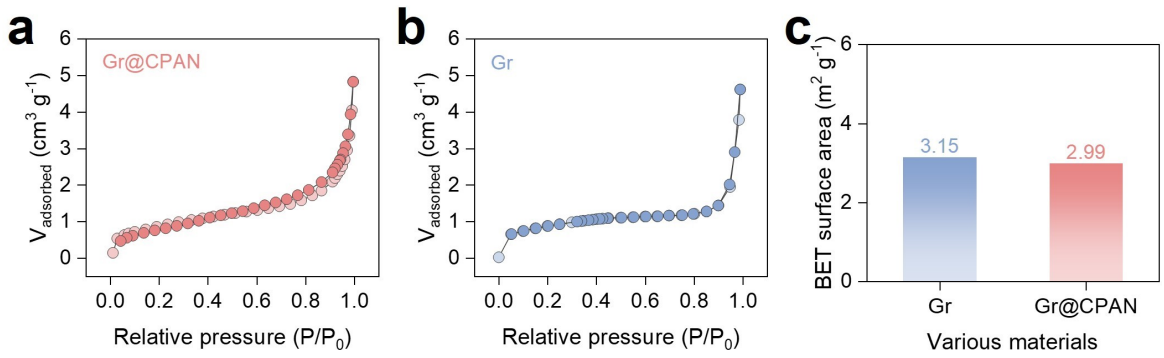

Fig. S6. (a) N_2 adsorption-desorption isotherms of Gr@CPAN. (b) N_2 adsorption-desorption isotherms of Gr. (c) Comparative BET surface areas of Gr and Gr@CPAN.

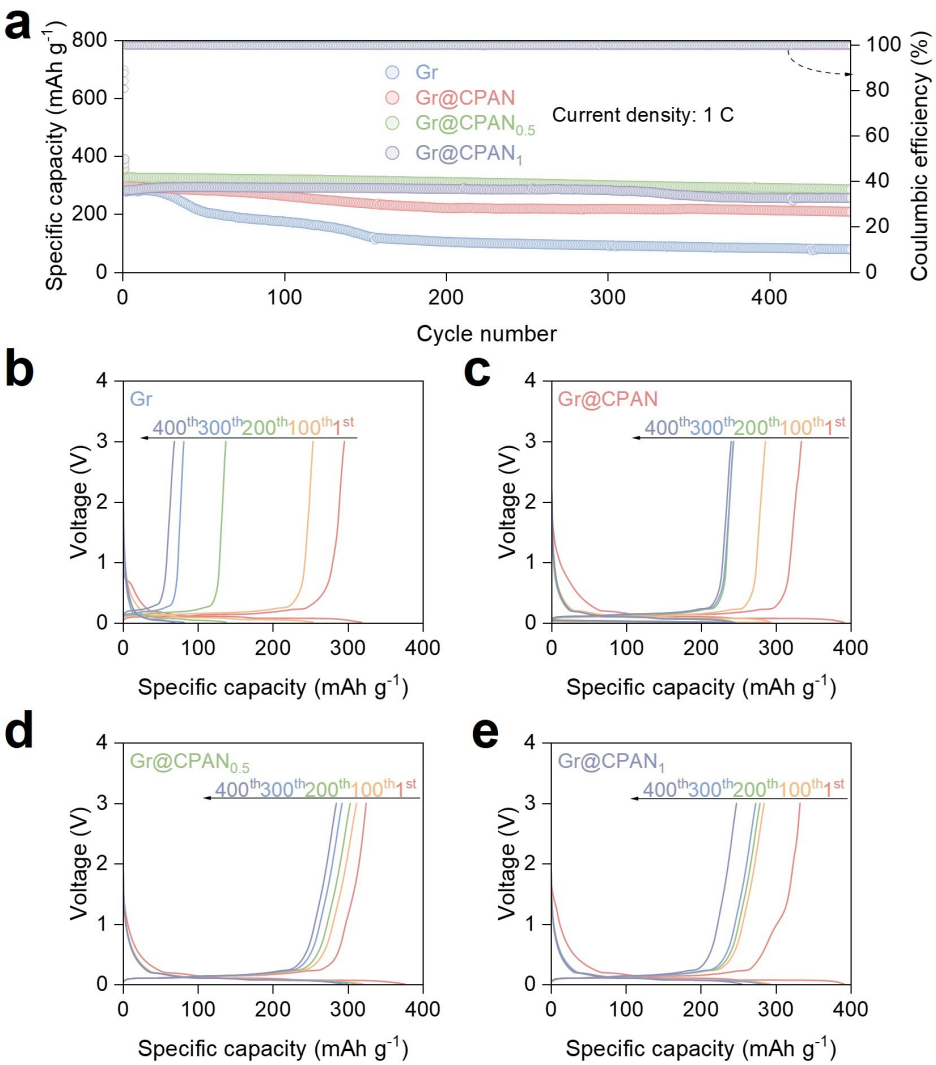

Fig. S7. (a) Long-term cycling performances of Gr, Gr@CPAN, Gr@CPAN$_{0.5}$, and Gr@CPAN$_1$ at a current density of 1 C.(b-e) Corresponding charge/discharge profile of Gr, Gr@CPAN, Gr@CPAN$_{0.5}$, and Gr@CPAN$_1$.

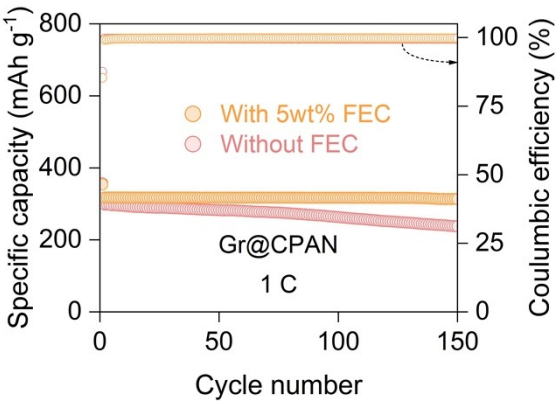

Fig. S8. Long-term cycling performances of Gr@CPAN with/without FEC-containing electrolyte at 1 C.

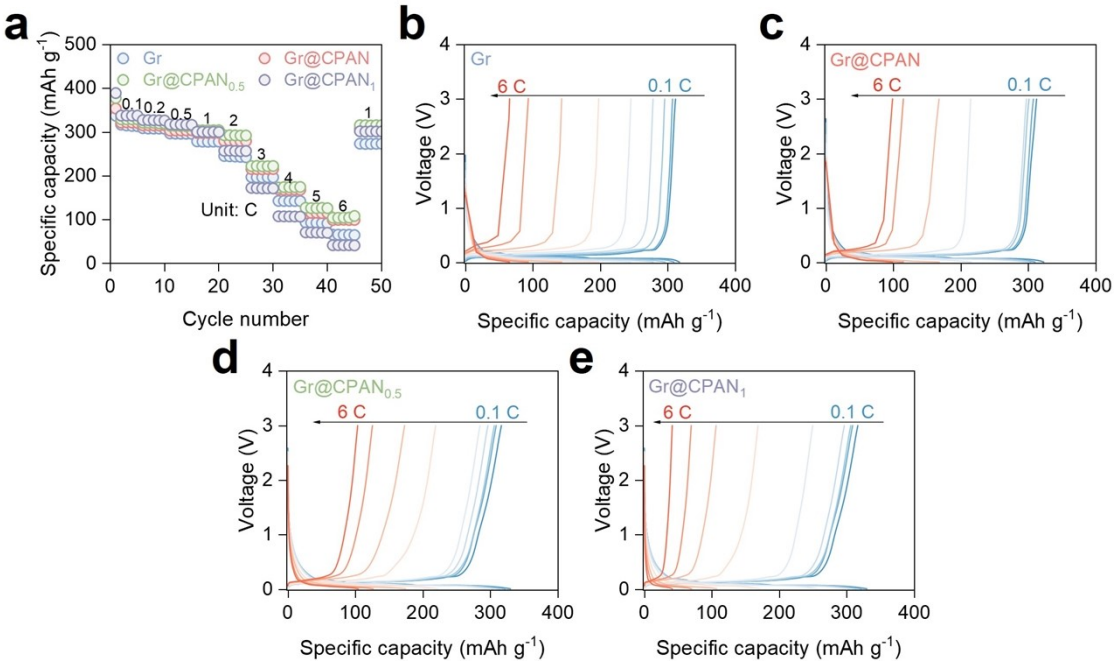

Fig. S9. (a) Rate capability of Gr, Gr@CPAN, Gr@CPAN$_{0.5}$, and Gr@CPAN$_1$ at a current rate of 0.1−6 C. (b-e) Corresponding charge/discharge profile of Gr, Gr@CPAN, Gr@CPAN$_{0.5}$, and Gr@CPAN$_1$.

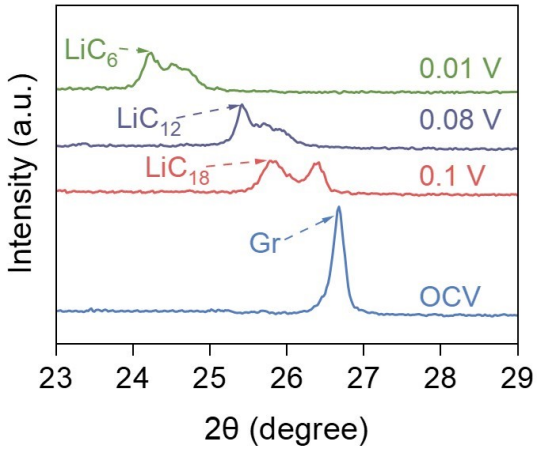

Fig. S10. XRD patterns of Gr@CPAN electrodes at different discharge states (fresh, 0.1 V, 0.08 V, and 0.01 V).

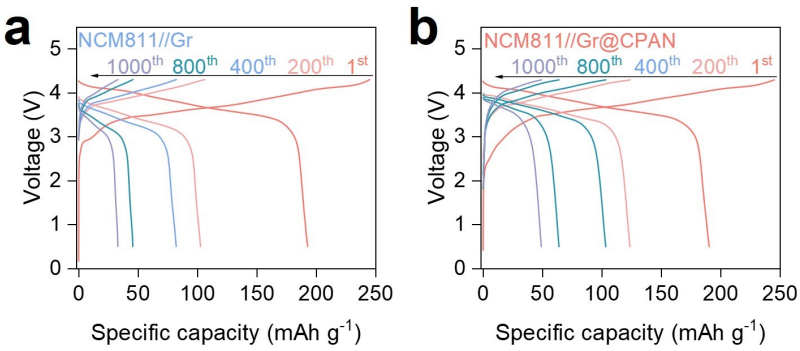

Fig. S11. (a-b) Charge/discharge profile of NCM811//Gr and NCM811//Gr@CPAN.

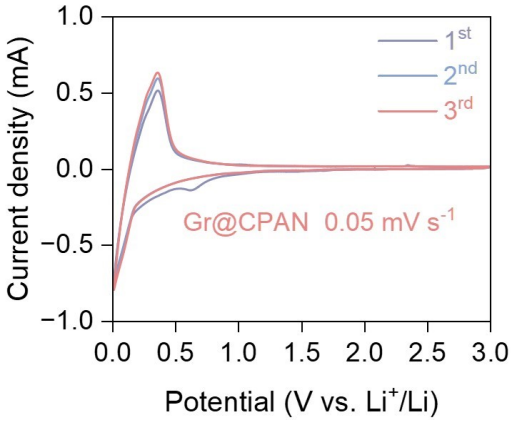

Fig. S12. CV curves of Gr@CPAN at 0.05 mV s^{-1} during the first three cycles.

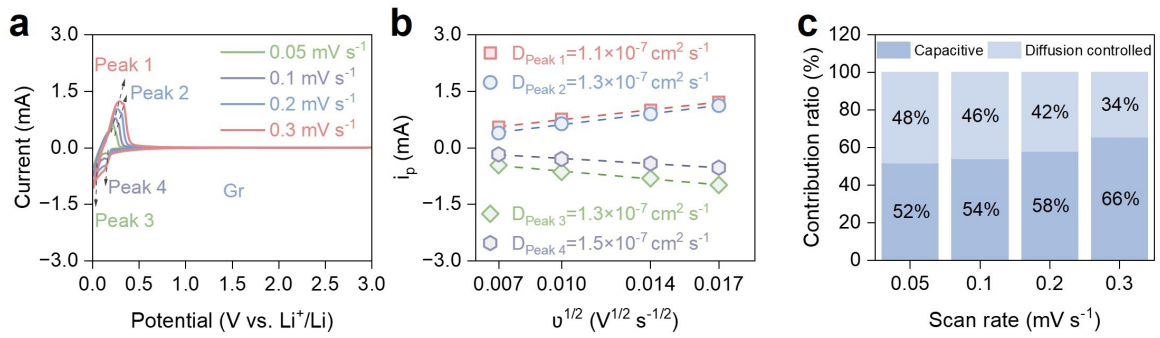

Fig. S13. (a) CV curves of Gr under various scan rates. (b) Calculated values of Li^+ diffusion of Gr. (c) Calculated capacity contribution of Gr.

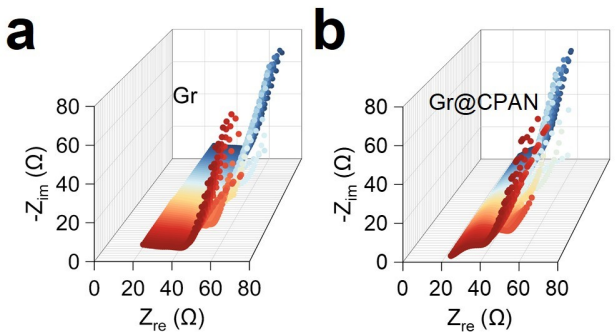

Fig.S14. (a) In situ EIS data of Gr after 100 cycles. (b) In situ EIS data of Gr@CPAN after 100 cycles.

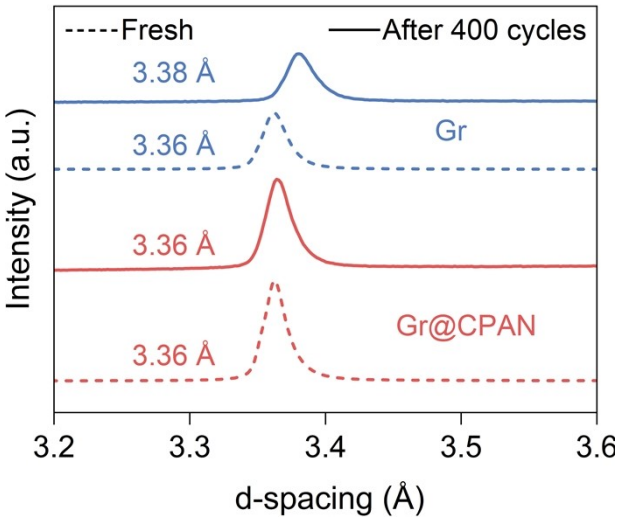

Fig. S15. XRD Patterns of fresh Gr anode, fresh Gr@CPAN anode, Gr anode after 400 cycles, and Gr@CPAN anode after 400 cycles with d-spacing axis.

Table S1. Elemental content based on EDS results of SEM of Gr@CPAN.

Element	Mass Fraction (%)	Mass Error (%)
C	99.88	1.15
N	0.12	1.38

Table S2. Elemental content based on EDS results of STEM of CPAN.

Element	Mass Fraction (%)	Mass Error (%)
C	93.72	1.02
N	6.28	0.16

Table S3. Performance comparison of different graphite modifications.

Materials	Electrolyte	Cycling performance (mAh g^{-1})	Cpacity decay per cycle	Refs.
Gr@S	**1.0 M $LiPF_6$ in EC:DMC:EMC (1:1:1 Vol%)**	**265 after 450 cycles_1 C**	**~0.042%**	**This work**
Al_2O_3@Graphite	1.0 M $LiPF_6$ in EC: EMC (3:7 Vol%)	~330 after 100 cycles_1 C	~0.060%	[1]
FRA	1.0 M $LiPF_6$ in EC:DEC:DMC (1:1:1 Vol%)	336 after 100 cycles_0.2 C	~0.090%	[2]
CS-Nf	1.0 M $LiPF_6$ in EC:DMC:EMC (1:1:1 Vol%)	~250 after 350 cycles_0.5 C	~0.063%	[3]
TiO_{2-x}/Graphite	1.0 M $LiPF_6$ in EC/EMC (3:7 Vol%)	~250 after 100 cycles_1 C	~0.219%	[4]

References

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