

Electronic Supplementary Information

Integrating commercial graphite with network-like carbon fibers for high-rate and long-cycling K⁺-storage

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Experimental section

Materials synthesis: Firstly, 0.2 g zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was added into 10 mL N, N-dimethylformamide (DMF) and completely dissolved, then 1 g PAN and 0.6 g spherical graphite were added to the above solution and ultrasonically dispersed for 30 min and then placed on a magnetic stirring table for 12 h at a speed of 500 rpm to obtain a dispersed black solution. Using an electrostatic spinner, the distance between the needle and the receiver was set at 18 cm, the voltage was 20 kV, the solution was advanced at a rate of 1 mL h^{-1} , the syringe translation distance was 80 mm, the translation speed was set at 40 mm min^{-1} and the receiver rotation speed was set at 60 rpm. The resulting film was removed and placed in a blower at $80 \text{ }^\circ\text{C}$ for 12 h. The dried spun filaments were placed in a muffle furnace and cured by annealing at $200 \text{ }^\circ\text{C}$ for 2 h at a temperature increase rate of $0.5 \text{ }^\circ\text{C min}^{-1}$ (denoted as Gr@PAN). Subsequently, black flexible films (referred to as Gr@CNF) were carbonized at high temperature for 2 h under an Ar atmosphere by ramping up to $800 \text{ }^\circ\text{C}$ at a rate of $1 \text{ }^\circ\text{C min}^{-1}$. The obtained membrane is washed by 1M HCl. For comparison, carbon fiber films without the addition of spherical graphite with $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (denoted as CNF) were prepared by the same procedure. The Gr/CNF composite was prepared by ball-milling spherical graphite with carbon fibers at 300 rpm for two hours.

Materials Characterization: The crystal structure and morphology of the as-prepared electrocatalysts were characterized by X-ray diffraction (XRD, Bruker, D8 Advance) with Cu K α radiation ($\lambda = 0.15418 \text{ nm}$) as an X-ray source, scanning electron microscopy (SEM, SU 3500) with 15 kV working voltage. Raman spectroscopy was obtained using the WITec system (alpha 300 R with a 532 nm wavelength laser). Nitrogen adsorption/desorption isotherms were collected from the samples, and the specific surface areas were calculated by the multipoint Brunauer–Emmett–Teller (BET) procedure. The surface electronic configuration of samples was determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi).

Electrochemical tests: Spherical graphite, Super P and polyvinylidene fluoride (PVDF) binder were mixed in a mass ratio of 8: 1:1 in N-methylpyrrolidone (NMP) and the paste was coated on copper foil to prepare anode and was dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for 12 h and then cut into small discs of 12 mm diameter to be used as electrode pieces. The average active substance loading of the negative electrode was about 1.2 mg cm^{-2} . Gr @CNF and CNF can be used directly as anode electrode. Electrolyte using 0.8M KPF₆/EC/DEC.

Galvanostatic charge-discharge and galvanostatic intermittent titration technique (GITT) tests were performed using a LAND battery test system over a voltage range of 0.01-3.0 V (vs K⁺/K). For the GITT tests, cells were discharged at 25 mA g⁻¹ for 20 min, followed by open-circuit relaxation for 2 h, and this process was continued until the potential was ≤ 0.01 V. Cyclic voltammogram (CV) profiles were scaled in a potential range of 0.01-2.5 V (vs. K⁺/K) on a CHI750E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) tests were performed on a Reference 3000 Gamry with a recording range of 0.1 Hz-100 kHz and an amplitude of 0.5 mV. All tests are conducted at room temperature.

The energy density and power density are calculated by using equations: $P = \Delta E_i / m$ and $E = Pt$, where $\Delta E = (E_{max} + E_{min}) / 2$, V_{max} and V_{min} are the beginning and end of the potential in the discharge curve, I is the charge-discharge current (A), t is the discharge time (h), and m is the mass of the active material, including both anode and cathode.

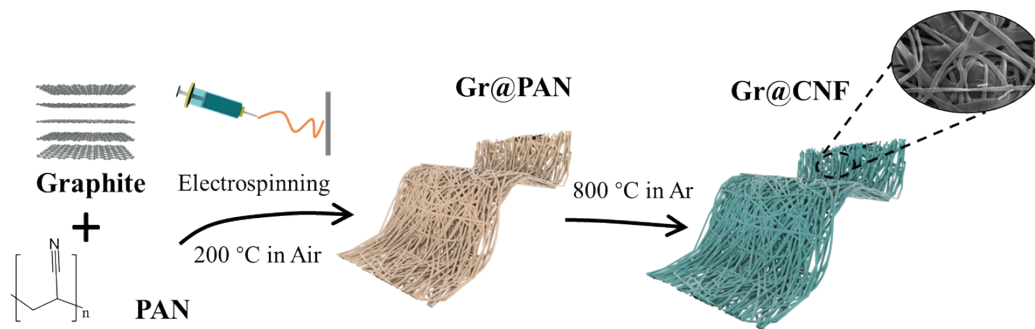


Figure S1. Schematic diagram of Gr@CNF synthesis by electrostatic spinning.

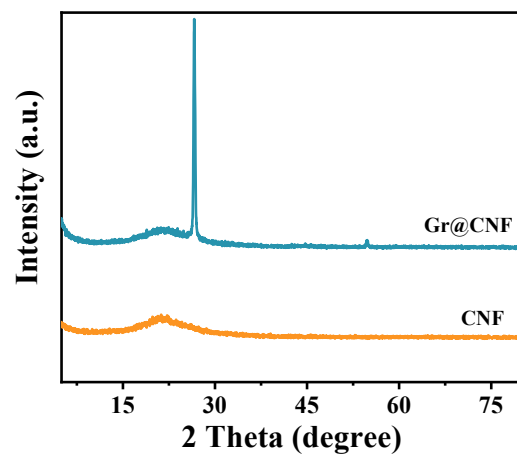


Figure S2. XRD patterns of Gr@CNF and CNF.

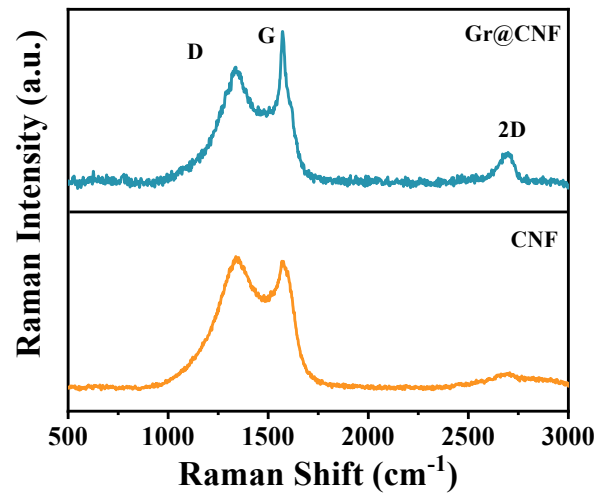


Figure S3. The Raman spectra of Gr@CNF and CNF.

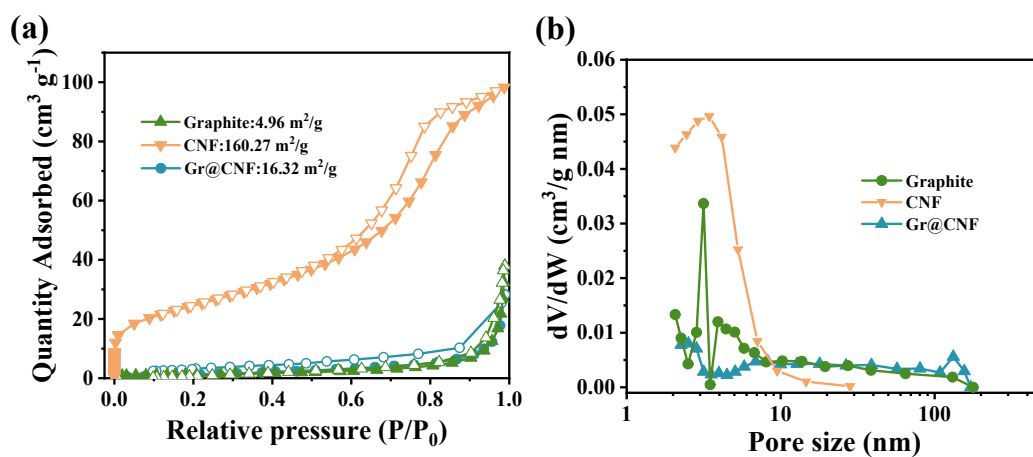


Figure S4. The N₂ adsorption and desorption curves and pore size distribution.

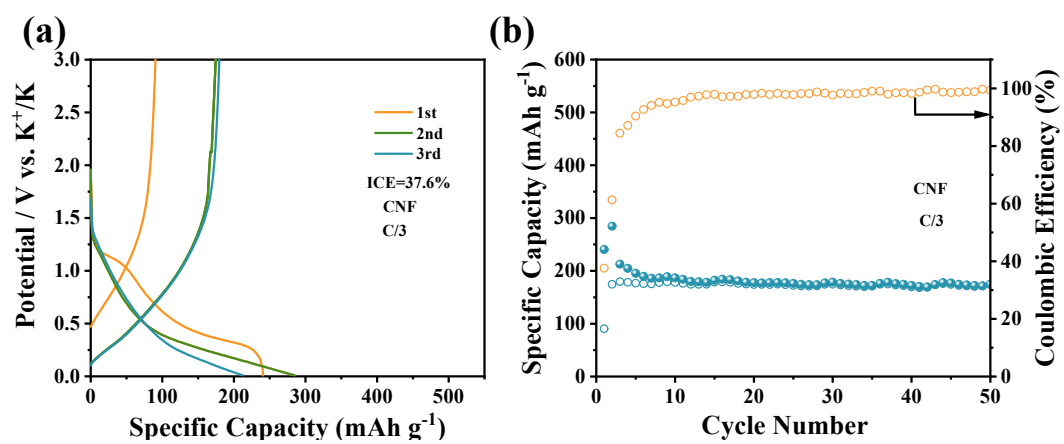


Figure S5. The GCD curves and 50 cycles of CNF at the current density of C/3.

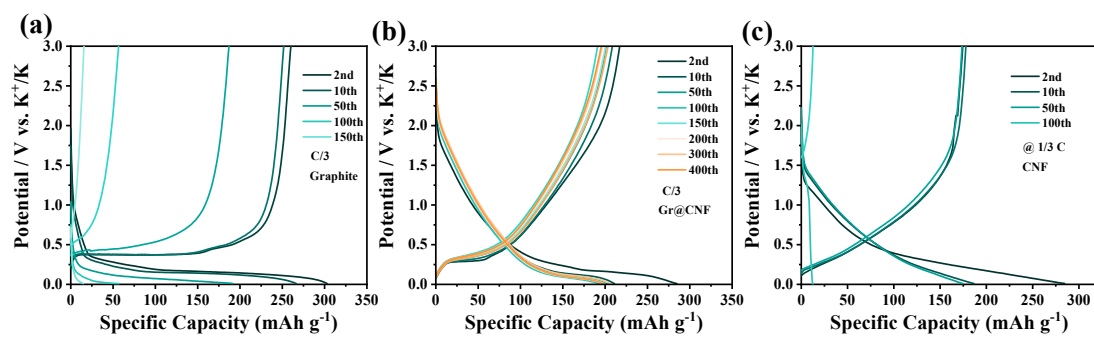


Figure S6. GCD curves with different number of turns of three electrodes cycled at a current density of C/3: (a) Graphite; (b) Gr@CNF; (c) CNF.

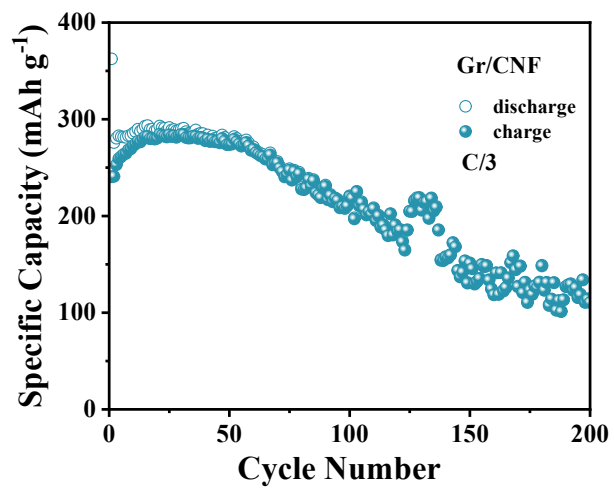


Figure S7. 200 cycles of Gr/CNF at the current density of C/3.

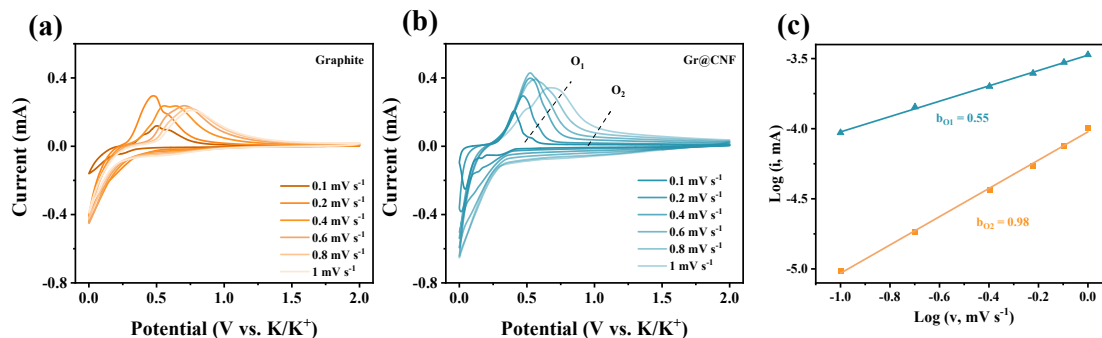


Figure S8. CV curves for two electrodes at different scan rates and b-values calculated from the curves.

Note to S8: Both materials show obvious reduction peaks in the low potential interval, as well as oxidation peaks around 0.5 V. The difference is that the peak shift of the Gr@CNF curves is smaller and the deformation is weaker with the increasing sweep rate. From the relationship between the peak current (i) and the scan rate (v) ($i = av^b$), the b value can be calculated to determine the electrochemical behavior of K⁺ during cycling.

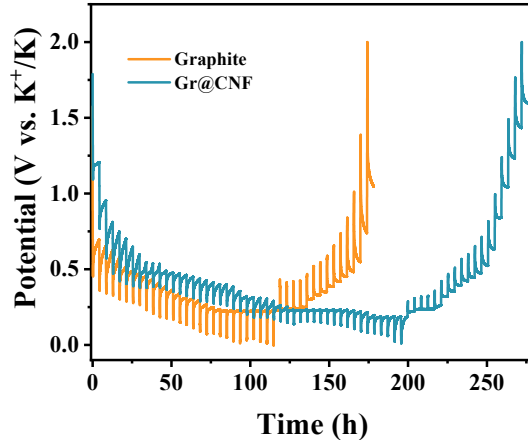


Figure S9. GITT curves for the two electrodes.

Note to S9: According to GITT test results, D_{K^+} can be calculated using the following equation

$$D_{K^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2$$

Where τ is the relaxation time, m_B is the mass of active material, M_B is the molar mass of active material, V_m is the molar volume of hard carbon, S is the surface area of active material, ΔE_S and ΔE_τ can be obtained from GITT curves.

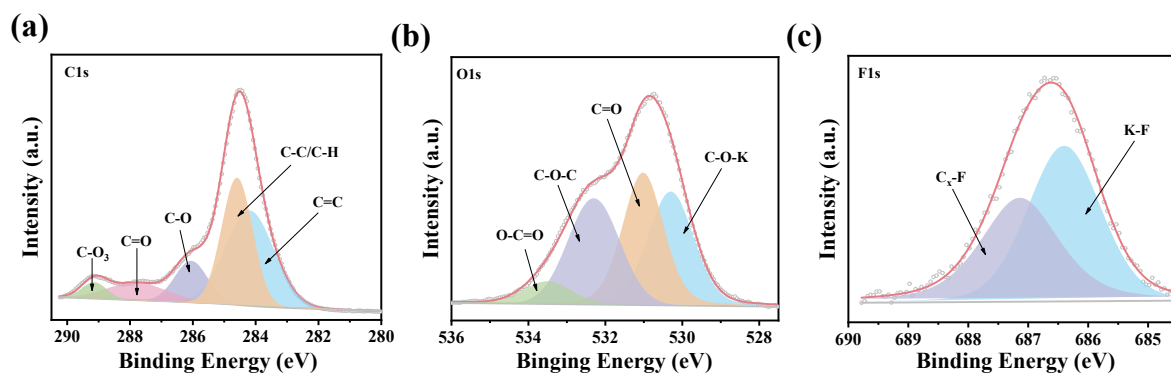


Figure S10. XPS spectra of Gr@CNF electrode after 20 cycles: (e) C 1s, (f) O 1s, (g) F 1s. Note to S10: The C-C/C-H, C=C, C-O-C, C-O, C=O and C-O₃ bonds located at 285, 284.2, 285.7, 287.2 and 288.4 eV in the C1s spectra, as well as the O1s spectra showing O-C=O (533.5 eV), -C-O-C- (532.3 eV), C=O (531.4 eV) and -C-O-K (530.3 eV) characteristic peaks, which are mainly due to organic matter produced by solvent decomposition.

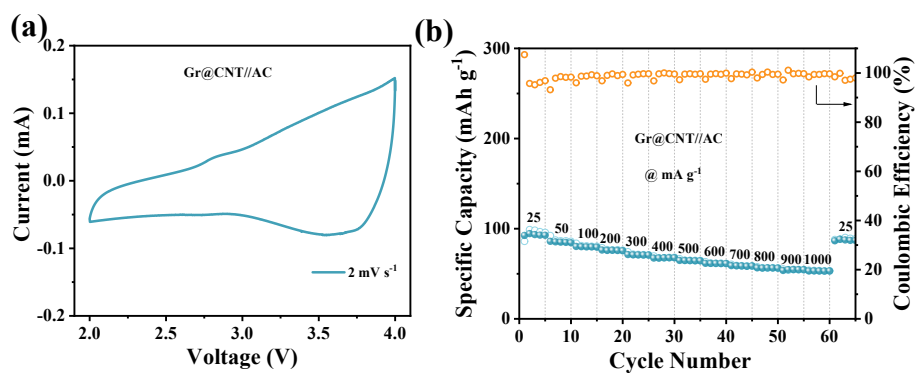


Figure S11. (a) CV curve of Gr@CNT//AC at 2 mV s⁻¹; (b) Rate performance at different current densities of Gr@CNT//AC.

Acknowledgement

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