Electronic Supplementary Information

ZIF-8 Coating on Graphite: A High-Rate and Long-Cycling Anode for Sodium-Ion Capacitors

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Experimental Section

Synthesis of ZIF-8@Gr: Firstly, 3 g of $Zn(CH3COO)_2$-$2H_2O$ was dissolved in 50 mL of deionized water, and then 0.6 g of spherical graphite, 9.11 mg of CTAB and 5 mg of SDS were added to the solution, and then 2-methylimidazole was dissolved in 50 mL of deionized water with rapid stirring for 20 minutes to make the solution homogeneously dispersed. Then the two solutions were mixed quickly and stirred for 30 min, and the final solution appeared dark gray. The powder was collected by vacuum filtration and then dried at 60°C for 12 h. In addition, spherical graphite without ZIF-8 coating was used as a comparison

Materials Characterization: The microscopic morphology and structure of the samples were obtained by scanning electron microscopy (SEM, Hitachi SU3500) and transmission electron microscopy (TEM, Philips CM12 TEM/STEM), and were measured by XRD (Bruker AXS D8-Focus, Cu), X-ray photoelectron spectroscopy (XPS, VG Multilab2000) and Raman microscope (Renishaw RM-1000, 532 nm excitation) to demonstrate the material phases and characteristics, followed by The specific surface area of the samples was determined by nitrogen adsorption-desorption isotherms (Micromeritics, ASAP 2460).

Electrochemical characterizations: A standard CR2032-type coin cell was assembled in an argon-filled glove box (Mbraun, Germany) to test the half-cell performance, using 1 M $NaPF_6$ in Diglyme as the electrolyte, glass fiber filter as the separator of the cell, and the counter electrodes of the half-cell were taken as sodium metal. The working electrode was fabricated by grinding and mixing the active material (80wt%), acetylene black (10wt%), and polyvinylidene fluoride (PVDF) (10wt%) and adding N-methyl pyrrolidone (NMP) to prepare a slurry coated on aluminum foil, dried in an oven at 60°C for 12 h and cut into 1.12 cm^2 circular electrodes for use. The average loading of ZIF-8@Gr and Graphite electrodes was 1-1.5 mg cm^{-2}. The ink for 3D printed electrodes was made by mixing ZIF-8@Gr (70wt%), acetylene black (20wt%) and polyvinylidene fluoride (PVDF) (10wt%), and N-methyl pyrrolidone (NMP) homogeneously, and the printed electrodes were dried in an oven at 60 ^oC for 12 h, and their loadings were all in the range of 8-10 mg cm^{-2}. Both the galvanostatic charge-discharge (GCD) cycle and the electrochemical intermittent titration technique (GITT) were tested on the LAND-CT2001A battery system, where GCD was tested in the voltage range of 0.01-2.0 V and GITT was charged and discharged at a constant current of 30 mA g^{-1} and left to stand for 2 hours after each 15-minute test. CV profiles were measured on a CHI 750E

electrochemical workstation in the potential window of 0.01-2.0 V *vs*. Na^+/Na, and EIS was measured by Gamry Reference 3000. Using the ZIF-8@Gr as the working electrode and the active carbon as the counter electrode, the ZIF-8@Gr//AC SIC was prepared with a mass ratio of about 3:1 between the anode and the cathode and the 1 M $NaPF_6$ in diglyme as the electrolyte. Glass fiber filter was used as the cell separator. The power and energy densities of SICs are calculated as follows:

$$P = \Delta V \times I/m \quad (2)$$

$$E = P \times t/3600 \quad (3)$$

$$\Delta V = (V_{max} + V_{min})/2 \quad (4)$$

Where V_{max} and V_{min} are the maximum and minimum operating voltages (V) during discharge, I is the current (A) during charging and discharging, t is the time it takes to complete the discharge process, and m is the mass of active material in total for the cathode and anode.

The formula for the diffusion coefficient of Na^+ is as follows:

$$D_{Na+} = \frac{4}{\pi}\left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_S}{\tau\left(dE_\tau/d\sqrt{\tau}\right)}\right)^2 \left(\tau \ll L^2/D_{Na+}\right) \quad (5)$$

Where m_B, V_M, M_B, and A are the mass, molar volume and molecular weight, and surface area of the electrode of the material, respectively. L is the thickness of the electrode.

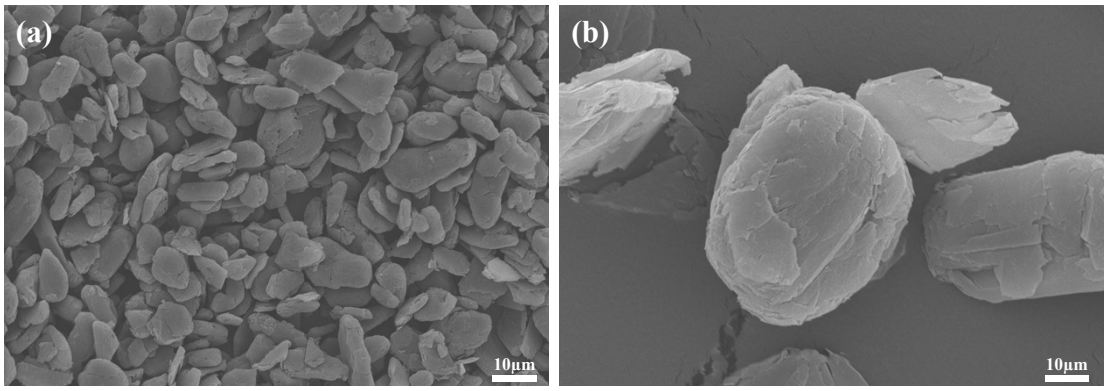

Fig. S1 (a and b) SEM images of the graphite.

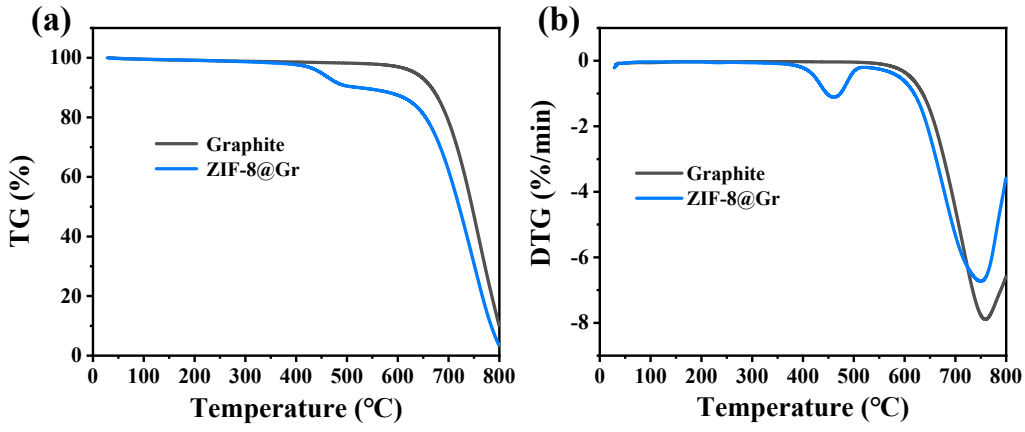

Fig. S2. (a) TG and (b) DTG curves of graphite and ZIF-8@Gr at the heating rate of 10 °C min^{-1}.

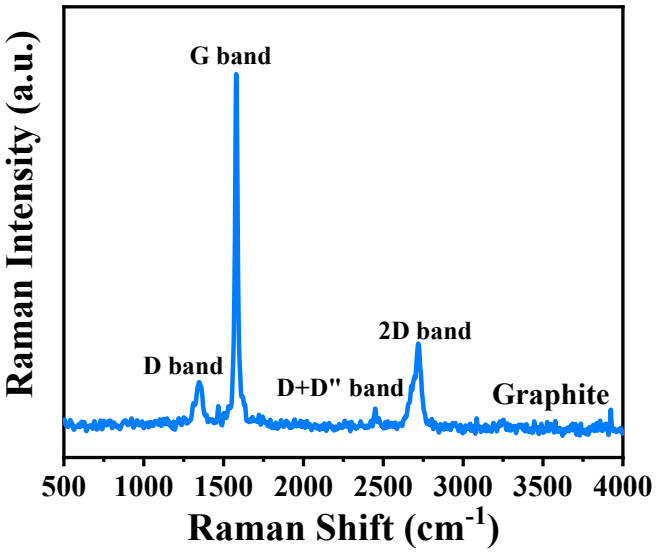

Fig. S3 Raman spectra of graphite.

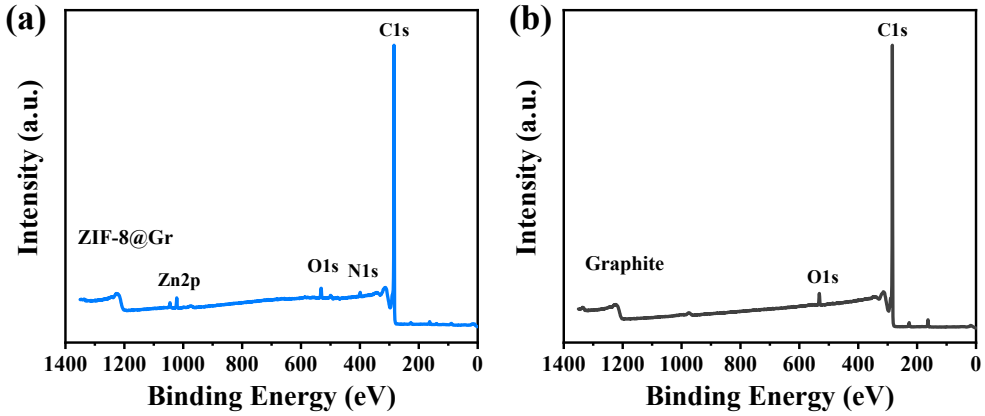

Fig. S4 XPS spectra of (a) ZIF-8@Gr and (b) graphite.

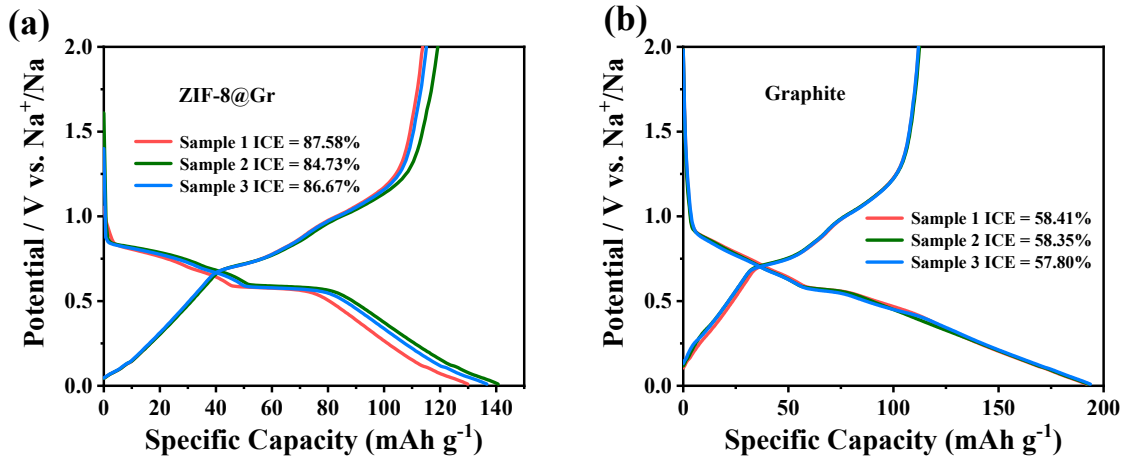

Fig. S5 The initial coulombic efficiency of three parallel cells at 0.5Ag^{-1} (a) ZIF-8@Gr and (b) graphite.

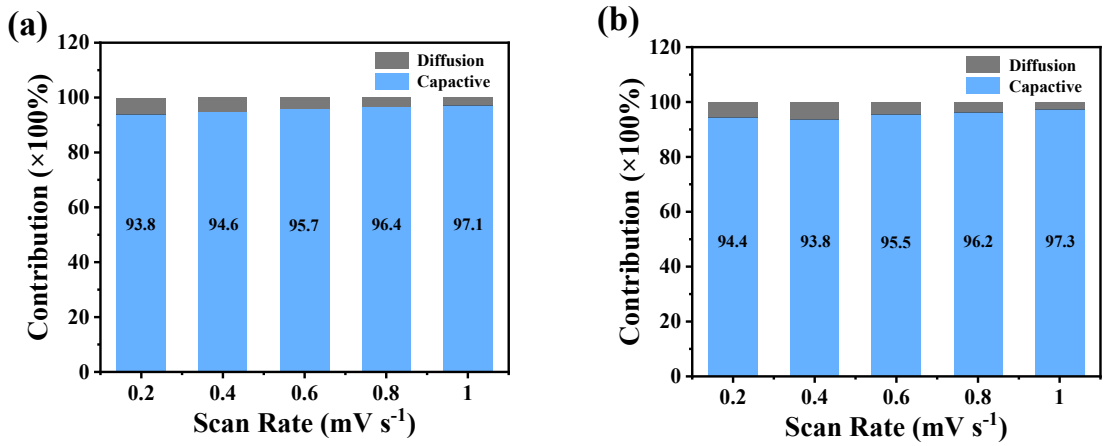

Fig. S6 Capacitive contributions at various scan rates of (a) ZIF-8@Gr and (b) graphite.

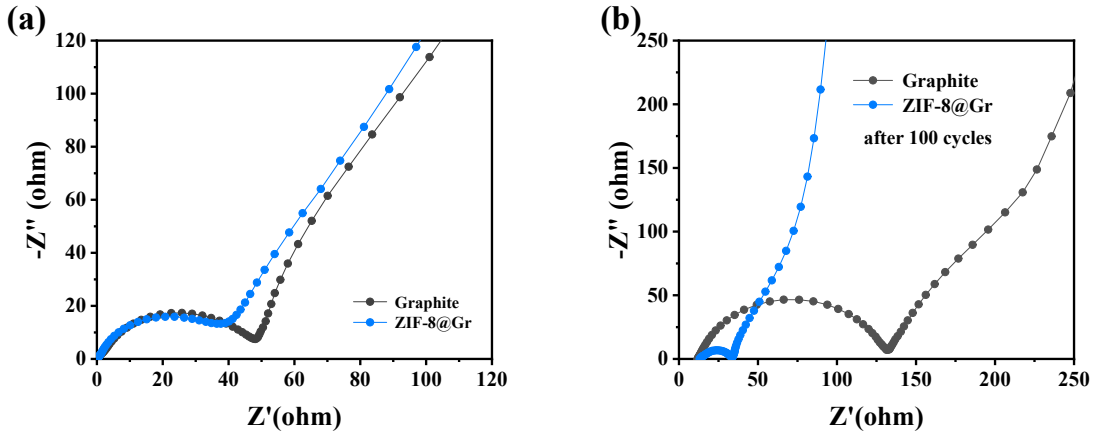

Fig. S7 EIS spectra (a) the pristine electrodes and (b) after 100 times charging and discharging.

Table S1. The sodium storage performance of ZIF-8@Gr and other graphite materials in the literature

Anode	*ICE %*	*Rate performance mA h g^{-1}/(A g^{-1})*	*cycling stability A g^{-1}/(number)*	*Ref.*
ZIF-8@Gr	**86%**	**117 (0.05) 90 (20)**	**10 (20000)**	**This work**
Graphite	**58%**	**83 (2) 45 (35)**	**15 (5000)**	**1**
Expanded graphite	**66%**	**120 (0.12) 78.2 (0.24)**	**0.12 (100)**	**2**
FGC2200	**93%**	**129 (0.1) 106 (10)**	**10 (8000)**	**3**
MCGF	**92.5%**	**107 (0.1) 88.4 (1.6)**	**0.4 (800)**	**4**
rGO	**24%**	**176.4(0.08) 95.6(1)**	**0.04(1000)**	**5**
Graphene foam	**54%**	**150(1) 100(30)**	**12(8000)**	**6**
Graphite	**87%**	**111(0.1) 102(10)**	**0.2(6000)**	**7**

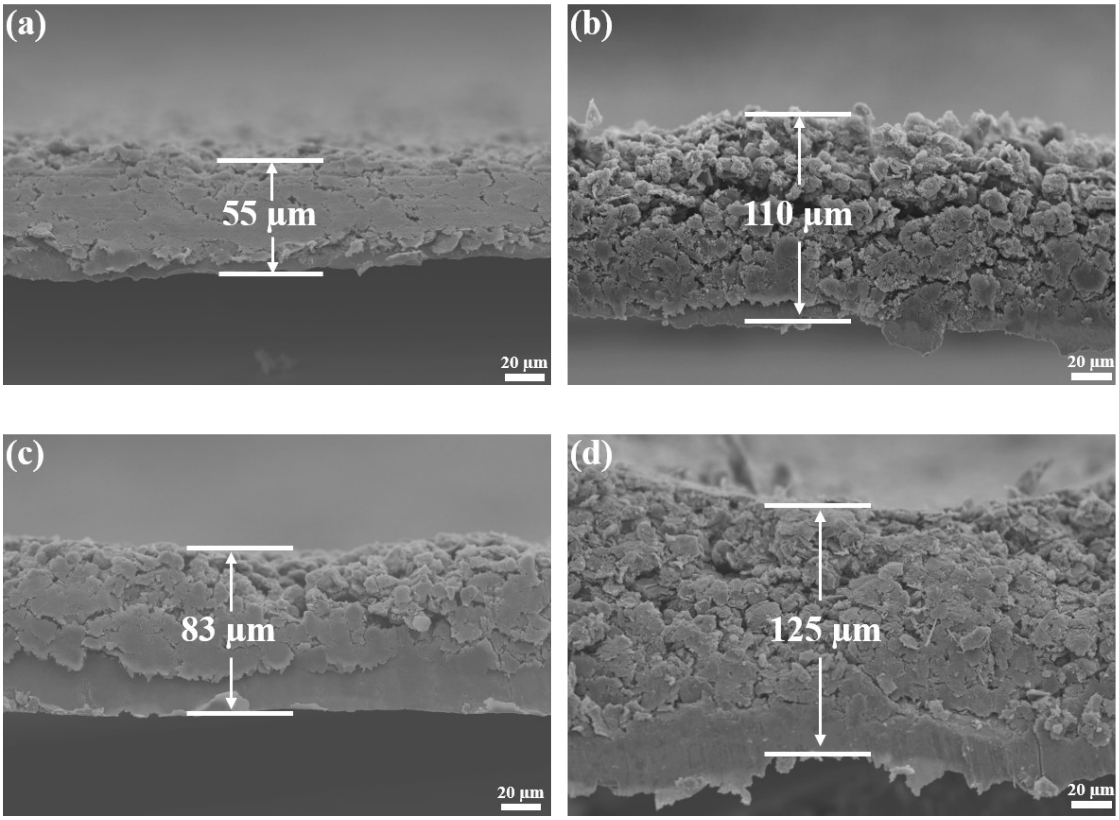

Fig. S8 SEM images of (a-b) the graphite electrode and (c-d) the ZIF-8@Gr electrode after the first discharge.

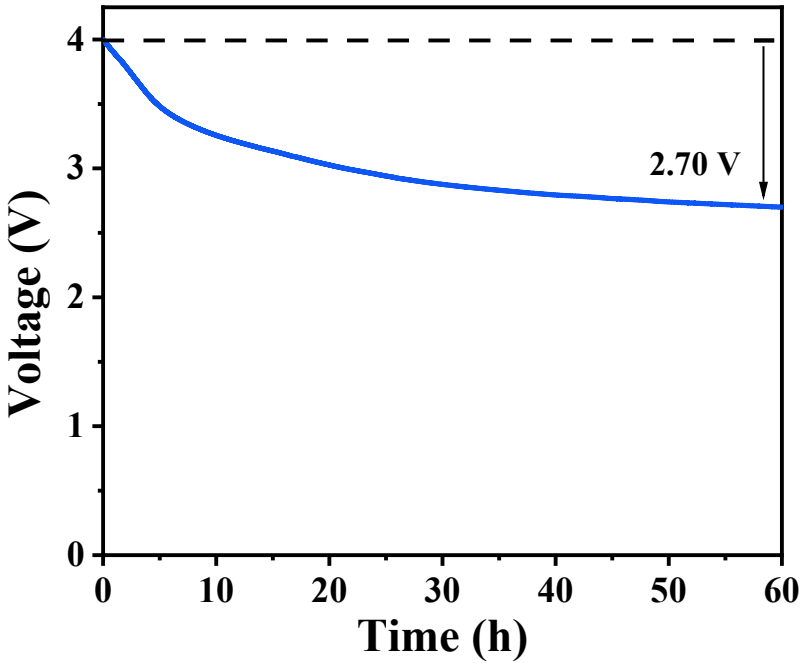

Fig. S9 The relationship between open-circuit voltage and time.

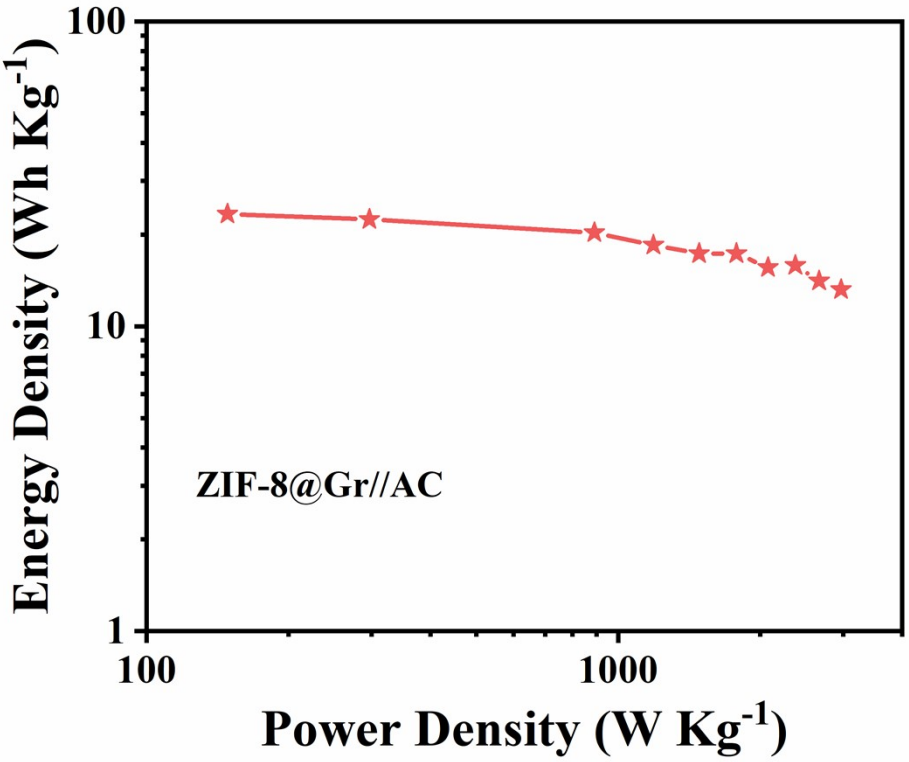

Fig. S10 Ragone plot of the total mass of both electrodes.

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