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Electronic Supplementary Material

A synergistic graphene–hard carbon shell enables fast-charging graphite anode

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Experimental

Chemicals and materials

Graphite, hard carbon, graphene and binder pitch were purchased from Guangdong Canrd New Energy Technology Co., Ltd. All chemical reagents were used as received without further purification.

Synthesis of G, G/Gr@C, G/HC@C and G/Gr/HC@C

Here, G, Gr, and HC represent pristine graphite, graphene, and hard carbon, respectively. Typically, 9.8 g of G, 0.2 g of Gr, and 1.0 g of pitch were homogeneously mixed in a high-shear mixer. The mixture was then transferred to a tube furnace and heated under a nitrogen atmosphere at a ramp rate of 5 °C·min^{-1} to 800 °C, followed by a dwell time of 1 h to obtain G/Gr@C. Similarly, 9.8 g of G, 0.2 g of HC, and 1.0 g of pitch were mixed under the same conditions and subjected to identical thermal treatment to produce G/HC@C. To prepare G/Gr/HC@C, 9.3 g of G, 0.5 g of HC, 0.2 g of Gr, and 1.0 g of pitch were uniformly mixed in a high-shear mixer and subsequently heated under a nitrogen atmosphere at 5 °C·min^{-1} to 800 °C, with a holding time of 1 h.

Materials characterizations

The phase composition and crystal structure of the samples were analyzed using an X-ray diffractometer (XRD, PANalytical Empyrean) equipped with Cu Kα radiation (λ = 1.5418 Å) over a 2θ range of 10° to 90°. The specific surface areas of the as-prepared materials were measured with a nitrogen adsorption analyzer (JW-BK222, Beijing JWGB) and calculated using the Brunauer–Emmett–Teller (BET) method, with N_2 as the adsorbate. Raman spectra were collected at room temperature on a dispersive Raman microscope (HORIBA XploRA PLUS) using a 532 nm excitation laser. The carbon content was determined via thermogravimetric analysis (TGA) on an STA 7200 thermal analysis system (Hitachi) in an air atmosphere, heating from 20 to 900 °C at a rate of 10 °C·min^{-1}. The morphology of the samples and electrodes after cycling was examined using field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010) and field-emission transmission electron microscopy (FE-TEM, Tecnai G2 F20).

Electrochemical measurements

The electrochemical performance was evaluated using CR2032 coin-type half-cells. The working electrodes were prepared by homogenously mixing the active material, acetylene black, and a lithium polyacrylate binder (4 wt.% aqueous solution) in ultrapure water at a mass ratio of 92:5:3. The resulting slurry was uniformly coated onto copper foil and dried under vacuum at 60 °C for 12 h to form electrode films. These films were subsequently punched into disks with a diameter of 14 mm and weighed. The electrolyte consisted of 1 mol·L^{-1} $LiPF_6$ dissolved in a mixed solvent of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC), with 2 vol.% vinylene carbonate (VC) and 10 vol.% fluoroethylene carbonate (FEC) as additives. Celgard 2500 separators with a diameter of 17 mm were used. In half-cell configurations, lithium metal foils served as counter electrodes. Full cells were assembled using $LiFePO_4$ as the cathode and prelithiated G/Gr/HC@C as the anode. All cell assemblies were carried out in an argon-filled glovebox, where both moisture and oxygen concentrations were maintained below 0.1 ppm. Electrochemical measurements were conducted at room temperature over a voltage range of 1.0–4.2 V for full cells, and the specific capacities were calculated based on the anode mass. Galvanostatic charge–discharge tests, rate capability evaluations, and galvanostatic intermittent titration technique (GITT) measurements were performed using a battery test system (BTS-4008, Neware, Shenzhen, China) over a voltage range of 0.01–2.0 V. For the GITT experiments, a constant current pulse of 100 mA·g^{-1} was applied for 20 min, followed by an open-circuit relaxation period of 20 min. Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range from 0.01 to 10^5 Hz with an amplitude of 10 mV. Cyclic voltammetry (CV) measurements were performed on a CHI760E electrochemical workstation (Chenhua, Shanghai) within the voltage range of 0.01–2.0 V.

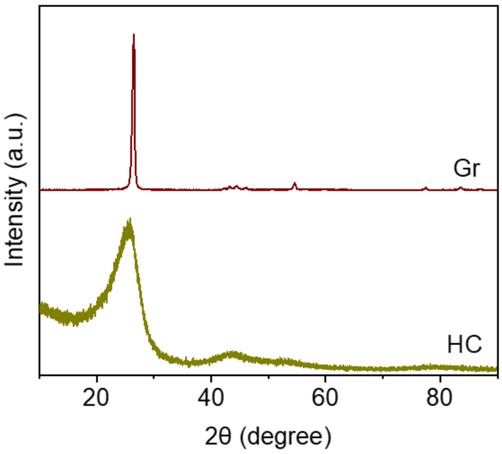

Fig. S1 XRD patterns of HC and Gr.

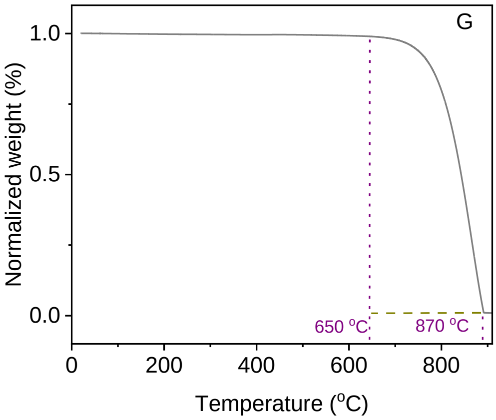

Fig. S2 Thermogravimetric analysis curve of G.

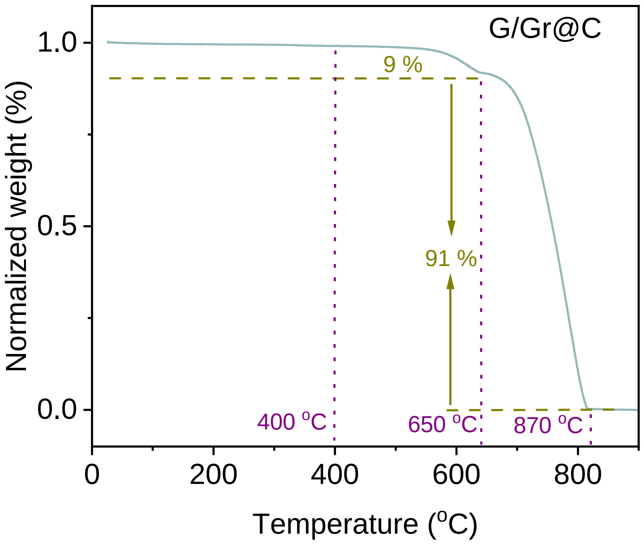

Fig. S3 Thermogravimetric analysis curve of G/Gr@C.

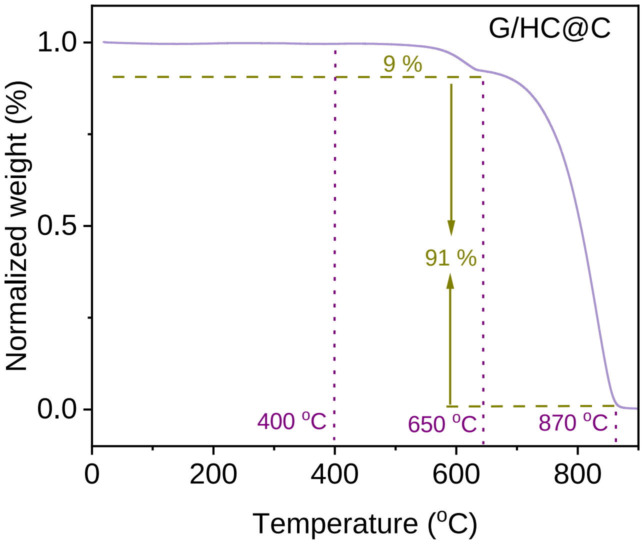

Fig. S4 Thermogravimetric analysis curve of G/HC@C.

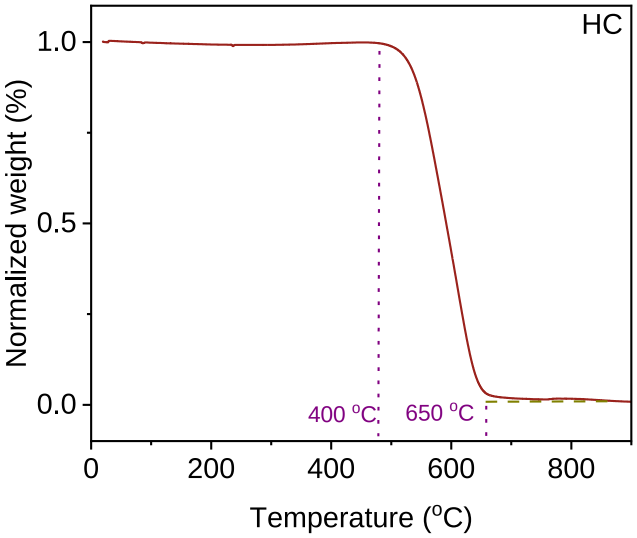

Fig. S5 Thermogravimetric analysis curve of HC.

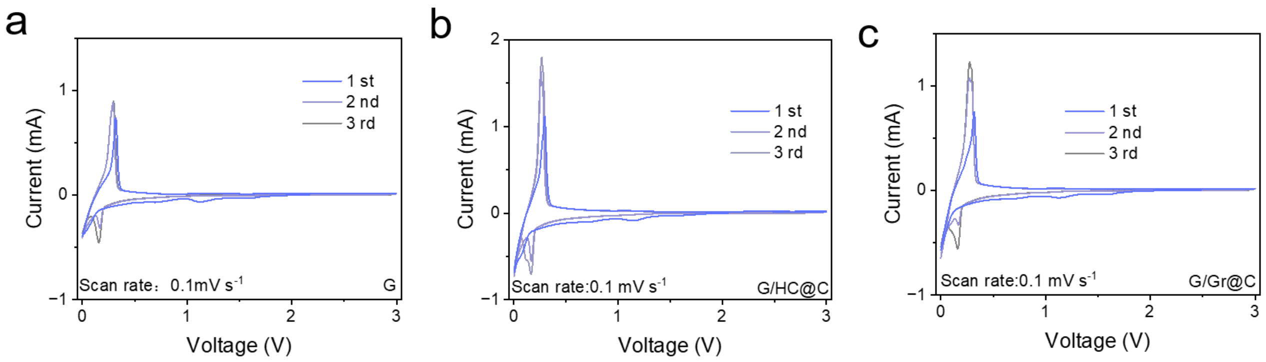

Fig. S6 CV profiles of **(a)** G, **(b)** G/HC@C, and **(c)** G/Gr@C anodes over the initial three cycles.

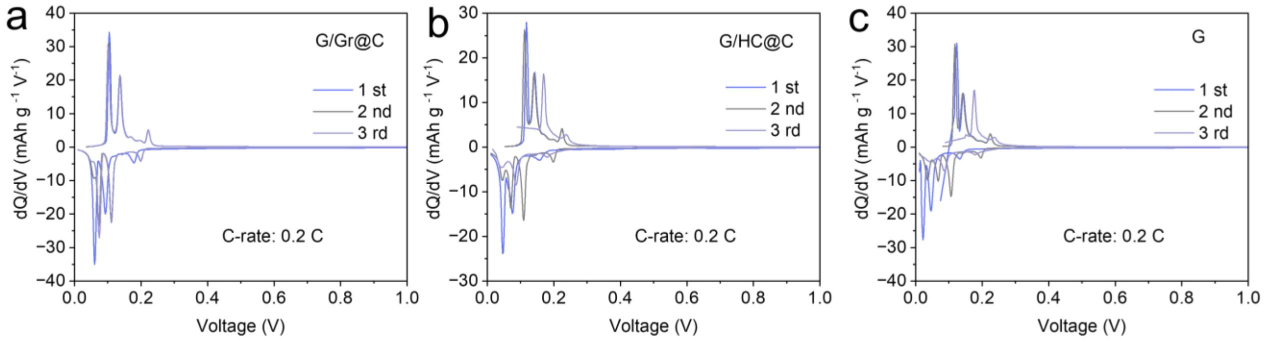

Fig. S7 dQ/dV curves of **(a)** G/Gr@C, **(b)** G/HC@C, and **(c)** G anodes over the initial three cycles.

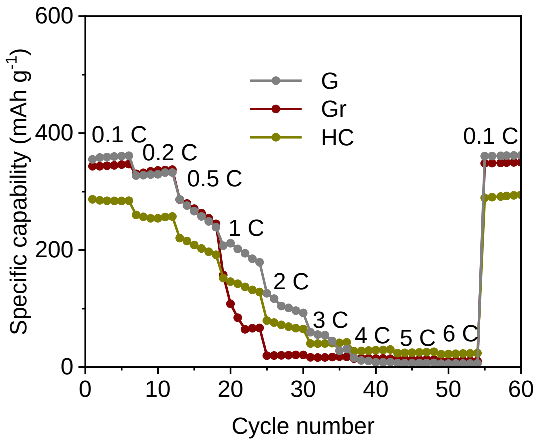

Fig. S8 Rate performances of G, Gr, and HC electrodes.

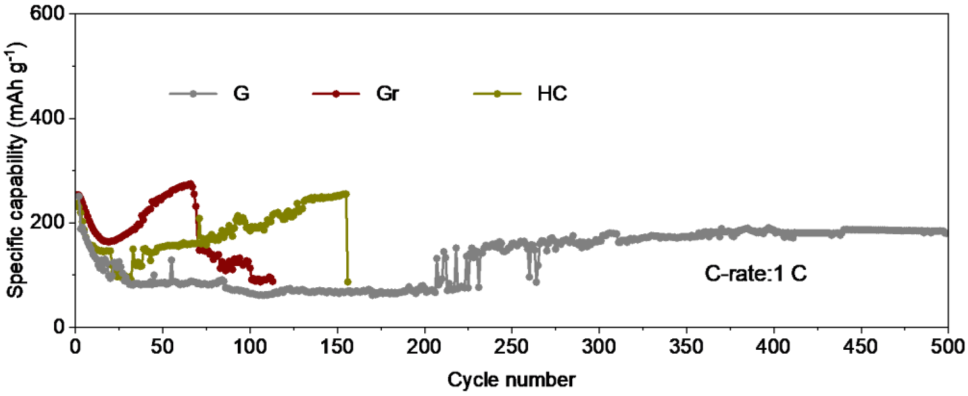

Fig. S9 Long-term cycle performance of G, Gr, and HC electrodes at the C-rate of 1C for 500 cycles.

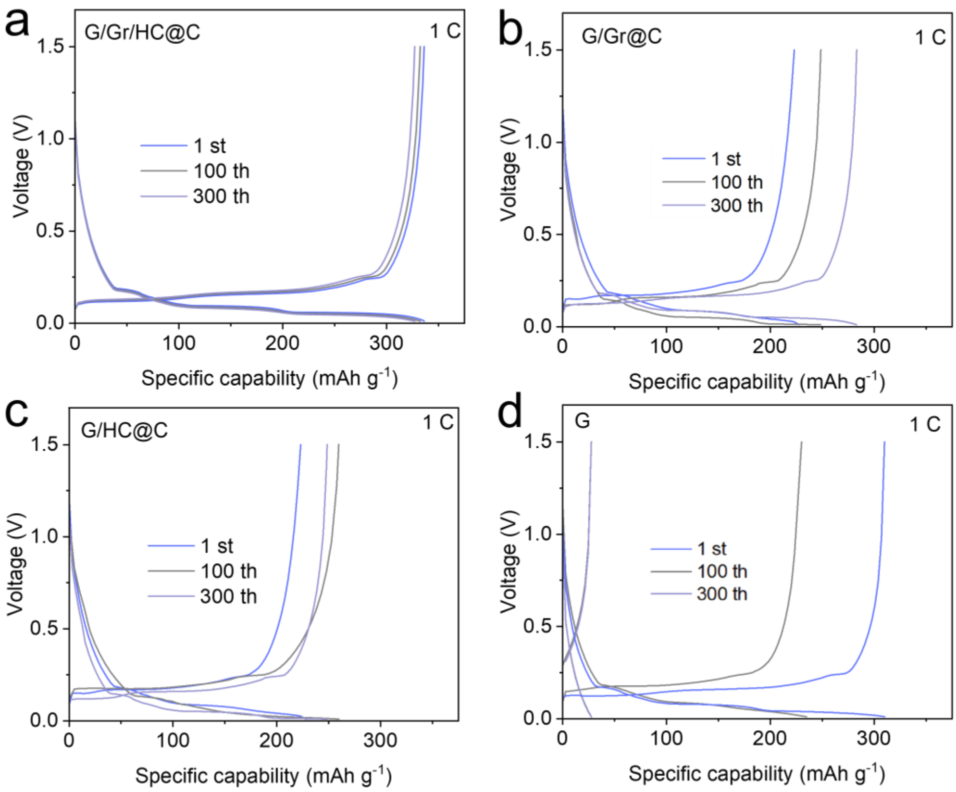

Fig. S10 GCD profiles of **(a)** G/Gr/HC@C, **(b)** G/Gr@C, **(c)** G/HC@C, and **(d)** G electrodes at 1C.

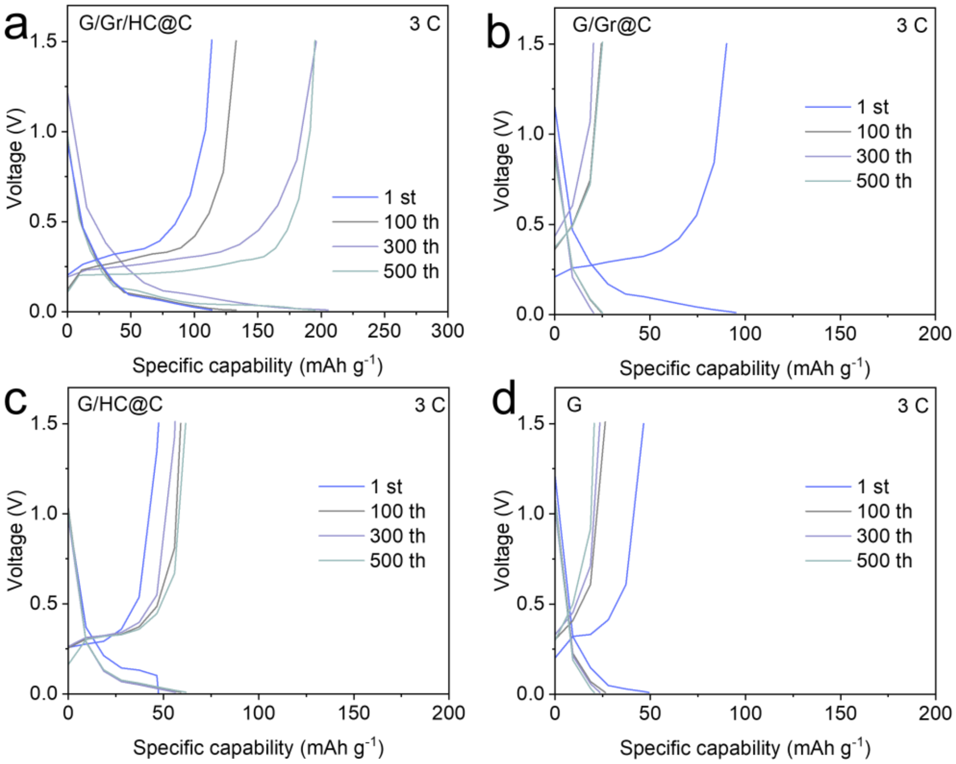

Fig. S11 GCD profiles of **(a)** G/Gr/HC@C, **(b)** G/Gr@C, **(c)** G/HC@C, and **(d)** G electrodes at 3C.