Core–Shell Structured Carbon @ Tin Sulfide @Hard Carbon Spheres as High-Performance Anode for Low Voltage Sodium-Ion Battery

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Materials and Methods

Materials. Thioacetamide (Sigma), Stannous chloride dihydrate (Sigma), Anhydrous ethanol (Shanghai Hushi)

Synthesis of Sn_xS_y@HCS

SnS nanoarrays on hard carbon spheres (Sn_xS_y@HCS) were synthesized via a chemical bath deposition (CBD) method. In a typical synthesis, 0.05 mol of $SnCl_2 \cdot 2H_2O$ and 0.15 mol of thioacetamide were dissolved in 240 mL of nitrogen-saturated ethanol within a glass container. The mixture was sonicated for 5 min to ensure complete dissolution, resulting in a clear solution. Subsequently, 2 grams of the hard carbon spheres (HCS) were introduced into the solution. The deposition process was conducted at 40 °C for 2 h, during which the initially transparent solution gradually turned opaque and brown. Upon completion, the reaction mixture was allowed to cool to room temperature (20–25°C), and the resulting Sn_xS_y@HCS was thoroughly washed with deionized water and ethanol. The final product was dried under vacuum at 60 °C.

Synthesis of C@Sn_xS_y@HCS

To prepare C@Sn_xS_y@HCS, the as-synthesized Sn_xS_y@HCS was immersed in 80 mL of a 0.1 M aqueous glucose solution at ambient conditions for 6 h. Without any further washing, the material was dried at room temperature and subsequently annealed at 300 °C for 1 h under an argon atmosphere, yielding the C@Sn_xS_y@HCS composite.

Materials Characterizations

The morphology of samples was characterized using a Scanning Electron Microscope (SEM) (Zeiss Sigma FESEM). X-ray diffraction (XRD) (Rigaku SmartLab 9 kW, tube voltage: 40 kV, current: 200 mA) with Cu Kα radiation (λ=0.15418 nm) was used as a structure characterize method. The specific surface area was detected through Micromeritics 3Flex# 350/00002/00. The molecular vibration and the rotation information of samples was qualitatively analyzed by confocal Raman microscopy (Thermo Fisher Scientific DXR3) with a 532 nm laser excitation. The elements of the electrode were characterized using X-ray photoelectron spectroscopy (XPS, ESCALAB 250i) under nitrogen protection.

Electrochemical Measurement

The HCS, Sn_xS_y@HCS and C@Sn_xS_y@HCS powders were mixed with conductive carbon black (EC 600JD) and polyvinylidene fluoride (PVDF) in a mass ratio of 8:1:1, followed by drying in a vacuum oven at 80 °C for 12 hours. The electrodes were then assembled into CR2025-type coin cells in an argon-filled glove box, using 160 μL of 1 mol L^{-1} $NaPF_6$ in diglyme as the electrolyte, Whatman GF/D glass-fiber separators, and 16 mm sodium sheets with aluminum foil as the current collector.

Charge-discharge tests and galvanostatic intermittent titration technique (GITT) measurements were performed using a NEWARE BTS4000 system at 30 °C, within a potential window of 0.01-2.5 V. The sodium-ion diffusivity coefficient (D_{Na^+}) was calculated based on a simplified form of Fick's second law:

$$D^{GITT} = \frac{4}{\Pi\tau}\left(\frac{m_B V_m}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_t}\right)^2$$

where τ is the pulse duration (s), m_B is the active mass of anodes (g), M_B is the molar mass of hard carbon (g mol^{-1}), V_m is the molar volume (cm^3 mol^{-1}), and S is the active

surface area of the anodes (m^2 g^{-1}). Additionally, ΔEs 10 min) and $\Delta E\tau$ (180 min) can be obtained from the GCD of GITT curves. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements, with a frequency range from 0.01 Hz to 100,000 Hz, were conducted using a CHI660E electrochemical workstation. The current densities for all electrochemical tests were normalized based on the active mass of the anodes.

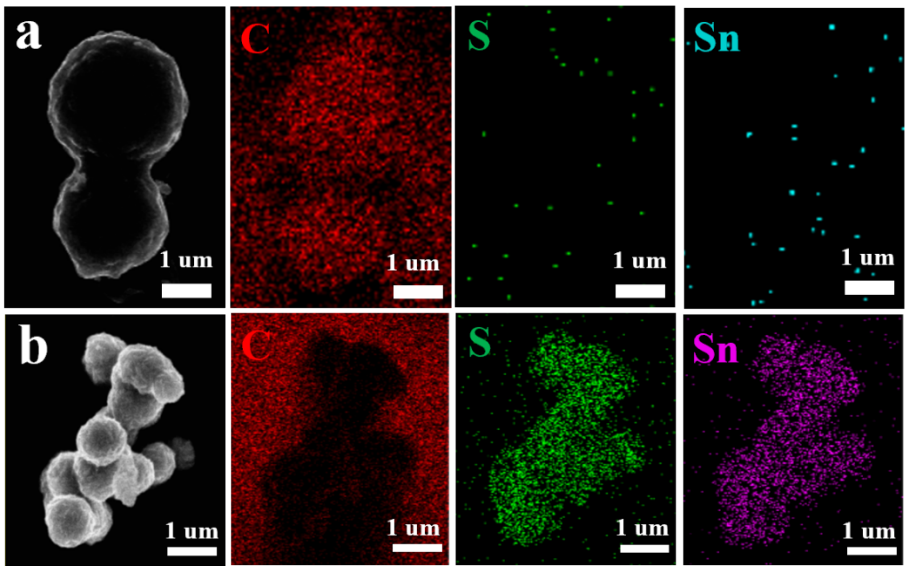

Figure S1 EDS analysis of a) HCS and b) Sn_xS_y@HCS.

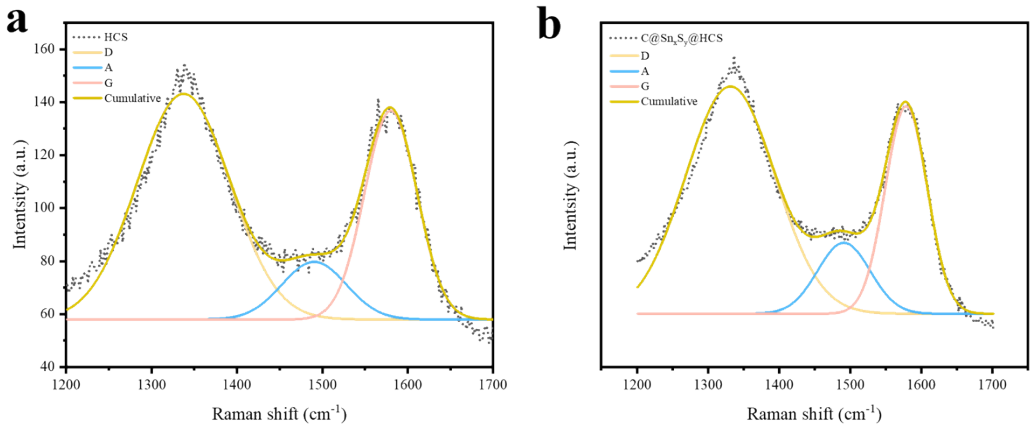

Figure S2 fitting of Raman spectrum. a) HCS. b) C@Sn_xS_y@HCS.

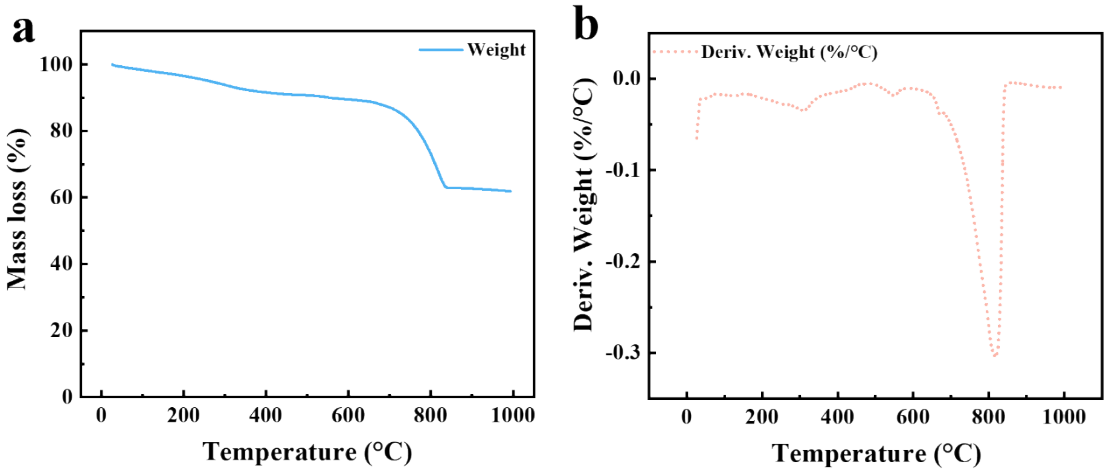

Figure S3 a) TGA and b) DTG curves of C@Sn_xS_y@HCS

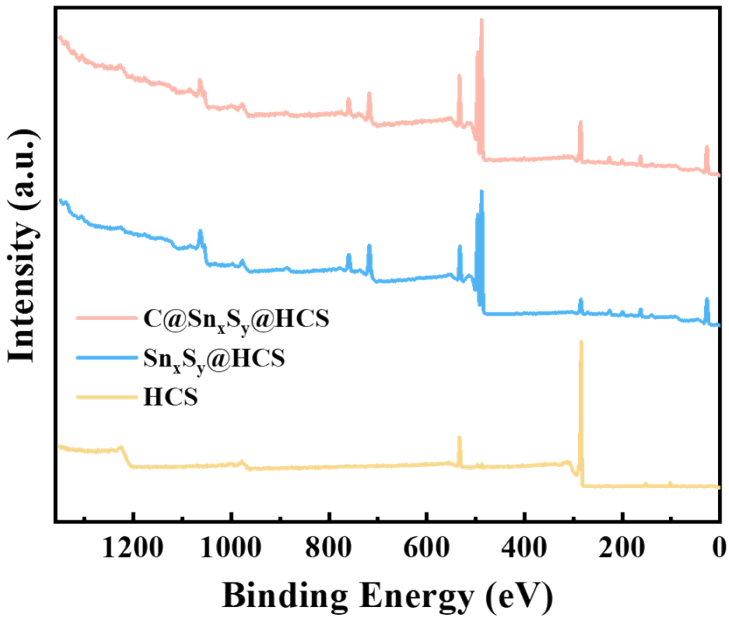

Figure S4 XPS full spectrum.

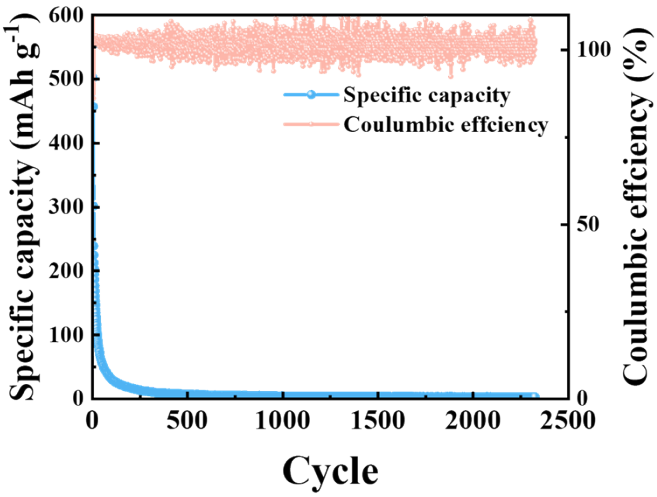

Figure S5 Cycle performance of C@Sn_xS_y@HCS in 1 M $NaClO_4$ in EC:PC:DMC = 1:1:1 electrolyte.

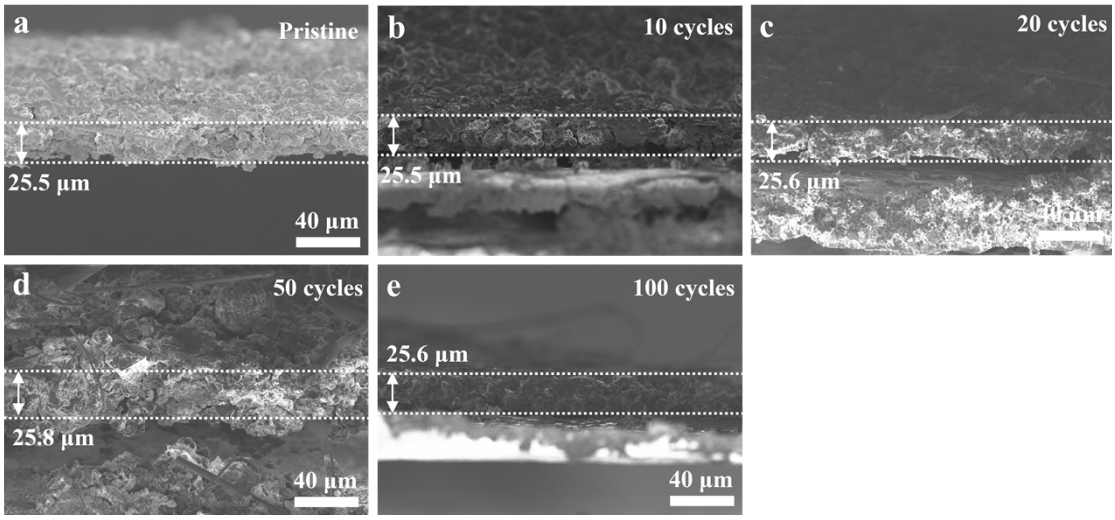

Figure S6 The thickness evolution of the hard carbon anode.

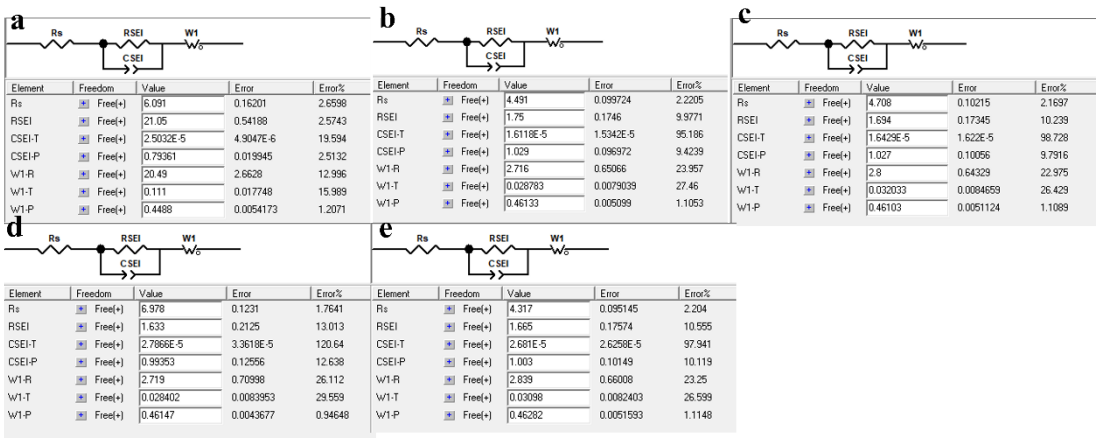

Figure S7 Fitting results of Nyquist plots, and values of R_{SEI} and R_{ct}. a) Pristine. b) 10 cycles. c) 20 cycles. d) 50 cycles. e) 100 cycles.