Supporting Information

The structural changes and sodium storage of carbon phase in the cobalt sulfides/carbon composites

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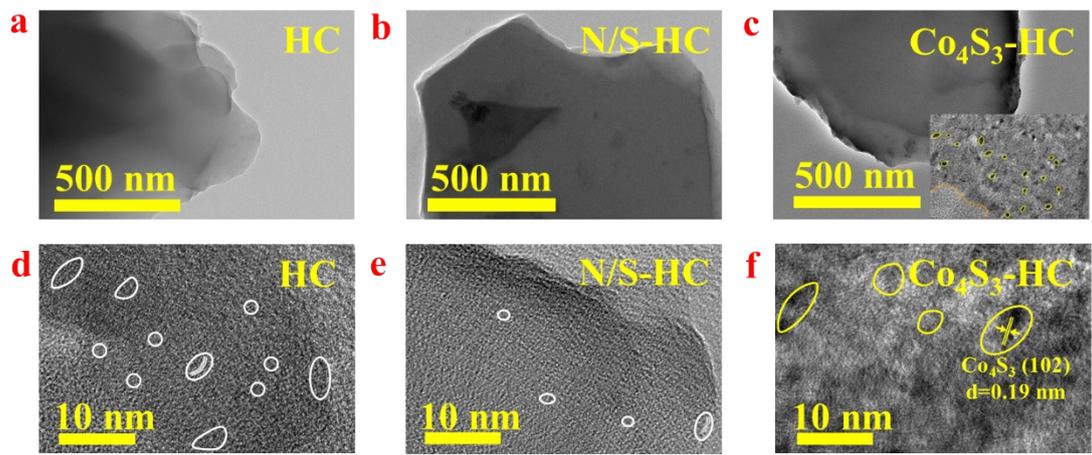
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Fig. S1. TEM images of (a) HC, (b) N/S-HC, (c) Co$_4$S$_3$-HC. HRTEM images of (d) HC, (e) N/S-HC, (f) Co$_4$S$_3$-HC.
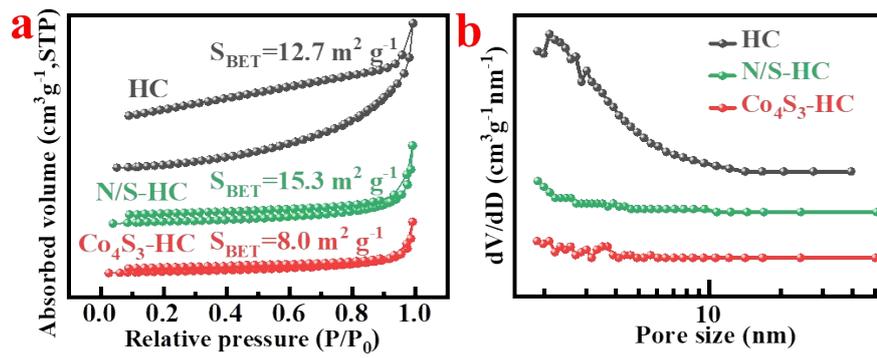
Fig. S2. (a) N_2 adsorption–desorption isothermal curves and (b) pore size distribution plots for HC, N/S-HC and Co_4S_3-HC.
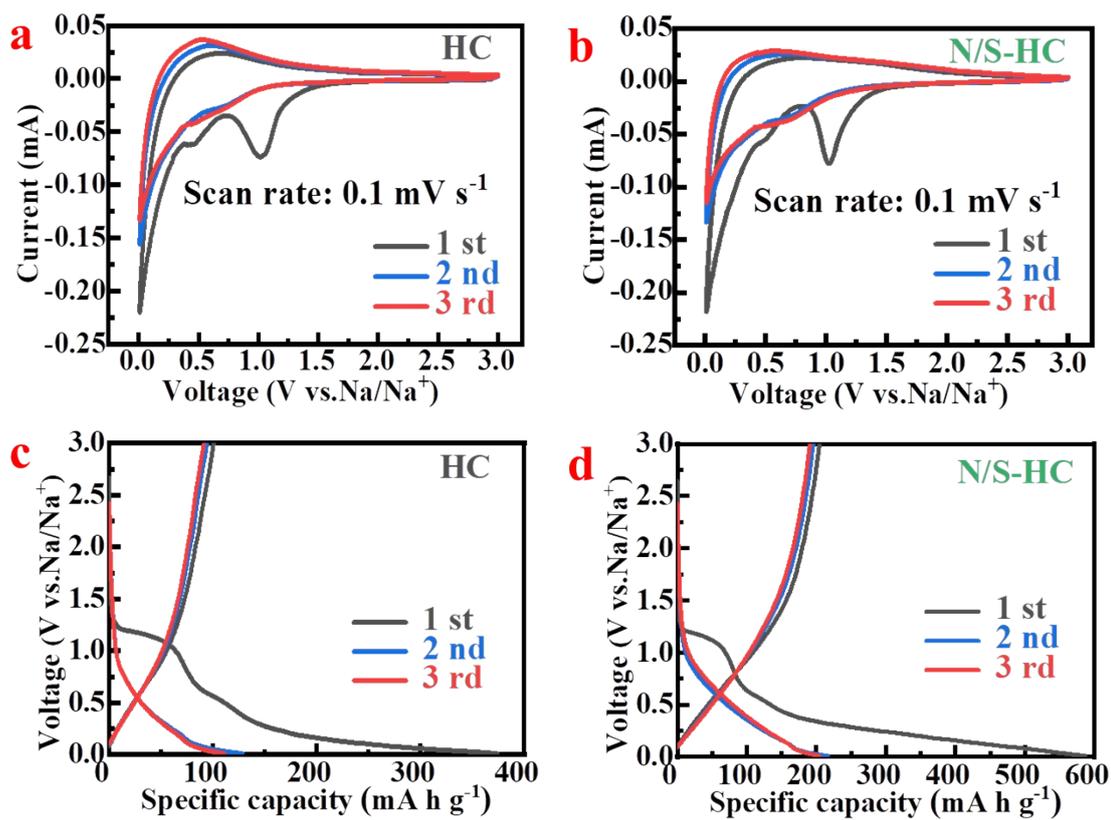
Fig. S3. The initial three CV curves at 0.1 mV s^{-1} of (a) HC and (b) N/S-HC and the galvanostatic discharge/charge curves at 0.05 A g^{-1} of (c) HC and (d) N/S-HC.
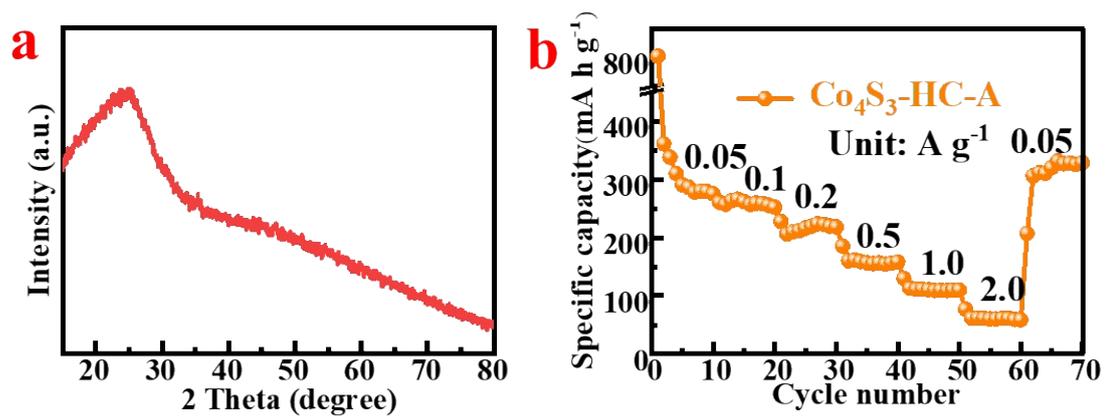
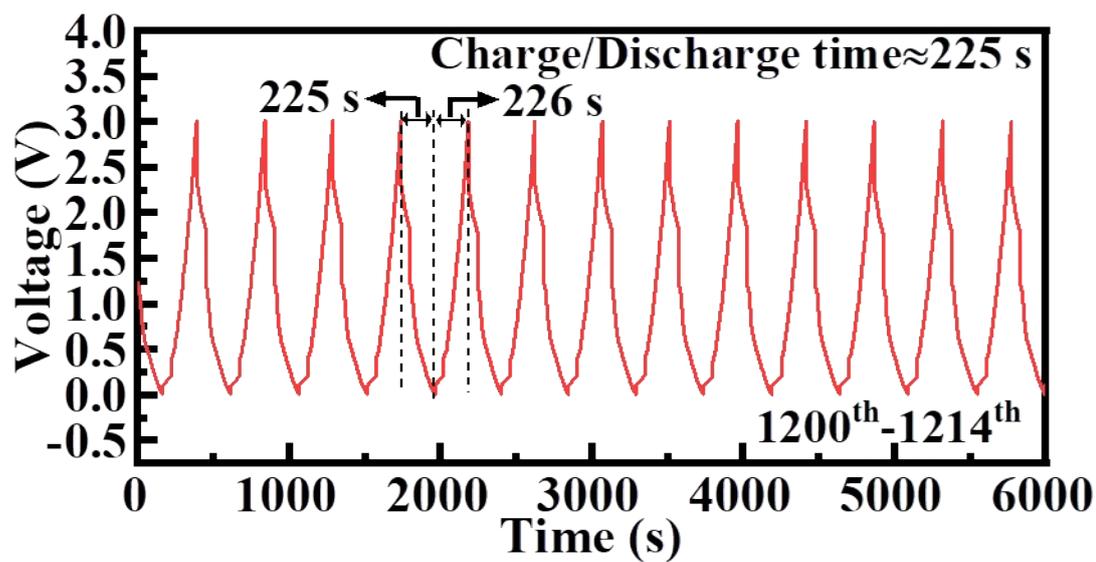**Fig. S4.** (a)XRD patterns and (b) rate performances of Co_4S_3-HC-A.

Fig. S5. Discharge/charge curves of the 1200th-1214th cycles at 2.0 A g^{-1}.
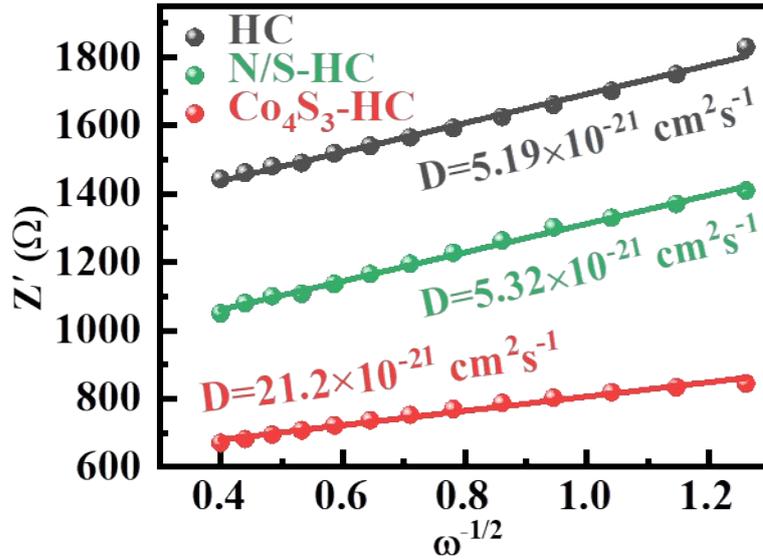
Fig. S6. Plots of real part of impedance (Z′) in the Warburg region as a function of inverse square root of angular frequency ($\omega^{-1/2}$) for all samples.

According to the following Eq. (1), the Warburg coefficient (σ_W) can be obtained from the slope of Fig. S4 plot.

$$Z' = R_s + R_{ct} + \sigma_W \omega^{-1/2} \tag{1}$$

Then, the Na$^+$ diffusion coefficient (D_{Na^+}) can be calculated from Eq. (2)

$$D_{Na^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_0^2 \sigma_\omega^2} \tag{2}$$

Where R is gas constant; T is temperature; A is contact area; n is number of electrons transfer per mole; F is Faraday constant; C_0 is concentration of Na$^+$ in the electrode; σ_W is Warburg coefficient.

Table. 1 The impedance, the Warburg coefficient and Na$^+$ diffusion coefficient of electrodes.

Samples	R_{ct} (Ω)	σ_W (Ω cm^2 s$^{-1/2}$)	D_{Na^+} (cm^2 s^{-1})
HC	988	424.46	5.19×10^{-21}
N/S-HC	672	419.29	5.32×10^{-21}

| Co$_4$S$_3$-HC | 573 | 210.05 | 21.2×10^{-21} |

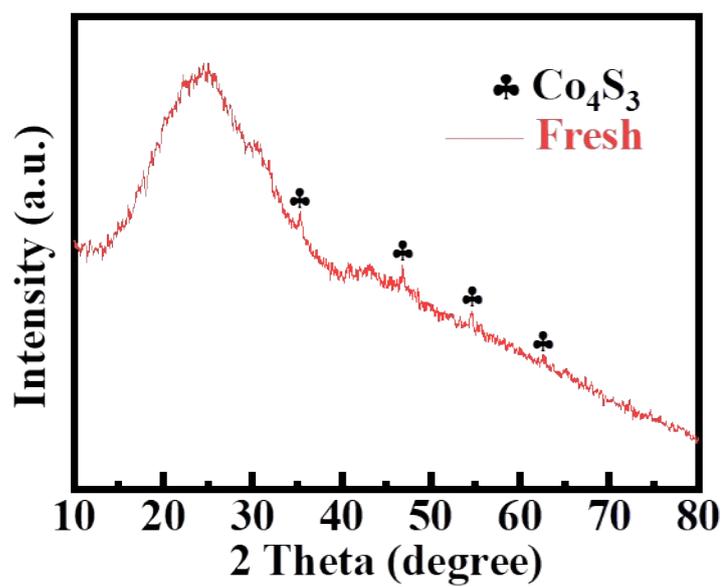**Fig. S7.** *Ex*-situ XRD pattern of the electrode material from the fresh cells.

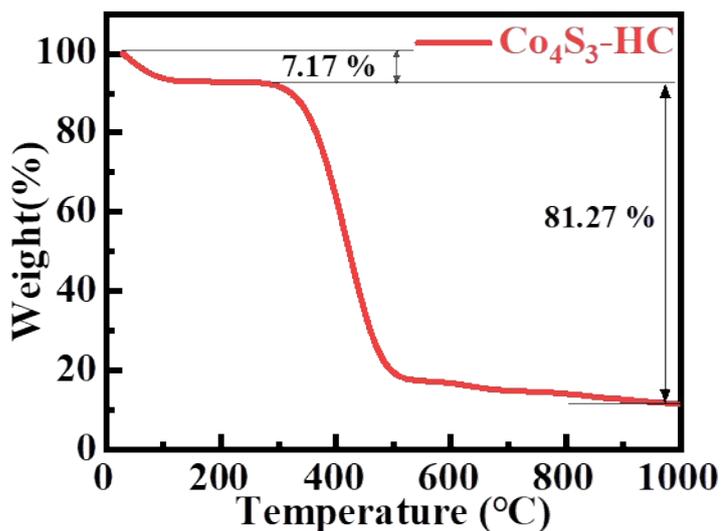**Fig. S8.** TG curve of Co_4S_3-HC in air.

Considering that the combustion product is Co_3O_4, and Co does not volatilize within the studied temperature range. Based on the amount of Co, we calculate that the content of Co_4S_3 in the Co_4S_3-HC is 11.9 wt%. And the Co_4S_3-HC powder, conductive carbon black and agglomerant polyvinylidene fluoride at the mass ratio of 7:2:1 are mixed and ground. The proportion of Co_4S_3 in electrode is 8.3 wt%.