Supporting Information

Multi-layered composite assembly of Bi nanospheres anchored on nitrogen-doped carbon nanosheets for ultrastable sodium storage

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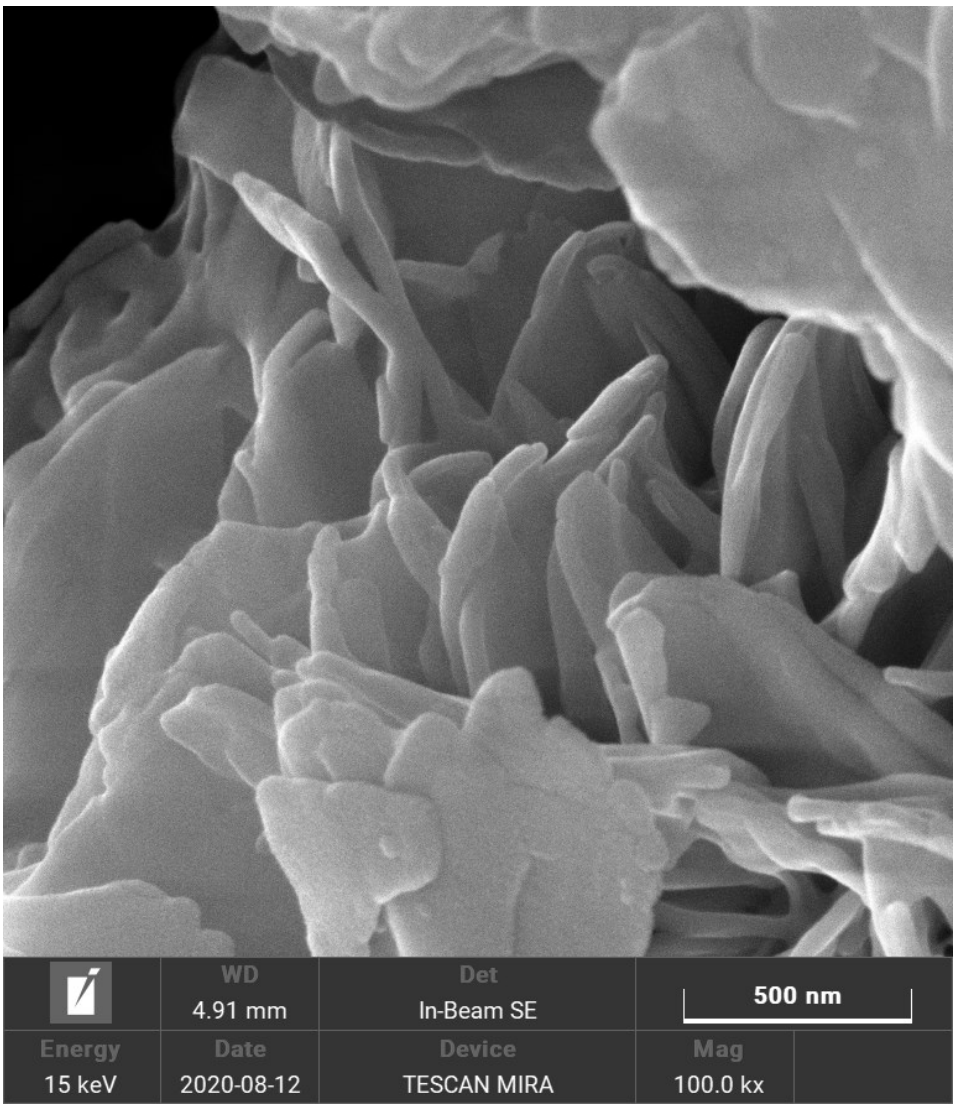

Figure S1. The SEM images of the precursor of ML-Bi@NCSs.

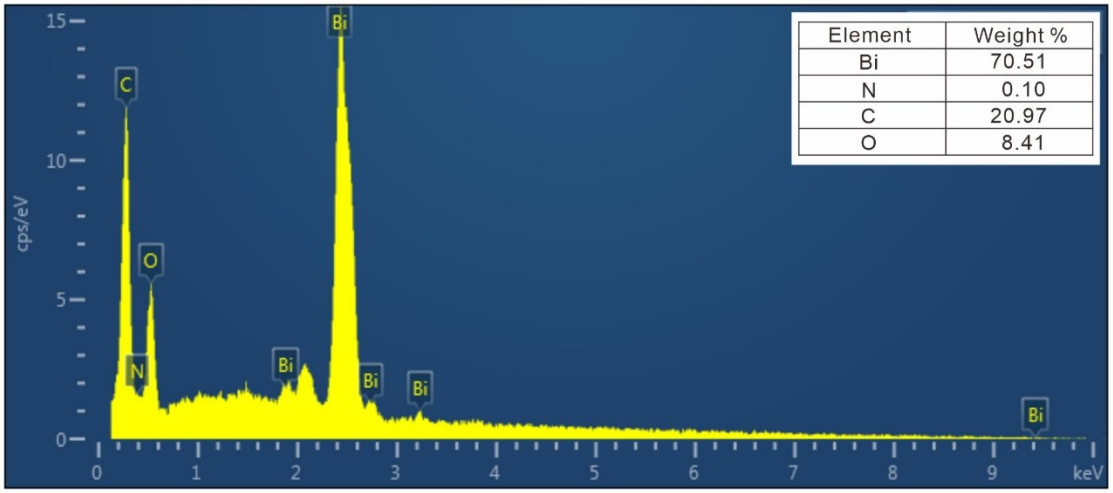

Figure S2. EDS patterns from SEM of ML-Bi@NCSs.

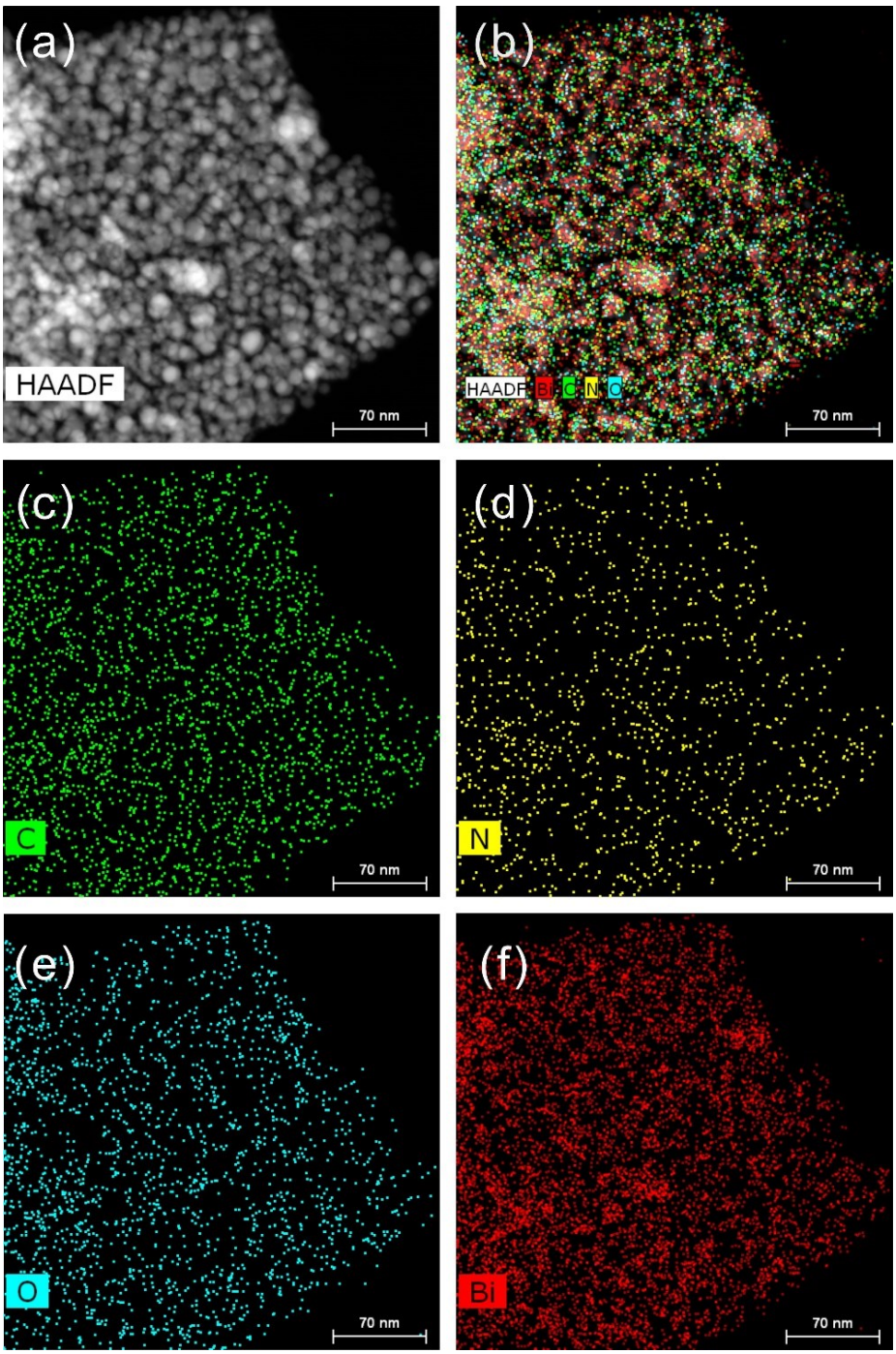

Figure S3. EDS mapping images (a-f) of from TEM of single layered ML-Bi@NCSs.

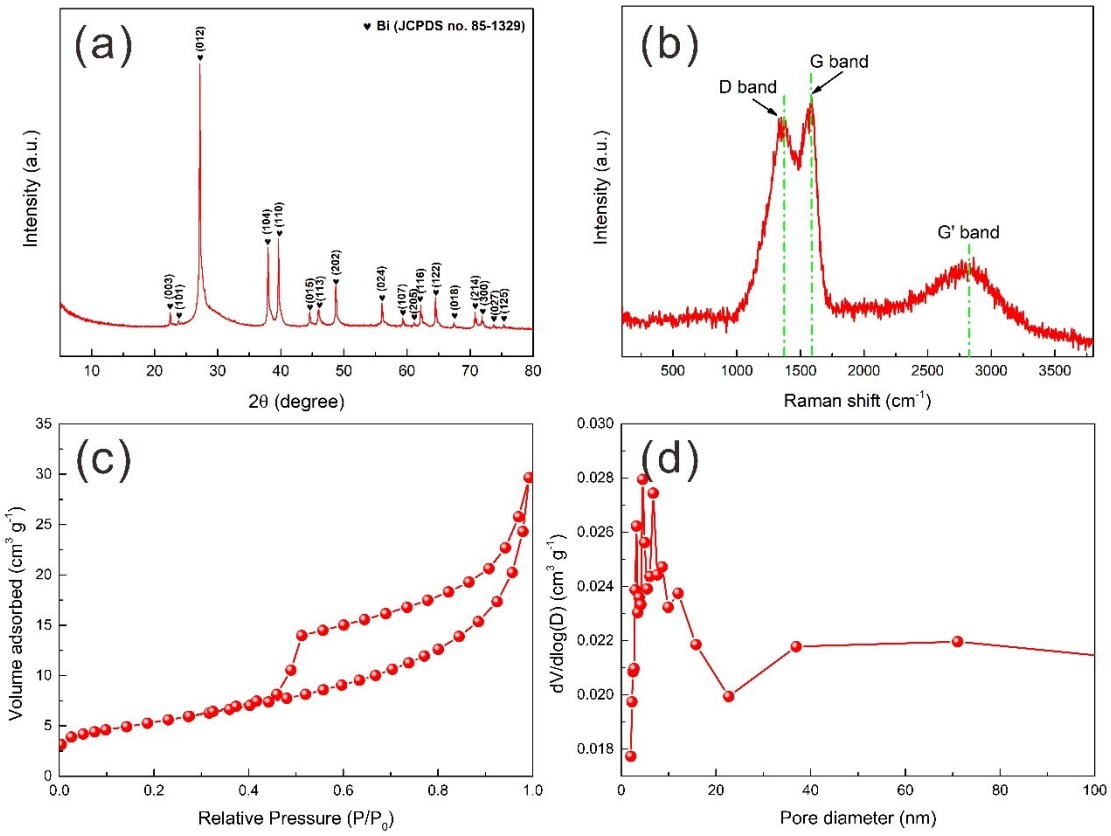

Figure S4. (a) XRD patterns and (b) Raman spectroscopy of ML-Bi@NCSs; The N2 adsorption-desorption isotherms and the pore size distribution curve of Bi NPs/NC (c, d) and ML-Bi@NCSs (e, f) sample.

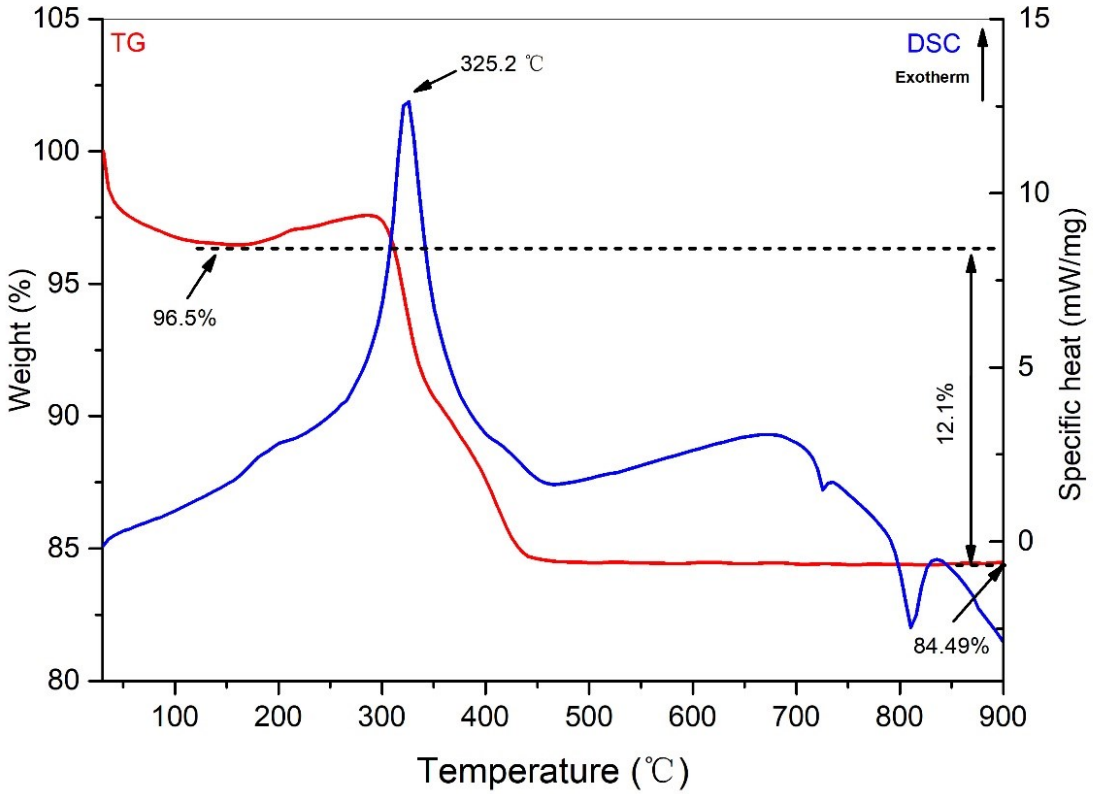

Figure S5. TGA and DSC curves of ML-Bi@NCSs in air (30-900 ℃).

The calculation process of weight ratio of N and C content:

$$N\ and\ C\ (wt\%) = (1 - \frac{2 \times W_{Bi}}{W_{Bi_2O_3}} \times \frac{w_2}{w_1}) \times 100 \quad (1)$$

Where W_{Bi}, $W_{Bi_2O_3}$, w_1 and w_2 are the molecular mass of Bi, the molecular mass of Bi_2O_3, the inital weight ratio of ML-Bi@NCSs (%) about 100℃ and the final weight ratio of Bi_2O_3 (%) at 900℃, respectively.

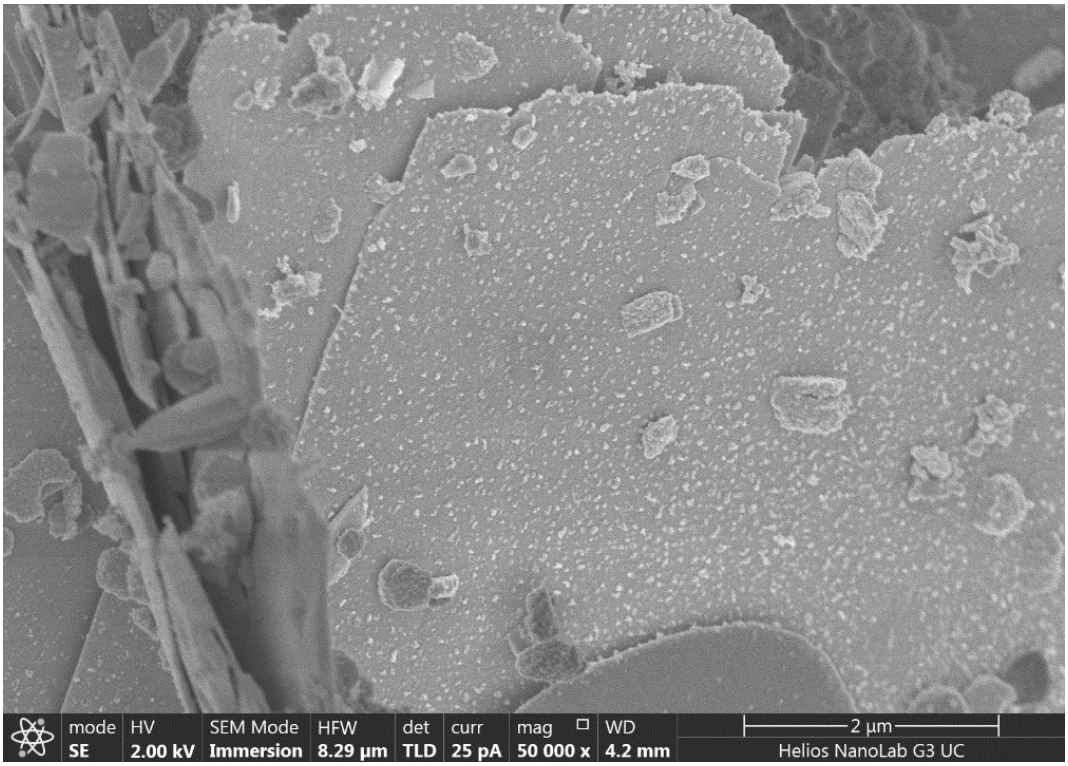

Figure S6. The SEM images of comparative sample of Bi NPs/NC.

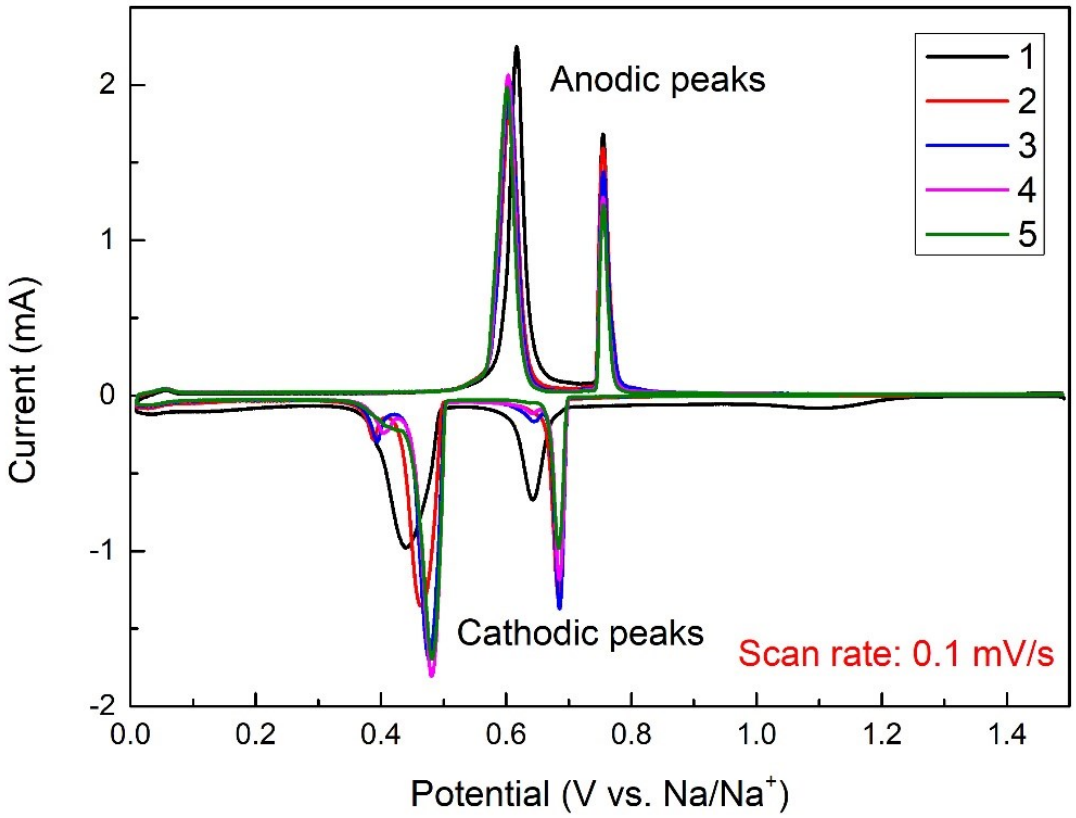

Figure S7. The CV curves at scan rate of 0.1 mV s^{-1} between 0.1 and 1.5 V of the Bi NPs/NC electrode.

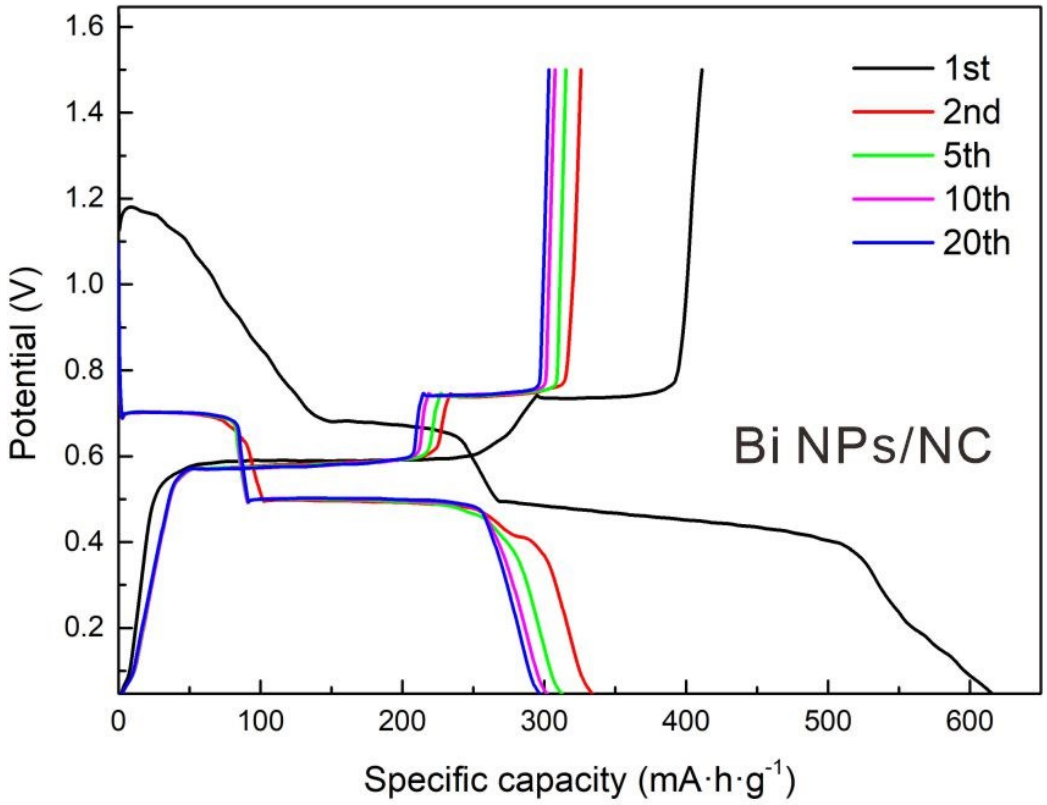

Figure S8. Galvanostatic charge-discharge curves at current density of 0.2A g^{-1} of the Bi NPs/NC electrode.

The analytical process of reaction kinetics mode:

The reaction kinetics mode was analyzed by the following equation and finite deformation:[1, 2]

$$I = av^b \tag{2}$$

$$\log(I) = b\log(v) + \log(a) \tag{3}$$

Where I and v are the peak current (mA) and sweep rate (mV s^{-1}), respectively. b and a are two parameters.

The detailed calculation process of contribution ratios of surface capacitive behavior:

The contribution ratios of surface capacitive behavior were estimated with the following equation and finite deformation:[2, 3]

$$I(V) = k_1 v + k_2 v^{0.5} \tag{4}$$

$$I(V)/v^{0.5} = k_1 v^{0.5} + k_2 \tag{5}$$

Where I, V and v are the current (mA), corresponding voltage (mV) and sweep rate (mV s^{-1}), respectively. k_1 and k_2 are constants, which can be calculated by current values at each given voltage on the CV curves and different sweep rate after linear fitting (Equation S4). $k_1 v$ and $k_2 v^{0.5}$ in Equation S3 are corresponding to the contribution of the surface capacitive behavior and diffusion-controlled process.

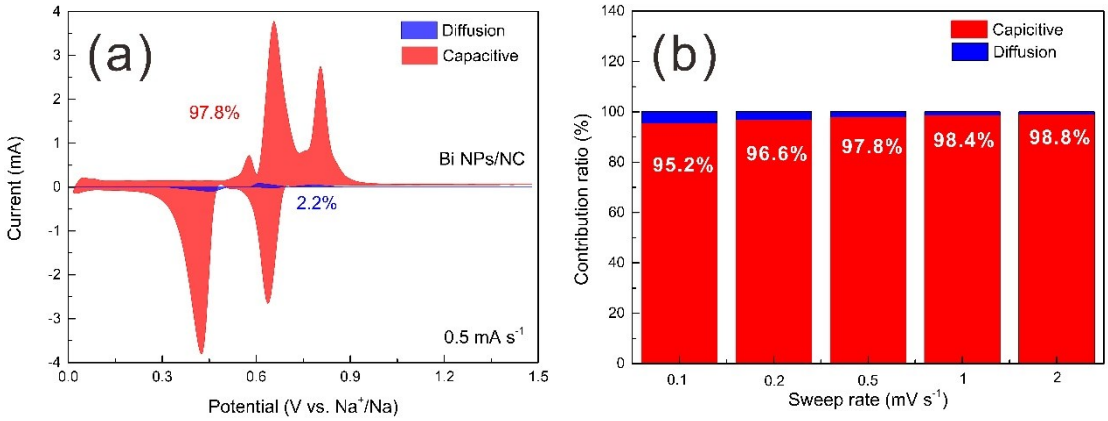

Figure S9 (a) Capacitive contribution of Bi NPs/NC electrode at the sweep rate of 0.5 mV s^{-1}; (b) Contribution ratio of capacitive behavior of Bi NPs/NC electrode at different sweep rate.

The detailed calculation process of the diffusion coefficients (D_{Na^+}) by CV measurements:

The diffusion coefficients (D_{Na^+}) were calculated by CV measurements based on Randles-Sevcik equation:[4-6]

$$I_p = 2.69 \times 10^5 n^{1.5} A C_0 D_{Na^+}^{0.5} v^{0.5} \quad (6)$$

Where I_p is the peak current (A), n is the number of electrons, A is the electrode surface area (cm^2), C_0 is the ion concentration of the electrolyte on the surface of the electrode (mol cm^{-3}), v is the sweep rate (V s^{-1}), D_{Na^+} is the diffusion coefficient (cm^2 s^{-1}).

The detailed calculation process of the diffusion coefficients ($D_{Na^+}^{GITT}$) in GITT:

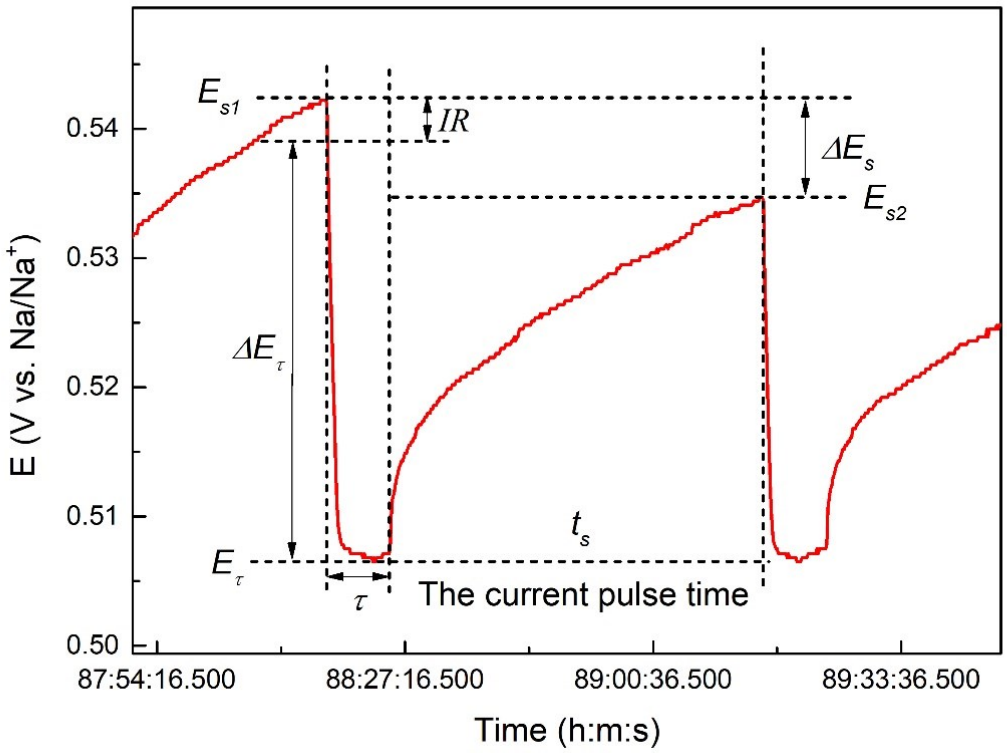

Figure S10 Potential vs. time curves of ML-Bi@NCSs electrode for a single GITT during discharge process.

The diffusion coefficients ($D_{Na^+}^{GITT}$) in galvanostatic intermittent titration technique (GITT) were calculated based on the following equation:[7, 8]

$$D_{Na^+}^{GITT} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad (7)$$

where τ is the constant current pulse time (s), m_B is the mass (g), V_M is the molar volume ($cm^3\ mol^{-1}$), M_B is the molar mass ($g\ mol^{-1}$), S is the contact area between the electrode and electrolyte (cm^2); ΔE_s is the steady-state potential change (V) by the current pulse, ΔE_T is the potential change (V) during the constant current pulse (s) after eliminating the *IR* drop (Figure S10).

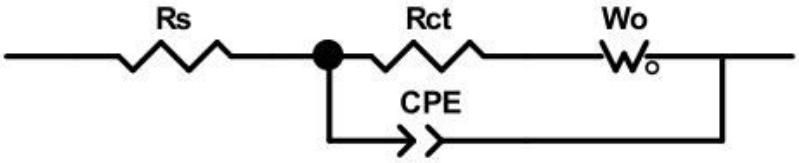

Figure S11. Equivalent circuit of the EIS fitting for ML-Bi@NCSs electrode.
Note: $\boldsymbol{R_s}$: the ohmic resistance; $\boldsymbol{R_{ct}}$: the charge transfer resistance; ***CPE***: the constant phase element of charge transfer; $\boldsymbol{W_o}$: the Warburg impedance related to the diffusion of sodium ions into the bulk electrode.

Table S1. The fitting data of the electrochemical impedance spectroscopy (EIS) for the Bi NPs/NC and ML-Bi@NCSs electrode from Figure 5a-d.

Cycle	Electrode	R_s (Ω)	R_{ct} (Ω)	CPE		W_o		
				CPE-T	CPE-P	W-R	W-T	W-P
Fresh	Bi NPs/NC	26.94	102.9	1.0154×10^{-5}	0.62561	258140	102.4	0.64149
	ML-Bi@NCSs	33.01	62.11	7.9302×10^{-5}	0.61028	46744	77.48	0.70339
1st	Bi NPs/NC	8.786	7	8.866×10^{-5}	0.7321	19193	146	0.68271
	ML-Bi@NCSs	2.01	1.7	3.3736×10^{-5}	0.87	15.7	0.25127	0.395
100th	Bi NPs/NC	1.52	1.58	8.926×10^{-5}	0.82013	19468	127.8	0.80392
	ML-Bi@NCSs	1.45	1.13	9.8561×10^{-5}	0.87144	997.9	1083	0.62853
3000th	Bi NPs/NC	2.864	16.5	0.000253	0.67187	5286	5500	0.555
	ML-Bi@NCSs	1.611	0.2445	0.005203	0.55608	0.20358	0.0003579	0.37357

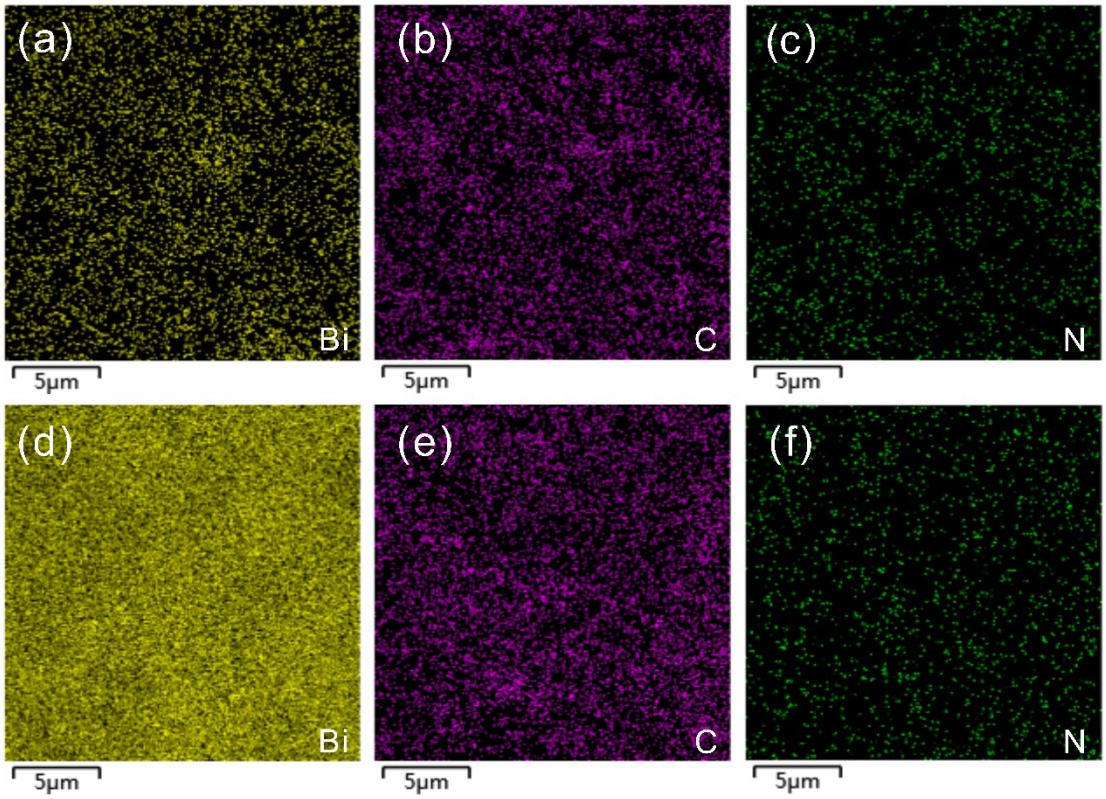

Figure S12. The EDS mapping (Bi, C, N) of Bi NPs/NC (a-c) and ML-Bi@NCSs electrode (d-f) after 3,500 cycles at 5 A g^{-1}.

References

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