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Electronic Supplementary Information:

In Situ Synthesis of Bi Nanoflakes on Ni Foam for Sodium-Ion Batteries

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Experimental section

Materials synthesis: Bismuth nitrate pentahydrate ($Bi(NO_3)_3$•$5H_2O$) was obtained from Tianjin Guangfu fine chemical research institute. Ethylene glycol was purchased from J&K. In order to removal the residual water, ethylene glycol was dehydrated by reduced pressure distillation. The Ni foam was punched into disks (diameter, 10mm; thickness, 1mm), which were carefully washed with 0.2 M of hydrochloric acid and subsequently with de-ionized water and ethanol to remove the passive layer. In a typical synthesis of Bi/Ni, 0.2 mmol of $Bi(NO_3)_3$•$5H_2O$ was dissolved in 2 ml of ethylene glycol in a glass bottle in an Ar-filled glove box. Then, the cleaned Ni foam was put into the prepared solution. The glass bottle was tightly sealed and maintained in an Ar-filled glove box at room temperature for 3-18 h. The as-synthesized Bi/Ni was washed with ethylene glycol, absolute ethanol and deionized water several times, and dried at 80 ºC in a vacuum overnight.

Materials characterization: XRD (Rigaku MiniFlex600 X-ray generator, Cu $K\alpha$ radiation, γ=1.5406 Å) was applied to characterize the pristine Ni foam and the Bi/Ni after discharge and charge at a scan rate of 2°/min from 20° to 80°. The morphologies and EDS elemental mappings were obtained on a field-emission SEM (JEOL JSM7500F) at an acceleration voltage of 5 kV and 20 kV, respectively. The mass loading of Bi on the Bi/Ni was verified by coupled plasma spectrometry (ICP, Perkin-Elmer Optima8300, Germany) analysis. Raman spectra were obtained on a confocal Raman microscope (DXR, Thermo-Fisher Scientific) with an argon-ion laser of 532 nm.

***Electrochemical measurements**:* The sodium-ion batteries were assembled in CR2032 coin cells. They are composed of the as-synthesized Bi/Ni, sodium foil, glass microfiber filters (16 mm in diameter, GF/F: 0.7µm, Whatman) as separator, and 1 M $NaPF_6$ (Sigma-Aladdin, 99%) in diethylene glycol dimethyl ether (DEGDME, Meryer, 99.5%) as electrolyte. The electrochemical performance was measured between 0.1 and 2.0 V on a Land battery-test instrument (CT2001A). The cyclic voltammetry was performed at various scanning rates on a LK2005A (Tianjin Lanlike Co. Ltd.) electrochemical workstation. EIS (Zahner IM6ex) was obtained at open-circuit voltage by applying a sine wave with an amplitude of 5.0 mV over the frequency range from 100 kHz to 100 mHz. The batteries were assembled in a glove box (Mikrouna Universal 2440/750) with H_2O and oxygen lower than 1 ppm. The electrode was disassembled from the batteries and rinsed with dimethoxyethane for SEM and TEM analyses.

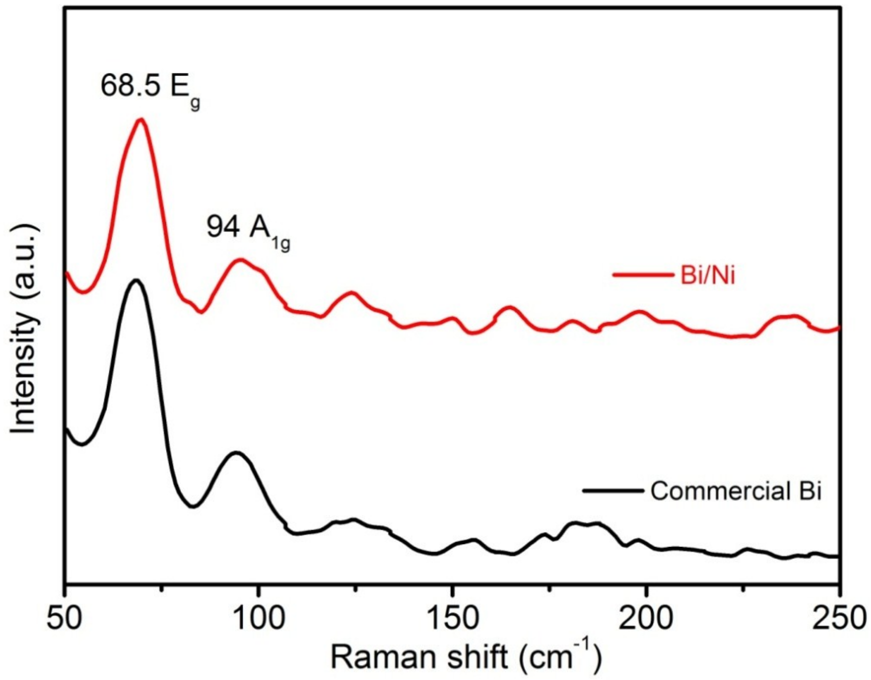

Fig. S1. Raman spectrum of the synthesized Bi/Ni electrode.

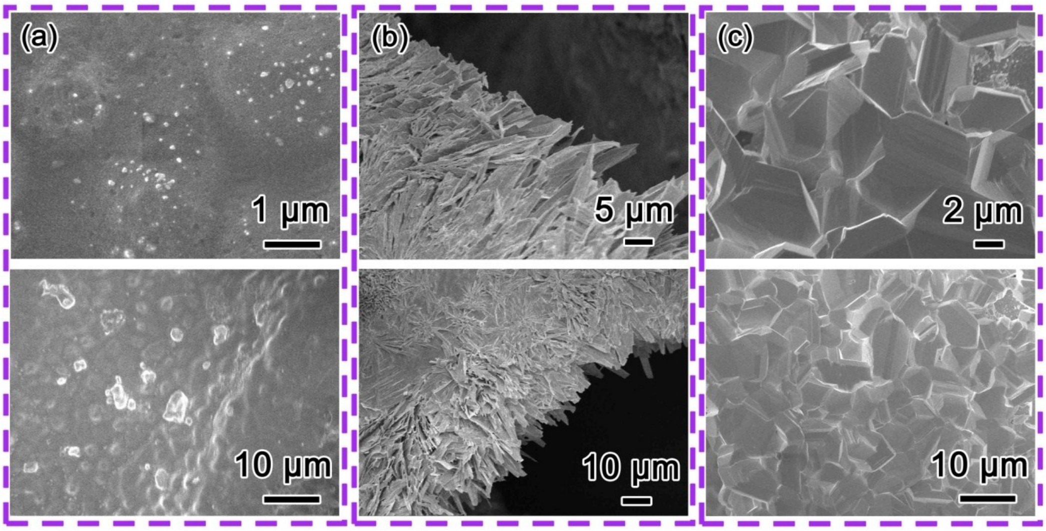

Fig. S2. SEM images of the Bi/Ni prepared at different reaction conditions: (a) 0.01 M, room temperature, 6h, (b) 0.5 M, room temperature, 6h, and (c) 0.1 M, 60 ºC, 6h.

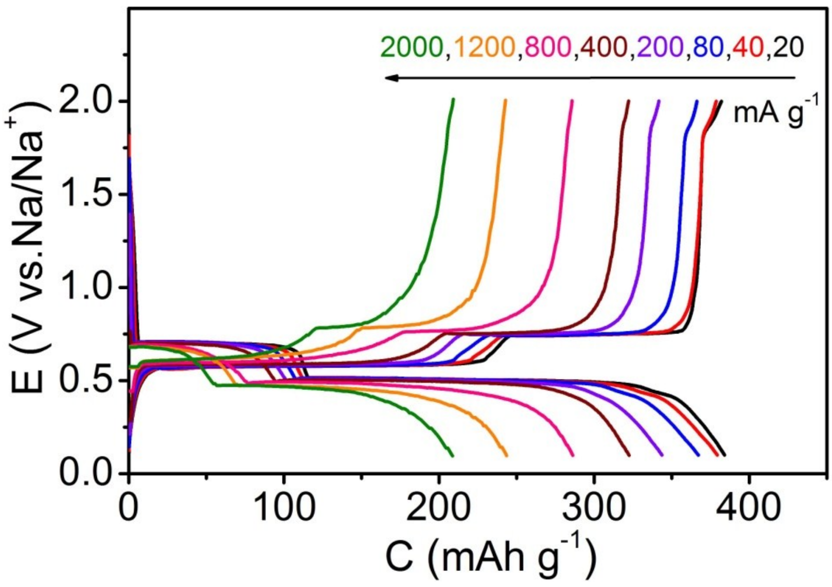

Fig. S3 Discharge/charge curves at different current densities.

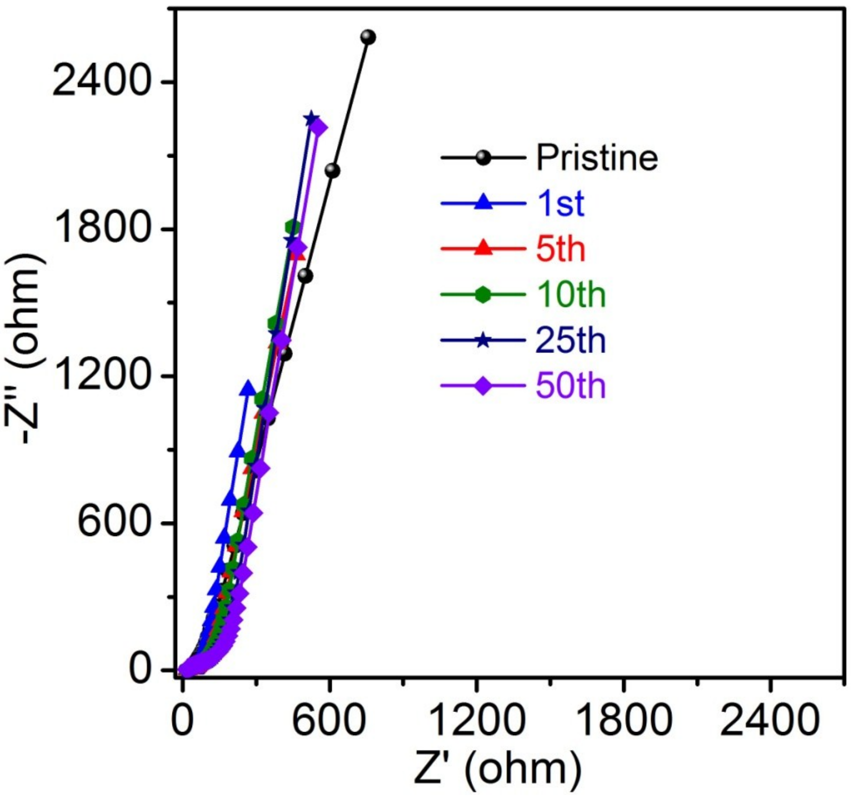

Fig. S4. EIS spectra of the Bi/Ni electrode at open-circuit voltage before test, and after 1st, 5th, 10th, 25th, and 50th charge.

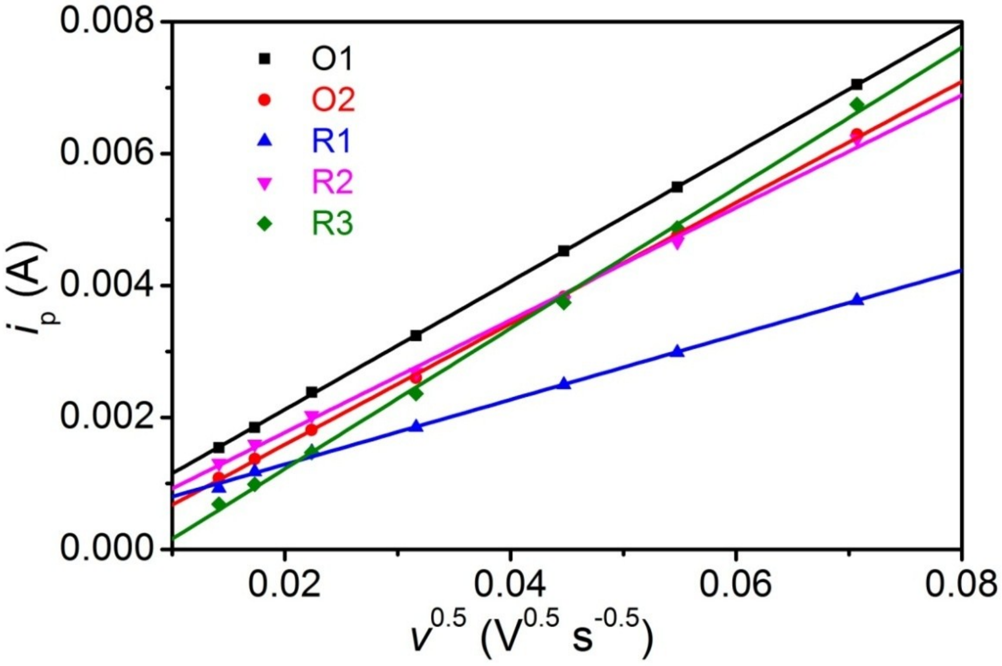

Fig. S5. Plot of peak currents (i_p) vs. square roots of scanning rates of the CVs in Figure 3e and the corresponding linear fittings.

As shown in Figure S5, with the increase of scan rate (v), the peak current (i_p) has a linear relationship with the square root of scan rate. It indicates that diffusion of Na^+ in Bi electrode is the rate-determining step. The relationship of peak current (i_p) and scan rate (v) is described as the Randles-Sevcik equation, as shown below:

$$i_p = (2.69*10^5)n^{3/2}AD^{1/2}_{Na^+}C_{Na^+}v^{1/2} \qquad (1)$$

Where i_p is the peak current (A), n is the charge-transfer number, A is the contact area between electrode and electrolyte, D_{Na^+} is the diffusion coefficient of Na^+ (cm^2 s^{-1}), C_{Na^+} is the concentration of Na^+ in the electrode material, v is the scan rate (V s^{-1}).