

Fast-response/stable Ni-Bi cells achieved by open-up Bi@carbon nanospheres: a preferred electricity collection choice to couple with clean energy harvesting

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1. Experimental Details:

Synthesis of $\text{NH}_4\text{Bi}_3\text{F}_{10}$ Precursors: The precursors of $\text{NH}_4\text{Bi}_3\text{F}_{10}$ nanosphere were produced beforehand by a liquid reaction process at room temperature. In details, 0.2 g $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.6 g NH_4F were vortically dissolved into 25 ml ethylene glycol and denoted as A and B solution, respectively. Next, the obtained A and B homogeneous solutions in two separate vortex tubes were simultaneously transferred into one beaker (volume: 150 mL), evenly mixed by magnetic stirring and aged for 12 h at 25 °C. Afterwards, the power products were then harvested by a filtration treatment, washed with deionized water and dried at 60°C in a vacuum oven.

Synthesis of Bi@C Nanospheres: 0.4 g $\text{NH}_4\text{Bi}_3\text{F}_{10}$ nanosphere powders and 0.1 g dopamine (DA) molecules were successively dispersed into 220 ml of *Tris*-buffer solution and magnetically stirred for 6 h. Next, gray intermediates of $\text{NH}_4\text{Bi}_3\text{F}_{10}$ @polydopamine (PDA) were centrifugally collected,

washed by ethanol for several times and then dried at 60 °C for further usage. The Bi@C nanospheres were eventually synthesized by annealing $\text{NH}_4\text{Bi}_3\text{F}_{10}$ @PDA under Ar atmosphere at 400 °C for 30 min. For comparison, bare Bi nanoparticles were also prepared by directly annealing $\text{NH}_4\text{Bi}_3\text{F}_{10}$ powders in the same condition mentioned above.

Synthesis of CoNi_3O_4 @C Nanowall Arrays (NWAs): The cathode of binder-free CoNi_3O_4 @C NWAs was prepared through a facile hydrothermal approach.⁴⁰ A piece of $25 \times 40 \times 0.3 \text{ mm}^3$ stainless steel (SS) substrate was put into a 100 mL Teflon-lined autoclave, where there involves a 50 mL mixed solution containing 0.75 g $\text{CO}(\text{NH}_2)_2$, 0.7 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.4 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 g NH_4F . The autoclave was then sealed, held at 120 °C for 4 h in an electric oven and then cooled down naturally. The SS with NWAs films grown were fetched out and rinsed with deionized water for several times. Afterwards, these SS samples were immersed into a 100 mL *Tris*-buffer solution (pre-dissolving 0.1 g DA molecules) and kept still for 6 h. The resultant film products were sequentially rinsed with deionized water and heated at 600 °C for 1 h under Ar atmosphere to form CoNi_3O_4 @C NWAs.

Materials Characterizations and Electrochemical Measurements: We detect the samples microstructure/composition by using field-emission scanning electron microscope (FE-SEM; JEOL JSM-7800F, Japan) coupled with high-precision energy dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM; JEM 2010F, USA), X-ray powder diffraction (XRD; Bruker D8 diffractometer, USA), X-ray photoelectron spectroscopy (XPS; Thermo Electron, VG ESCALAB 250 spectrometer, USA) and *Raman* spectroscopy (Witech CRM 200; Laser wavelength: 532 nm). The nitrogen adsorption-desorption isotherms were measured at 77 K with a Micromeritics analyzer (mode: Belsorp Mini).

A conventional slurry-coating method was used to make working anodes. Bi@C nanosphere actives, poly(vinylidene fluoride) (PVDF) binder and acetylene black were mixed in a mass ratio of 8:1:1 and dispersed into *N*-methyl-2-pyrrolidone (NMP) to form homogenous slurries. Then, the slurry was evenly pasted onto a Ni foam (thickness: $\sim 2.5 \text{ mm}$) and dried at 120 °C for 12 h under a vacuum condition (10^{-1} Pa). The electrode mass was determined on a microbalance with a high accuracy of 0.01 mg (Ohaus, USA). The mass loading of Bi@C products on each current collector was

controlled to be $\sim 3.5\text{-}4.2 \text{ mg cm}^{-2}$. The comparative electrode of bare Bi nanoparticles was also prepared according to the same procedures abovementioned. In addition, the $\text{CoNi}_3\text{O}_4@\text{C}$ NWAs with a central mass loading amount of $\sim 3.5 \text{ mg cm}^{-2}$ (estimated by mass differences before and after NWAs fabrication) was directly used as the counter cathode. Electrochemical measurements were all performed on a CS310 electrochemical workstation at ambient conditions. The single electrode testing was conducted by using a standard three-electrode setup; a Pt foil, an Ag/AgCl and 6 M KOH solution were utilized as the counter electrode, reference electrode and electrolyte, respectively. Full-cell battery devices were assembled with Bi@C nanosphere anodes and $\text{CoNi}_3\text{O}_4@\text{C}$ NWAs cathodes. In order to balance the charge storage, the cathode/anode mass ratio is eventually determined by according to their CV behaviors. Electrochemical impedance spectroscopy (EIS) measurements were carried out among a frequency range from 0.1 Hz to 10^2 kHz at an open circuit potential, by applying an AC voltage with 5 mV amplitude. The diffusion coefficient (D_{OH^-}) was calculated from the following formula:

$$D = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2}$$

where R , T , A , n , F and C successively represent the gas constant (8.314 J/K·mol), testing temperature (298 K), electrode surface area, total number of transferred electrons per molecule participating in reactions, Faraday constant (96500 C/mol) and the theoretical ionic concentration in electrodes. σ represents the Warburg factor, which can be calculated from the slope value of the line $Z' \sim \omega^{-1/2}$ by according to the formula of:

$$Z' = R_{ct} + R_e + \sigma \omega^{-1/2}$$

where R_{ct} , R_e and ω are the charge-transfer resistance, the bulky electrode resistance and the circular frequency, respectively. The specific stored charge (Q_{spec}) can be calculated based on galvanostatic charge/discharge curves according to:

$$Q_{\text{spec}} = I \times t / 3.6m,$$

where I , t and m represents the discharging current (A), the discharging time (t), and the actives mass

(g) on electrode, respectively. The specific energy and power densities (E and P) based on the total mass of actives on electrodes were calculated by:

$$E = \int_0^{\Delta t} IV(t)dt$$

$$P = E / \Delta t,$$

wherein $V(t)$ is the discharging voltage (V), dt is the time differential (t) and Δt is the discharging time (t).

2. Characterizations and additional testing results:

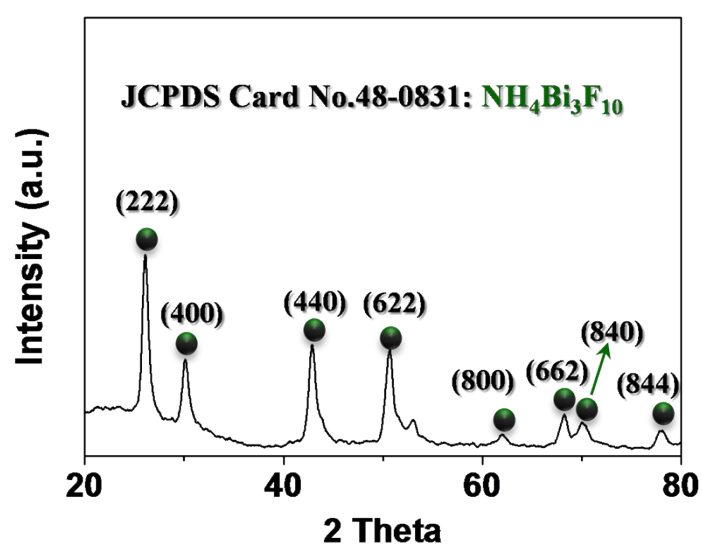


Fig. S1. XRD result of initial $\text{NH}_4\text{Bi}_3\text{F}_{10}$ nanospheres materials.

Fig. S2. (a, b) Additional TEM observations toward Bi@C hybrid nanoparticles.

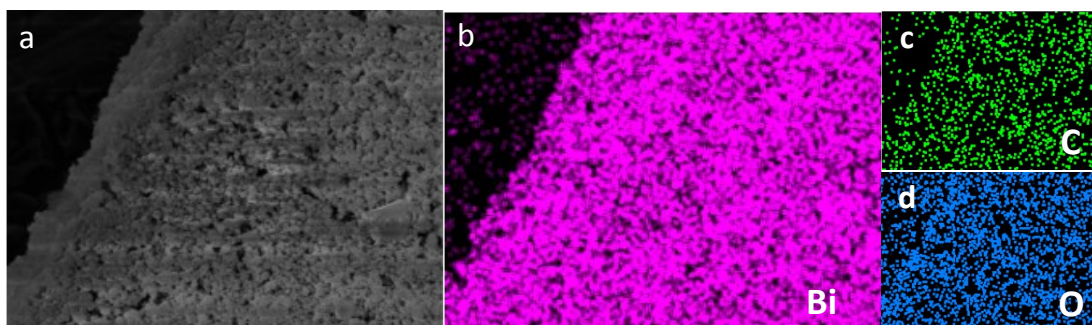


Fig. S3. EDS Elemental mapping results of Bi@C nano hybrids.

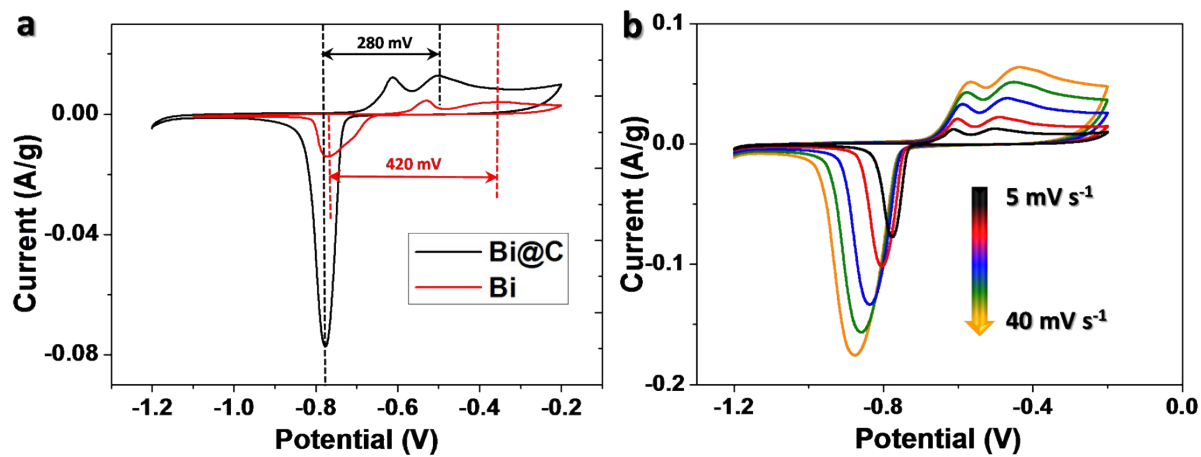


Fig. S4. (a) CV comparisons for Bi@C hybrid and bare Bi at a scan rate of 5 mV s⁻¹; (b) CV plots for Bi@C electrode at distinct scan rates.

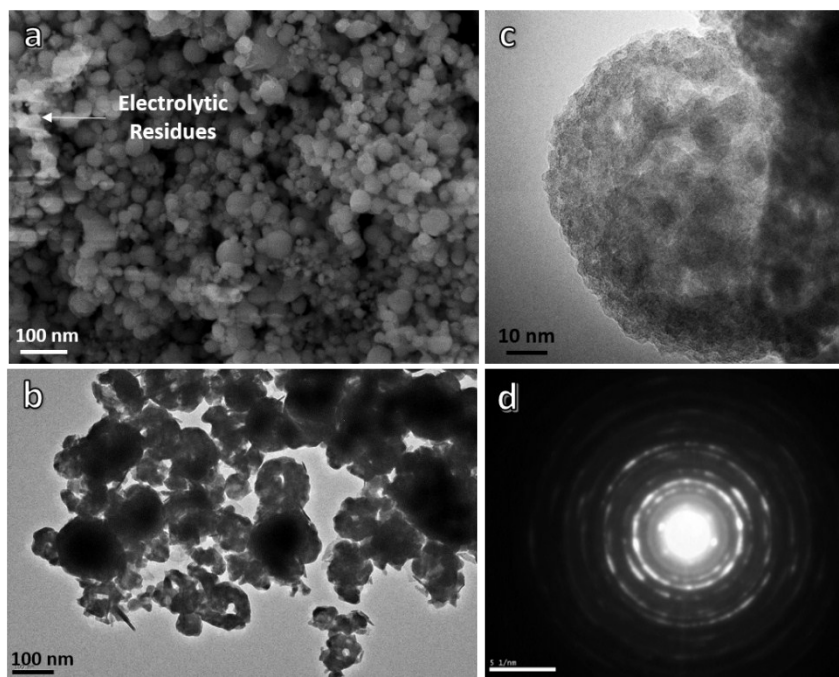


Fig. S5. (a,b) SEM and (c,d) TEM observations of Bi@C after 300 cycles.

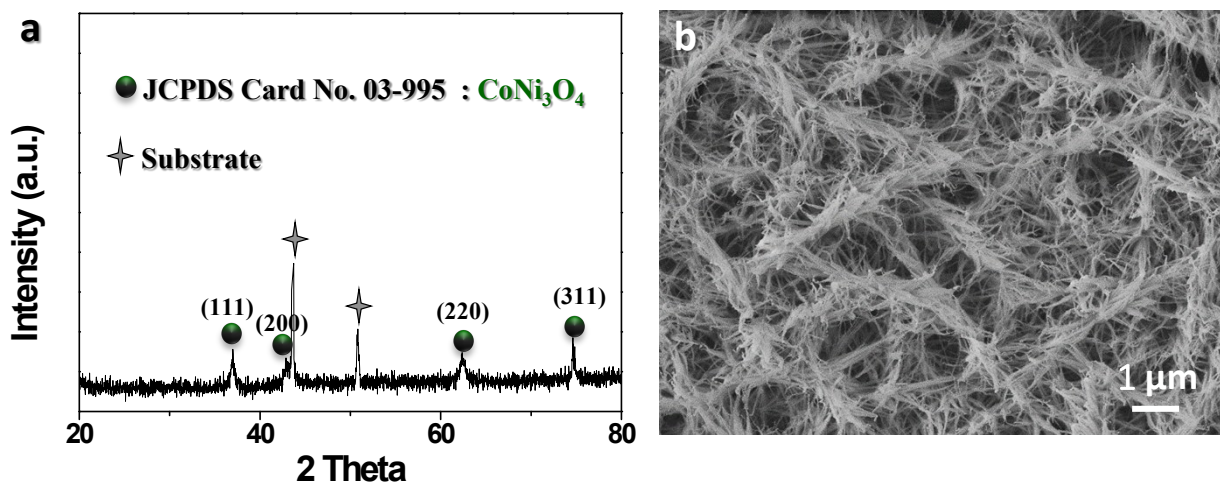


Fig. S6. (a) XRD plot and (b) SEM image of $\text{CoNi}_3\text{O}_4@\text{C}$ nanowall arrays on stainless substrate.

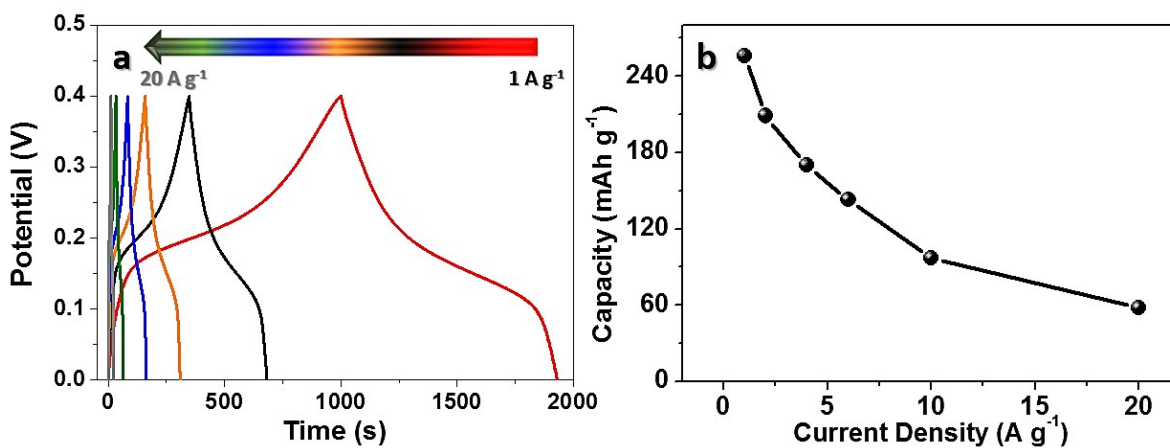


Fig. S7. (a) Galvanostatic discharge curves and (b) specific capacity as a function of current densities of $\text{CoNi}_3\text{O}_4@\text{C}$.

Fig. S8. Comparative CV scans of Bi@C anode and CoNi₃O₄@C cathode at a scan rate of 5 mV s⁻¹.