Supporting Information

Hierarchical Nanoarray Materials for Advanced Nickel-Zinc Batteries

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Experimental section

Synthesis of Co_3O_4@NiO nanostrips@nanorods arrays:

All of the chemicals were of analytical grade and used without any further purification. β-$Co(OH)_2$ nanosheet arrays were prepared by the following steps. Firstly, a piece of nickel foam (approximately 2 cm * 3 cm, the pore size of the nickel foam we used is around 0.2~0.4 mm with a Pores Per Linear Inch (PPI) value of 110.) was cleaned by concentrated HCl solution, ethanol and distilled water with assistance of ultrasonication for several minutes. Afterward, the purified Ni foam was put against the wall of a Teflon lined stainless steel autoclave which contained a homogeneous solution of $Co(NO_3)_2 \cdot 6H_2O$ (2 mmol), NH_4F (8 mmol), $CO(NH_2)_2$ (10 mmol) and 36 ml distilled water. Then the autoclave was sealed and maintained at 120℃ for 12 h to synthesize the β-$Co(OH)_2$ nanowire arrays. After a further calcination at 250℃ for 3 h, Co_3O_4 nanowire arrays (NWAs) were obtained. To synthesize the Co_3O_4 nanostrip arrays, a secondary hydrothermal reaction was adopted. Typically, the obtained β-$Co(OH)_2$ nanowire arrays were put into the solution containing 1 mmol $Co(NO_3)_2 \cdot 6H_2O$, 10 mmol urea and 36 ml distilled water in autoclaves, and maintained at 100℃ for 10 h. After the hydrothermal reactions, the thin films on the metal substrate were taken out and rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80℃ for 6 h. Then the as-prepared products were calcinated at 250℃ for 3 h. The obtained Co_3O_4 nanostrip arrays were denoted as NSAs. To synthesize hierarchical nanoarrays, the final hydrothermal reaction was adopted. Typically, the obtained β-$Co(OH)_2$ nanostrip arrays were put into the solution containing 2 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 10 mmol urea and 36 ml distilled water in autoclaves, and maintained at 100℃ for 10 h. After the hydrothermal reactions, the thin films on the metal substrate were taken out and rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80℃ for 6 h. Then the as-prepared products were calcinated at 250℃ for 3 h. The

obtained Co_3O_4@NiO nanostrips@nanorods arrays were denoted as NSRAs.

Characterizations:

X-ray powder diffraction patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10 (°)/min in the range from 5 to 90°. The size and morphology of the samples were characterized using a field-emission SEM (JEOL JSM6335) operating at 20 kV. High-resolution transmission electron microscopy (HRTEM) measurements were carried out using a JEOL JEM 2100 system operating at 200 kV.

Electrochemical measurements:

The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, chenghua, shanghai.). Fresh film on the metal substrate (1 cm × 1 cm) was used as the working electrode. A platinum electrode and an Hg/HgO electrode were used as counter and reference electrodes, respectively. Freshly prepared 6 mol L^{-1} KOH aqueous solution was used as the electrolyte. The Ni-Zn battery was performed in a ZnO saturated 6 mol L^{-1} KOH solution with the copper foil as the counter electrode. The assembled pouch cell was fabricated by assembling Co_3O_4@NiO NSRAs and a copper foil separated by a Nafion film.

Electrochemical Performance Calculation:

The specific capacities of the electrode and battery were calculated from the galvanostatic discharge curves using following equation, where 'C' is the specific capacity, 'i' is the discharge current, 'Δt' is the discharge time, and 'm' is the mass

$$C = \frac{i \times \Delta t}{m}$$

For single electrode measurement, m is the loaded mass of active materials, while for the assembled Ni-Zn battery, m is the total mass of both cathodic material and anodic Zn. The mass of the Zn anode is calculated from the stoichiometrically deposition during the first charging process, and it was about 4.2 mg cm^{-2}.

Figures

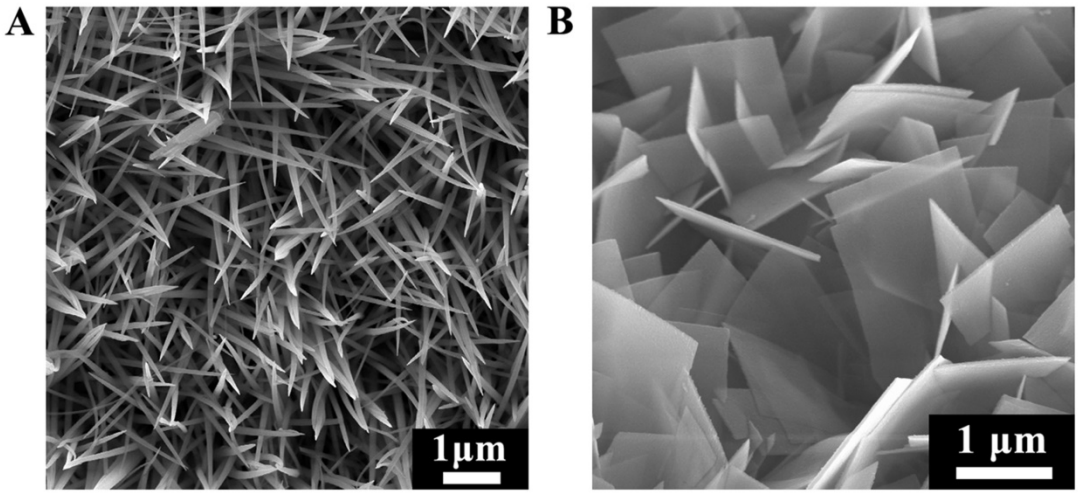

Figure S1. The SEM images of the Co_3O_4 nanowire arrays (A) and Co_3O_4 nanostrips arrays (B).

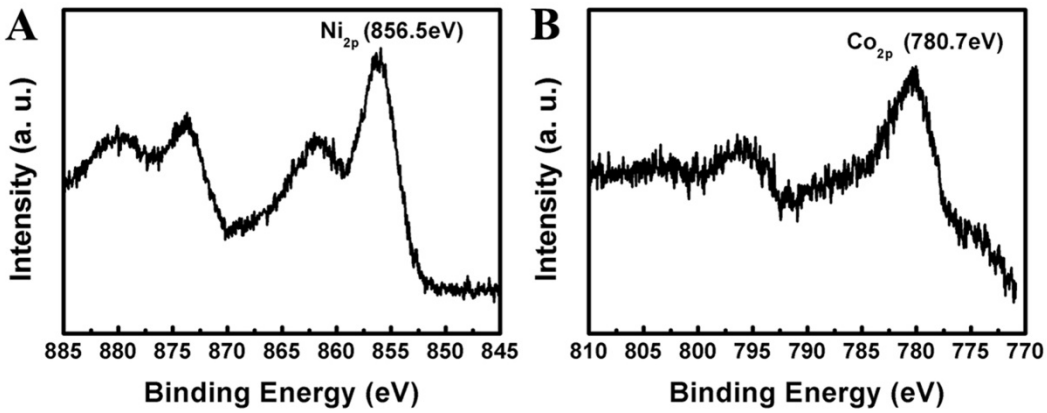

Figure S2. XPS spectra of Ni 2p region (A) and Co 2p region (B) for the hierarchical Co_3O_4@NiO NSRAs, indicating a 2+ oxidation state and mixed oxidation state (2+ and 3+) of Ni and Co, respectively. The Ni/Co ratio from the XPS data is 4:1.

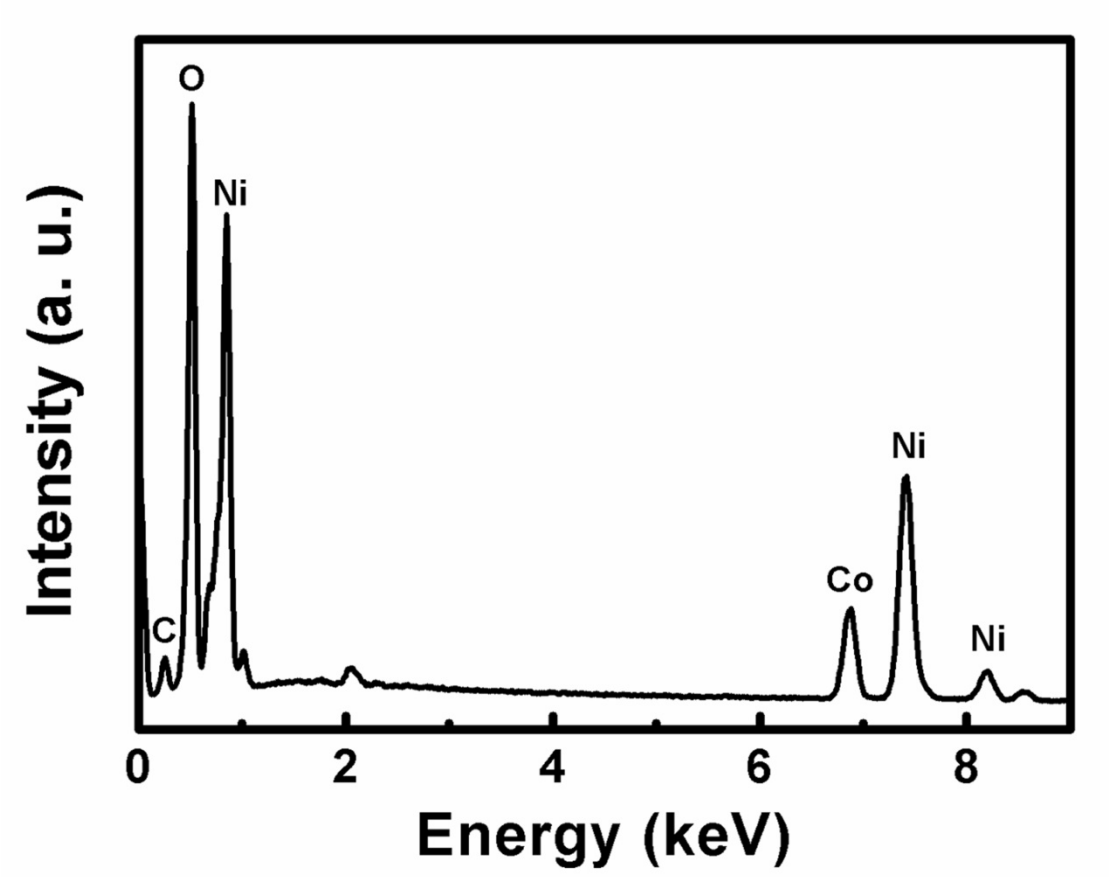

Figure S3. EDS of the hierarchical Co_3O_4@NiO NSRAs. The Ni/Co ratio from the EDS data is 2.5:1.

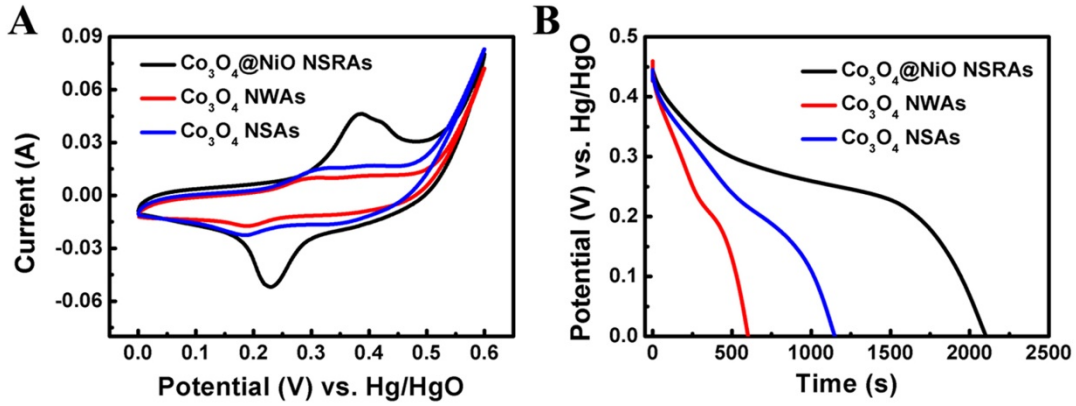

Figure S4. (A) and (B), comparison of the CV curves at a scan rate of 1 mV s^{-1} and the discharge curves at 5 mA cm^{-2} of the Co_3O_4 NWAs, Co_3O_4 NSAs and hierarchical Co_3O_4@NiO NSRAs.

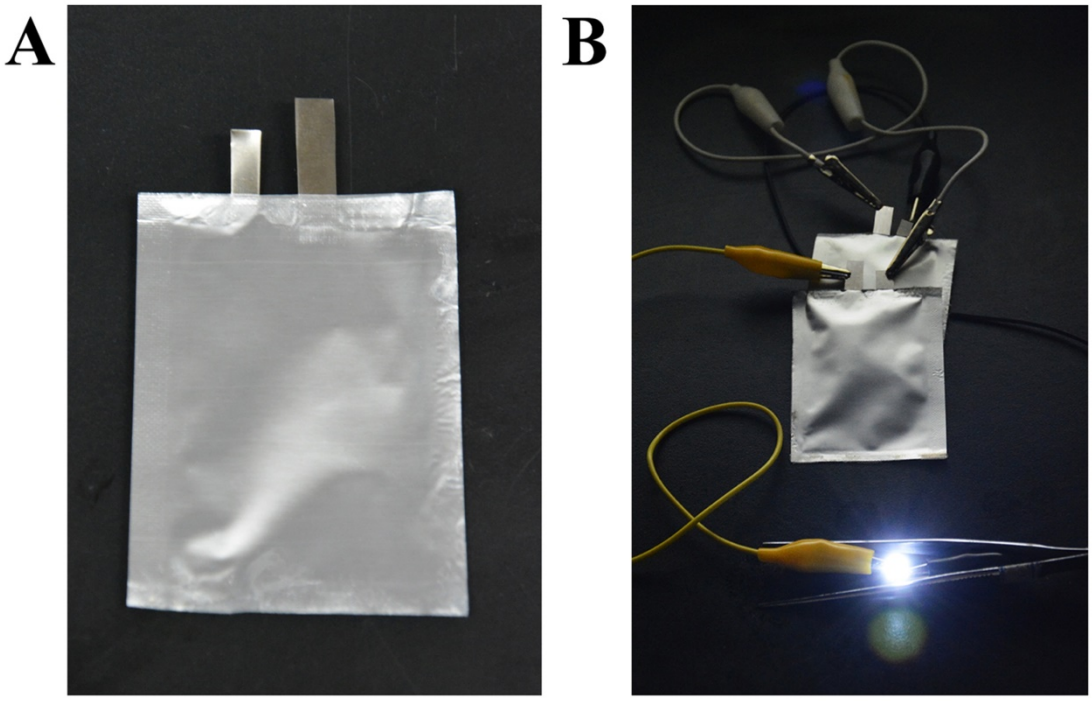

Figure S5. (A), optical image of a pouch cell of as-assembled NiZn battery; (B), optical image of two tandem NiZn pouch cells powering a LED light.

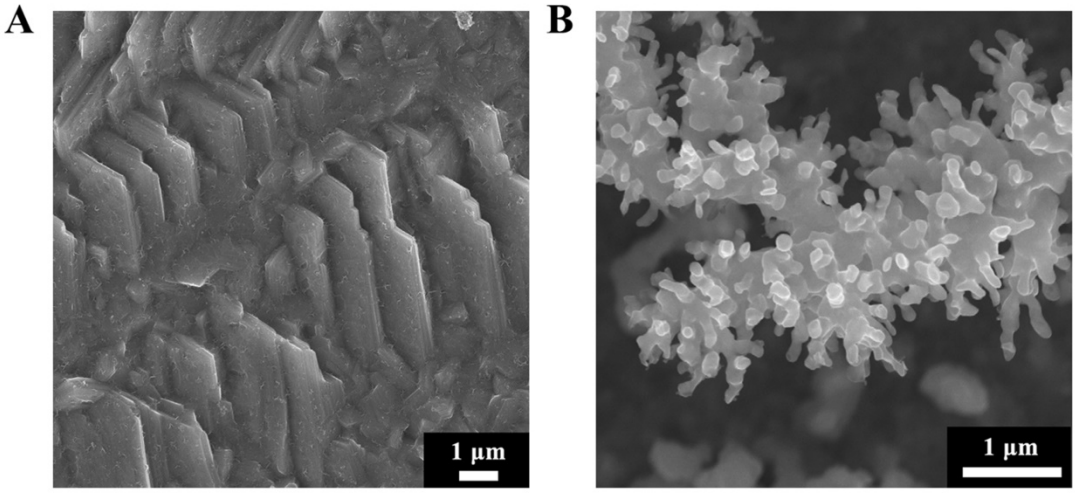

Figure S6. The SEM image of the zinc electrode after 5 cycles (A) and 500 cycles (B).