Supporting Information

Synergistic Effects of Engineered Spinel Hetero-Metallic Cobaltites on Electrochemical Pseudo-Capacitive Behaviors

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Experimental method

Material Synthesis

All chemicals were of analytical grade and used for synthesis without any further purification. The ZNCH electrodes on Ni foam were synthesized through a one-step hydrothermal synthesis. First, the conductive Ni foam was cleaned using 1.0 M HCl, ethanol, and deionized water. 0.5 mmol of $Zn(NO_3)_2 \cdot 6H_2O$, 0.5 mmol of $Ni(NO_3) \cdot 6H_2O$, 2.0 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 5.0 mmol of urea, and 3.0 mmol of NH_4F were then dissolved in deionized water. Next, the solution and Ni foam were transferred into a Teflon-lined stainless-steel autoclave. The autoclave was kept at 150 ^oC for 12 hr before the sample was rinsed with deionized water and dried at 60 ^oC for another 12 hr. Finally, the sample was annealed at 400 ^oC for 2 hr with a heating rate of 1 °C min^{-1} under Ar. The $ZnCo_2O_4$ and $NiCo_2O_4$ electrodes were similarly synthesized while only using 1.0 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ and 1.0 mmol of $Ni(NO_3) \cdot 6H_2O$ for the $ZnCo_2O_4$ and $NiCo_2O_4$ electrodes, respectively. The solutions were then transferred into a Teflon-lined stainless-steel autoclave and kept at 150 ^oC for 12 hr. Finally, the samples were annealed at 400 ^oC for 2 hr under the same heating rate and environmental conditions as above.

Electrochemical Measurements

The electrochemical properties of the ZNCH electrodes were measured in a three-electrode system using a working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode (in saturated 3 M KCl) as the reference electrode. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were conducted with a potentiostat (PGSTAT302N, Metrohm, Autolab) at different current densities. The active carbon (AC) electrodes were fabricated by mixing the active carbon,

super-P, and Polyvinylidene Fluoride (PVDF) binder as the active material, conductive material, and binding material, respectively, in a weight ratio of 80:10:10 to obtain a slurry

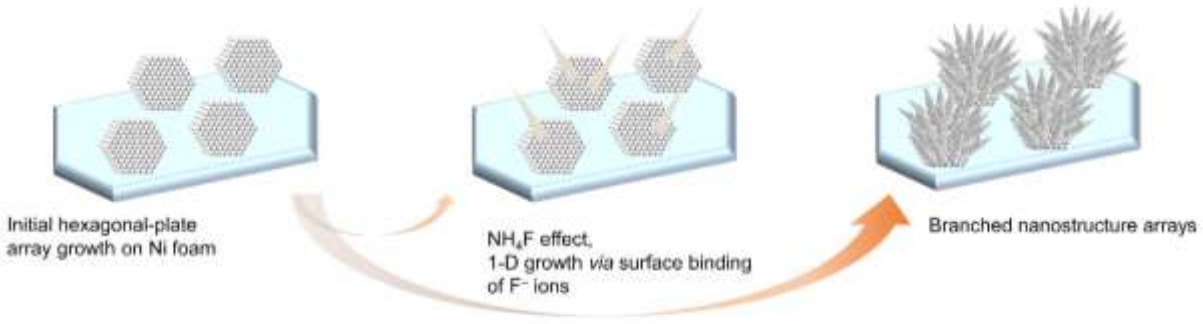

Figure S1. Synthetic illustration of hierarchically branched nanostructures of the ZNCH.

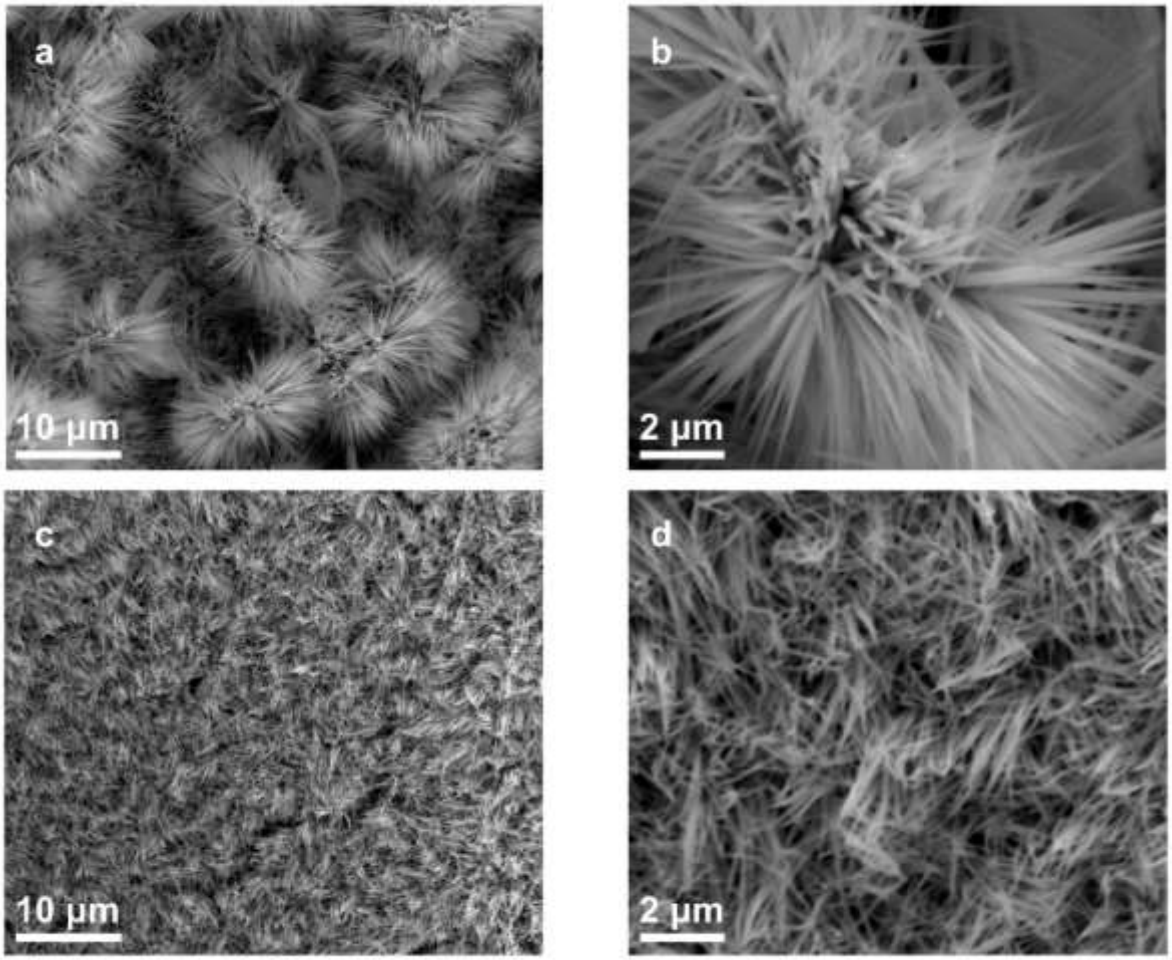

Figure S2. SEM images of (a,b) $ZnCo_2O_4$ and (c,d) $NiCo_2O_4$.

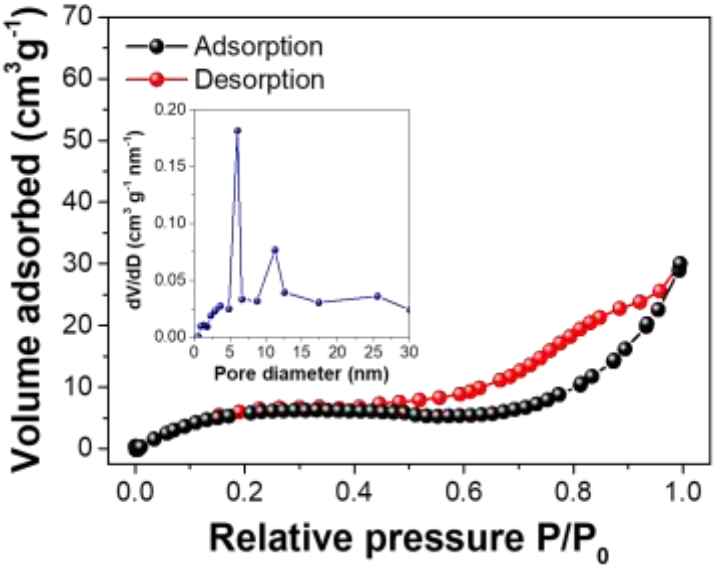

Figure S3. Nitrogen adsorption-desorption isotherms of the ZNCH. The inset indicates the pore size distribution of ZNCH.

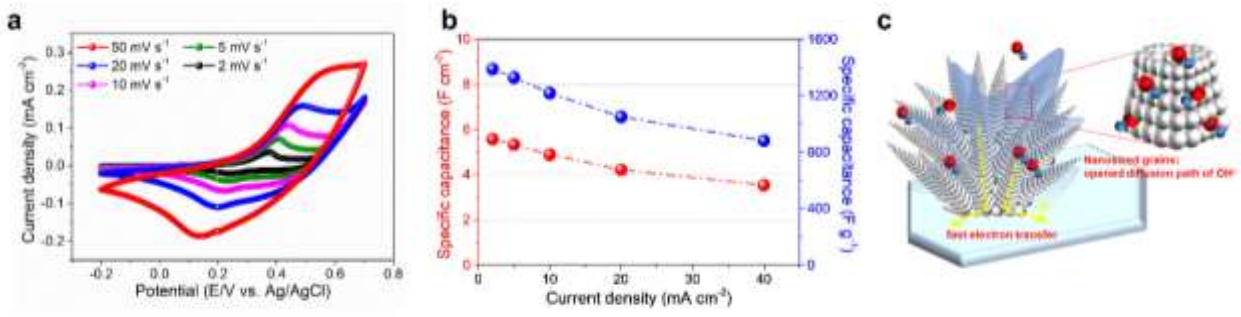

Figure S4. (a) CV and (b) Calculated capacitance curves of the ZNCH. (c) Schematic illustration of electrochemical kinetics of the ZNCH.

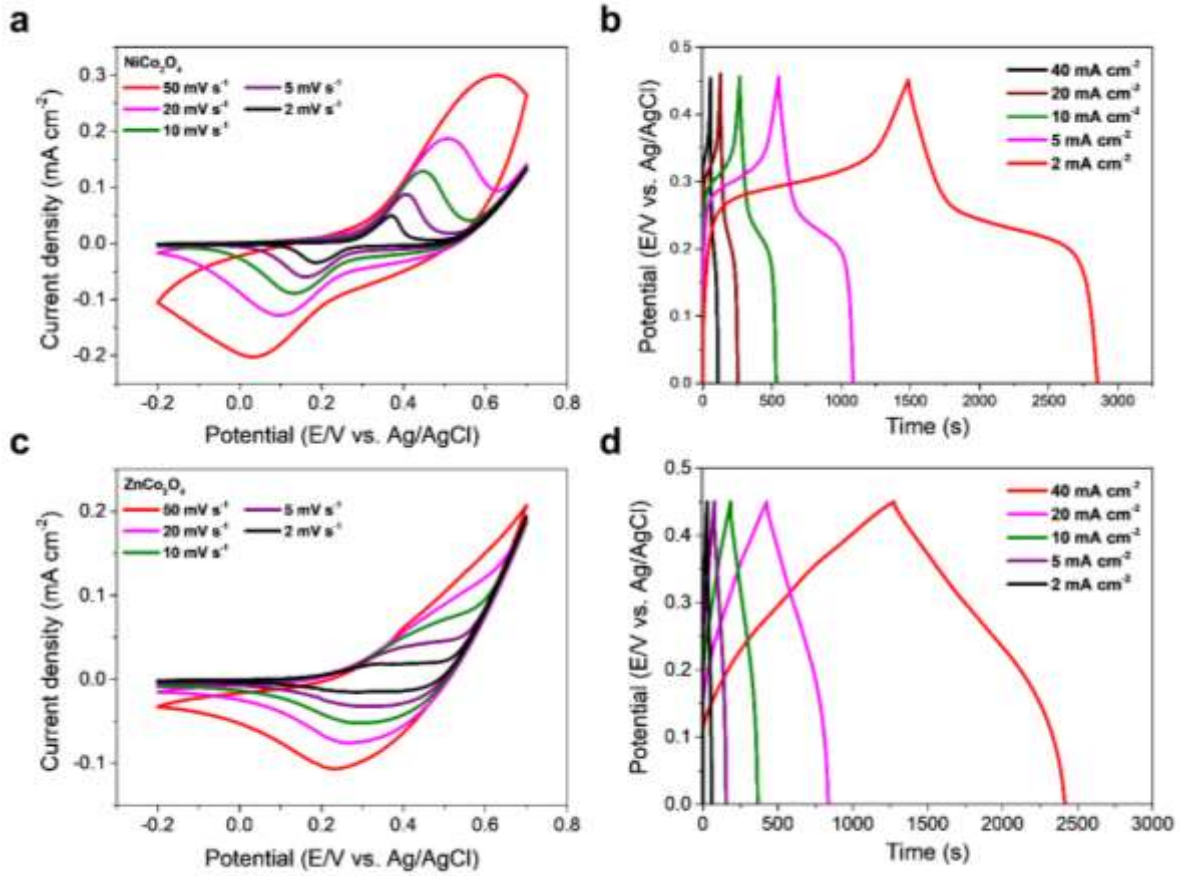

Figure S5. CV and GCD curves of (a) $NiCo_2O_4$ and (b) $ZnCo_2O_4$.

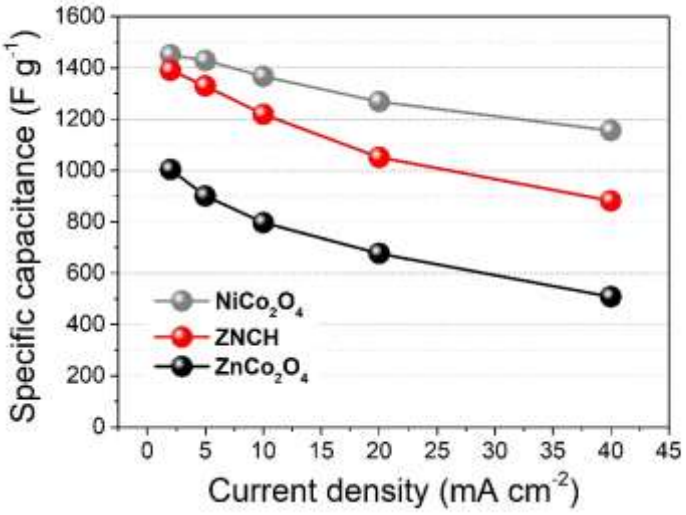

Figure S6. Mass capacitance comparison of the transition metal cobaltite samples.

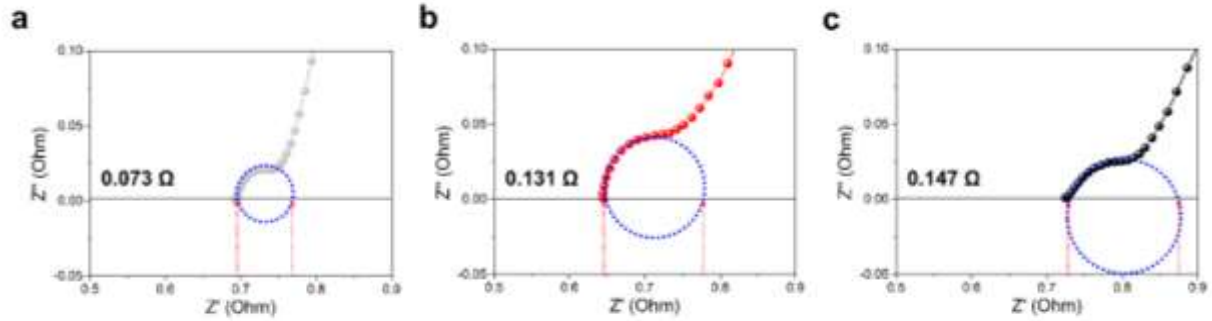

Figure S7. EIS curves of (a) $NiCo_2O_4$, (b) ZNCH and (c) $ZnCo_2O_4$.

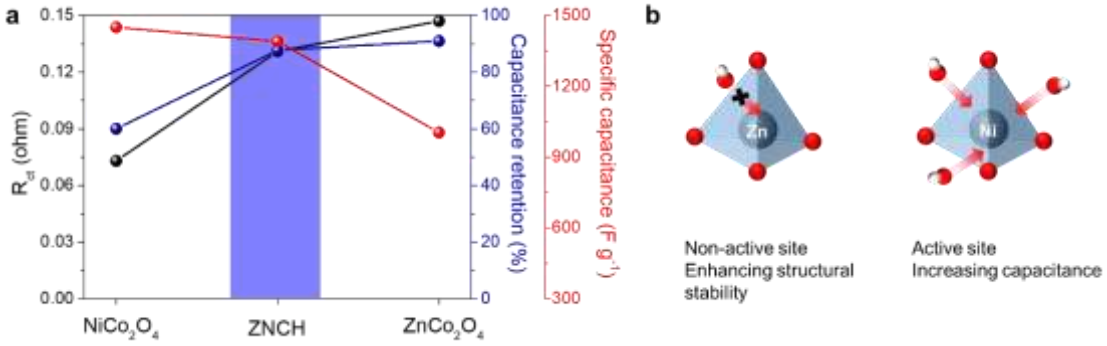

Figure S8. (a) A comparison of various electrochemical characteristics such as charge transfer resistance (R_{ct}), capacity retention, and specific mass capacitance for three different electrodes. (b) Illustration images showing the electrochemical role for Zn and Ni in the tetrahedral site of spinel cobaltite structure.