Electronic Supplementary Information

Hierarchical $NiCo_2O_4$@MnO_2 core-shell heterostructured nanowire arrays on Ni foam as high-performance supercapacitor electrodes

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Experimental Section

Materials Synthesis. In a typical synthesis, Ni foam (2 cm x 10 cm in rectangular shape) was immersed in a 3 M HCl solution for 15 min to get rid of the surface oxide layer. 1.16 g of $Co(NO_3)_2 \cdot 6H_2O$, 0.58 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.44 g of urea were dissolved in 160 mL of mixed solution with ethanol and H_2O (V : V = 1 : 1) at room temperature to form a clear pink solution. The solution was transferred into a 250 mL bottle, and the pretreated Ni foam was placed in the bottle. Then, the bottle was capped tightly, heated to 90 ^oC and maintained at the temperature for 8 h in an electric oven. After cleaned with the assistance of ultrasonication and dried in air at 60 ^oC, the Ni foam with grown precursor was further put into a 40 mL Teflon-lined stainless steel autoclave containing 1.6 mM $KMnO_4$ solution, which was subsequently heated to and maintained at 160 °C for 30 min. For comparison, 14 and 28 mM $KMnO_4$ solutions were further used to fabricate other $NiCo_2O_4@MnO_2$ core-shell NW arrays. Finally, the Ni foam with the as-grown hybrid precursor arrays was annealed at 350 ^oC for 2 h to obtain hierarchical $NiCo_2O_4@MnO_2$ core-shell heterostructured NW arrays grown on Ni foam. As a control, the $NiCo_2O_4$ NW arrays supported on Ni foam were also obtained under the same condition but without the following coating of the MnO_2 phase.

Materials Characterization. X-ray diffraction (XRD) patterns were collected on a Bruker D2 Phaser X-Ray Diffractometer with Ni filtered Cu *Kα* radiation (λ = 1.5406 Å) at a voltage of 30 kV and a current of 10 mA. Field-emission scanning electron microscope (FESEM) images and energy dispersive X-ray spectroscopy (EDX) spectra were acquired on a JEOL JSM 6700F microscope operated at 5 kV. Transmission electron microscope (TEM) images were taken on JEOL 2010 and JEOL 2100F microscopes.

Electrochemical Measurements. Electrochemical measurements (CHI 660D electrochemical workstation) were conducted in a three-electrode configuration at room temperature using a 1.0 M LiOH as electrolyte. The nickel foam supported electroactive materials (~ 1 cm^2 in area) serves directly as the working electrode. Pt foil and standard calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The mass loading of the hybrid $NiCo_2O_4$@MnO_2 core-shell NWs on Ni foam is about 1.4 mg cm^{-2}. Meanwhile, the mass loading of the $NiCo_2O_4$ NWs on Ni foam is about 1.15 mg cm^{-2}. The area specific capacitance of the electrodes was calculated from the CP curves based on equation (1):

$$C = \frac{It}{\Delta V} \qquad (1)$$

where C, I, t and ΔV are the SC (F cm^{-2}) of the electroactive materials, the discharging current density (A cm^{-2}), the discharging time (s), and the discharging potential range (V), respectively. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 1 mV amplitude in a frequency range from 0.1 Hz to 100 kHz at open circuit potential.

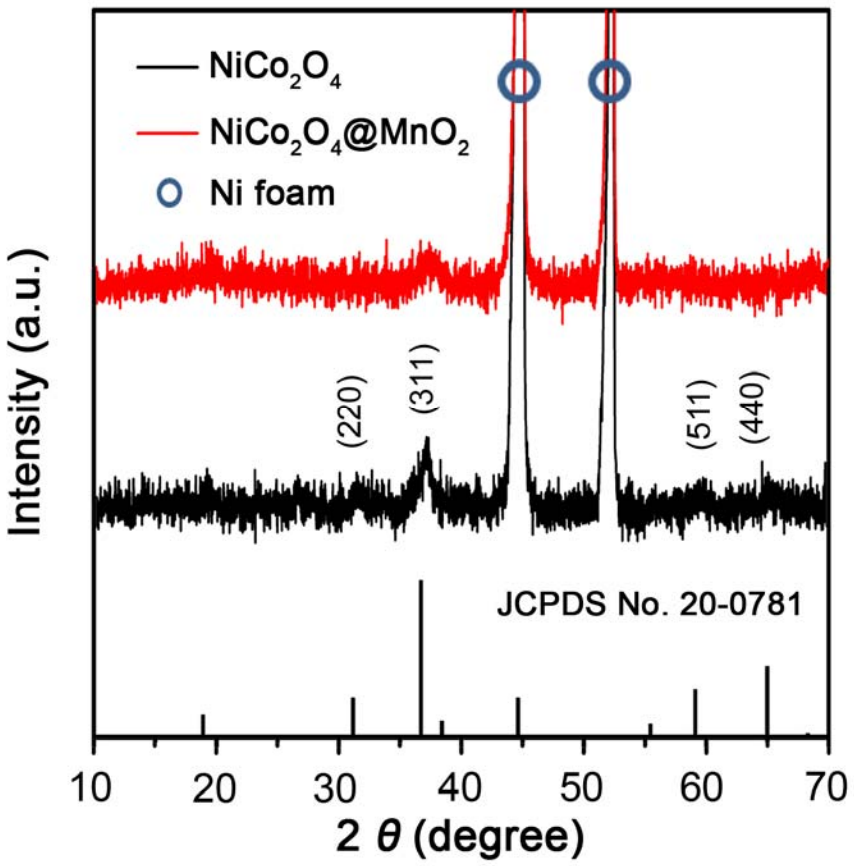

Fig. S1 XRD patterns of $NiCo_2O_4$ NW arrays and hierarchical $NiCo_2O_4$@MnO_2 core-shell heterostructured NW arrays on Ni foam

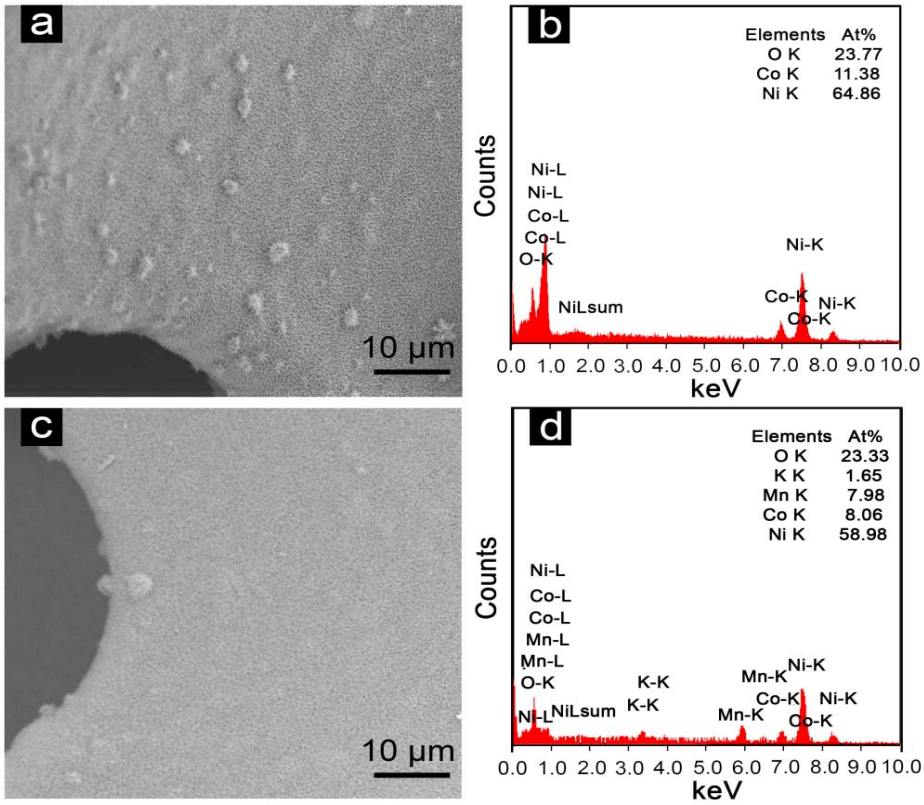

Fig. S2 Typical FESEM images and corresponding EDX data of (a, b) $NiCo_2O_4$ and (c, d) hierarchical $NiCo_2O_4$@MnO_2 core-shell NW arrays grown on Ni foam.

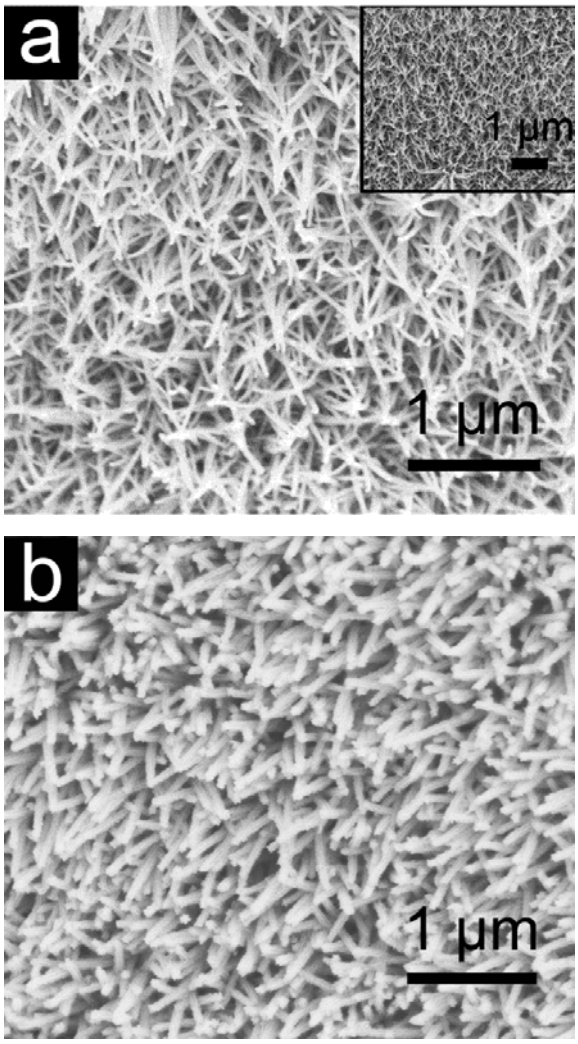

Fig. S3 Low-magnification FESEM images of (a) derived $NiCo_2O_4$ NW arrays and (b) hierarchical $NiCo_2O_4$@MnO_2 core-shell NW arrays grown on Ni foam. (The inset in (a) shows the precursor of $NiCo_2O_4$ NW arrays supported on Ni foam).

As seen from Fig. S3a, after the annealing treatment at 350 ºC, the $NiCo_2O_4$ NW arrays sample maintain the same morphology as its precursor (the inset in a) without any noticeable alteration. Moreover, both the $NiCo_2O_4$ NW arrays and hierarchical $NiCo_2O_4$@MnO_2 core-shell NW arrays were uniformly grown on Ni foam on a large scale.

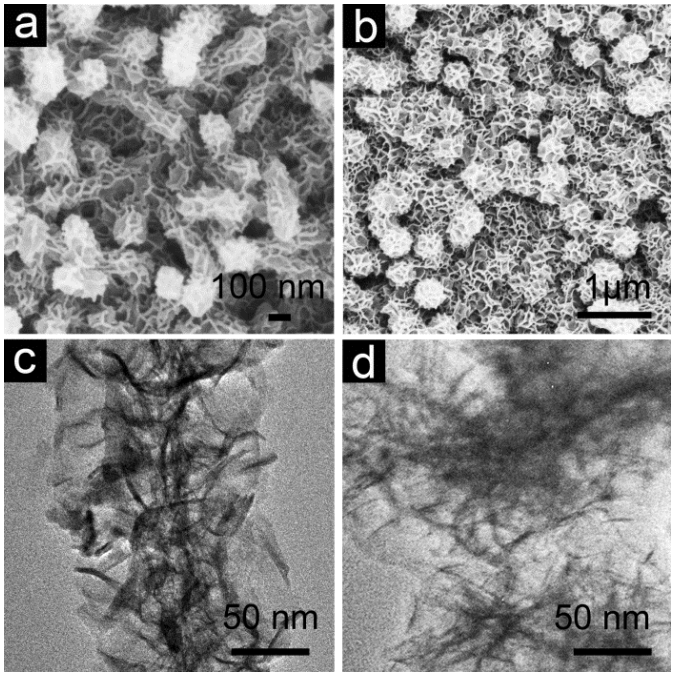

Fig. S4 FESEM and TEM images of as-fabricated hierarchical $NiCo_2O_4$@MnO_2 core-shell NW arrays grown on Ni foam by using $KMnO_4$ solutions with different concentrations: (a, c) 14 mM and (b, d) 28 mM.

Clearly, when the higher concentration of $KMnO_4$ is used, much thicker MnO_2 layer can be seen. In the case of 14 mM $KMnO_4$, the shell thickness of ultrathin MnO_2 nanoflakes is *ca.* 50 nm. When the $KMnO_4$ concentration is increased to 28 mM, the thickness of MnO_2 layer increases up to *ca.* 100 nm.

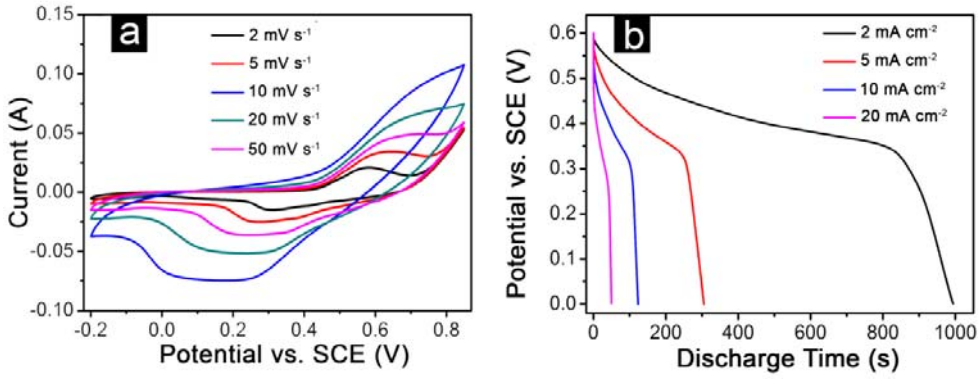

Fig. S5 Electrochemical characterizations of the hierarchical $NiCo_2O_4$@MnO_2 core-shell NW arrays grown on Ni foam: (a) CVs curves at various scan rates ranging from 2 to 50 mV s^{-1}, (b) discharge voltage profiles at different current densities.

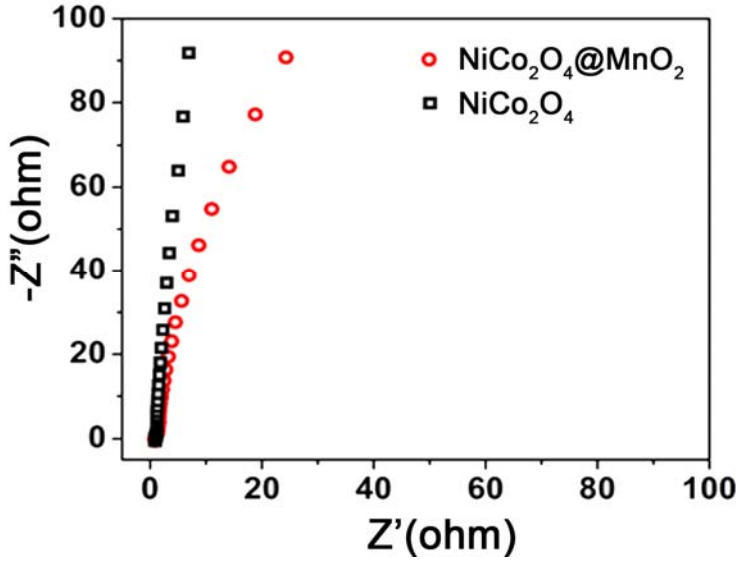

Fig. S6 Impedance Nyquist plots of the MnO_2, $NiCo_2O_4$ NW arrays and the hierarchical $NiCo_2O_4$@MnO_2 core-shell NW arrays grown on Ni foam at open circuit potential.