Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
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Hierarchical Mesoporous $NiCo_2O_4$@MnO_2 Core-Shell nanowires Arrays on Nickel Foam for Aqueous Asymmetric Supercapacitor

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Calculations: the mass loading of the mesoporous $NiCo_2O_4$ nanowires on nickle foam was calculated to be around 1.2 mg cm^{-2} by the following method: firstly, a piece of nickel foam was carefully cleaned with 3 M HCl solution in an ultrasound bath for 30 min to remove the NiO layer on the surface, and then washed by deionized water and absolute ethanol several times. And we weighed the mass of such cleaned nickle foam substrate by a XS analytical balance (Mettler Toledo; $\delta = 0.01$ mg) and labeled for m_1. Secondly, the experiment has been performed with such nickel foam, the products on the nickel foam were carefully washed with deionized water and absolute ethanol with the assistance of ultrasonication, and then dried at 60 °C overnight. Afterwards, the samples were calcined at 300 °C for 2 h in air. And then we weighted the mass of $NiCo_2O_4$/nickle foam by a XS analytical balance and labeled for m_2. Finally, the mass of the $NiCo_2O_4$ was calculated according to the equation: $m_{NiCo_2O_4} = m_2 - m_1$.

The discharge specific capacitance (C_{sp}) or areal capacitance(C_a) in the three-electrode was calculated from the discharge curves using the following equation:[1,2] $C_{sp} = It/m\Delta V$ and $C_a = It/S\Delta V$, where I (A) is the current used for the charge/discharge, t (s) is the discharge time, m (g) is the total weight of the active electrode and ΔV (V) is the voltage interval of the discharge, *S* is the geometrical area of the electrode.

The power density and energy density are calculated from the following equations, respectively:[3,4] $E = 0.5C\Delta V^2$, $P = E/t$, where E (Wh kg^{-1}) is the energy density, P (kW kg^{-1}) is the power density, C (F g^{-1}) is the specific capacitance, ΔV (V) is the potential window of discharge, and t (s) is the discharge time.

For supercapacitors, the charge balance between the two electrodes will follow the relationship $q^+ = q^-$, where q^+ means the charges stored at the positive electrode, q^- means the charges stored at the negative electrode. The charge stored by each electrode usually depends on the specific capacitance (C), the potential window for the charge/discharge process (ΔE), and the mass of the electrode (m) following Equation: $q = C \times \Delta E \times m$. The mass ratio between the positive and negative electrodes needs to follow: [5]

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+}$$

Therefore, the optimal mass ratio between such two electrodes can be determined by the specific capacitance values and potential windows.

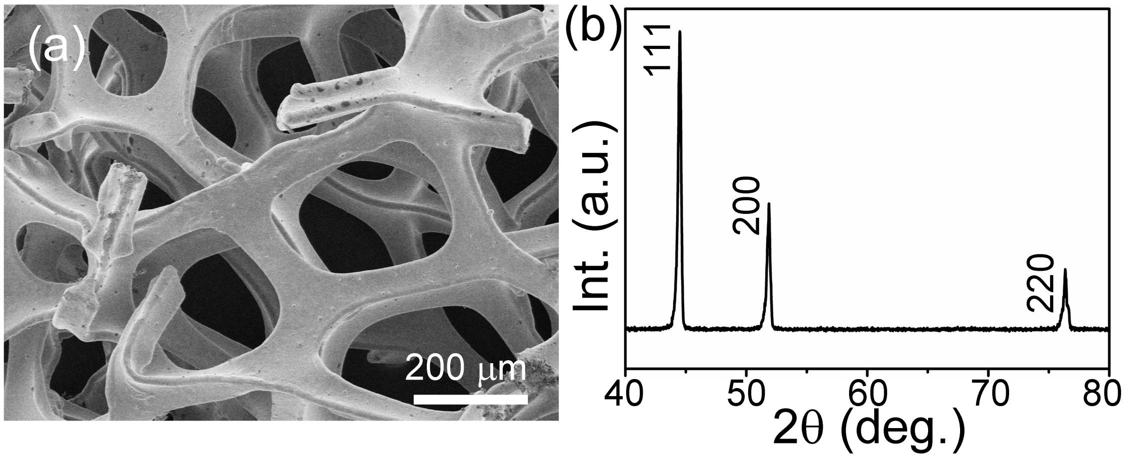

Figure S1. (a) SEM image and (b) XRD pattern of the treated Ni foam by HCl.

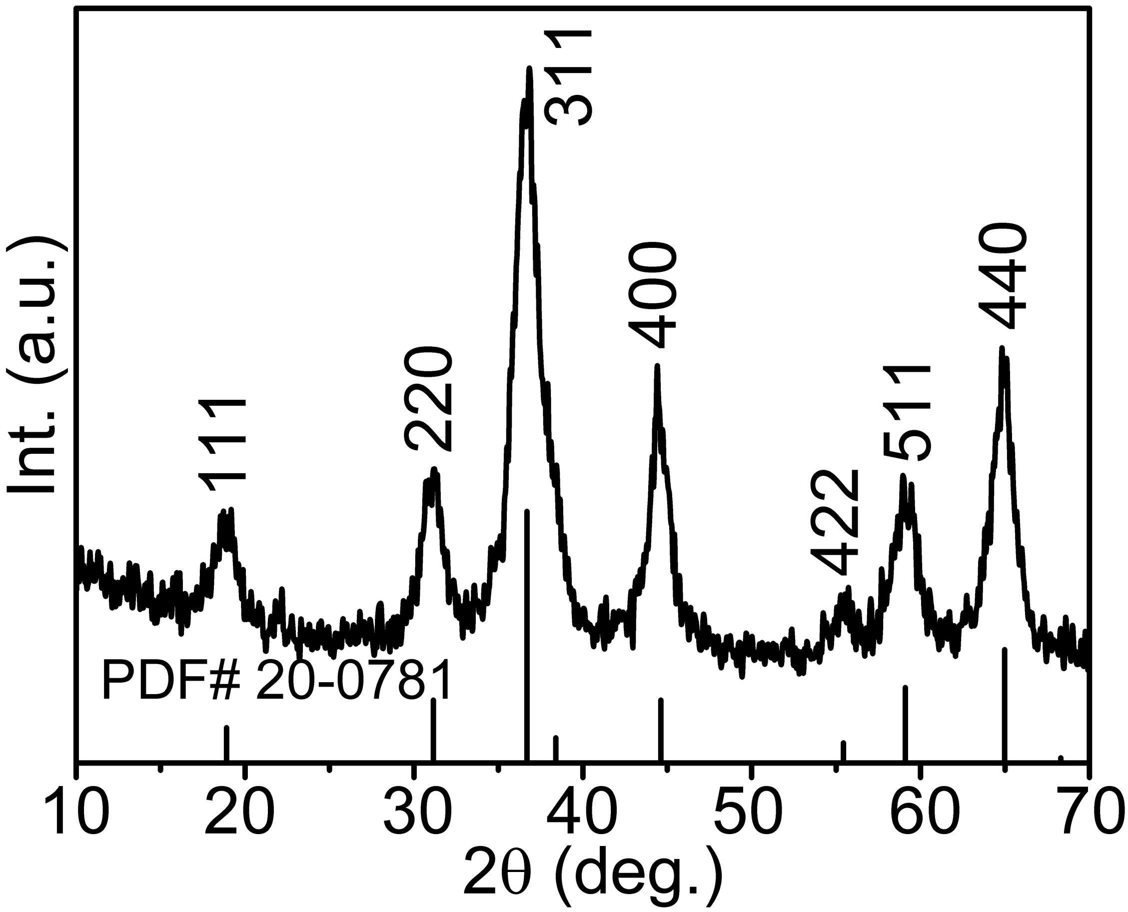

Figure S2. XRD pattern of the synthesized $NiCo_2O_4$ material scratched from the Ni foam.

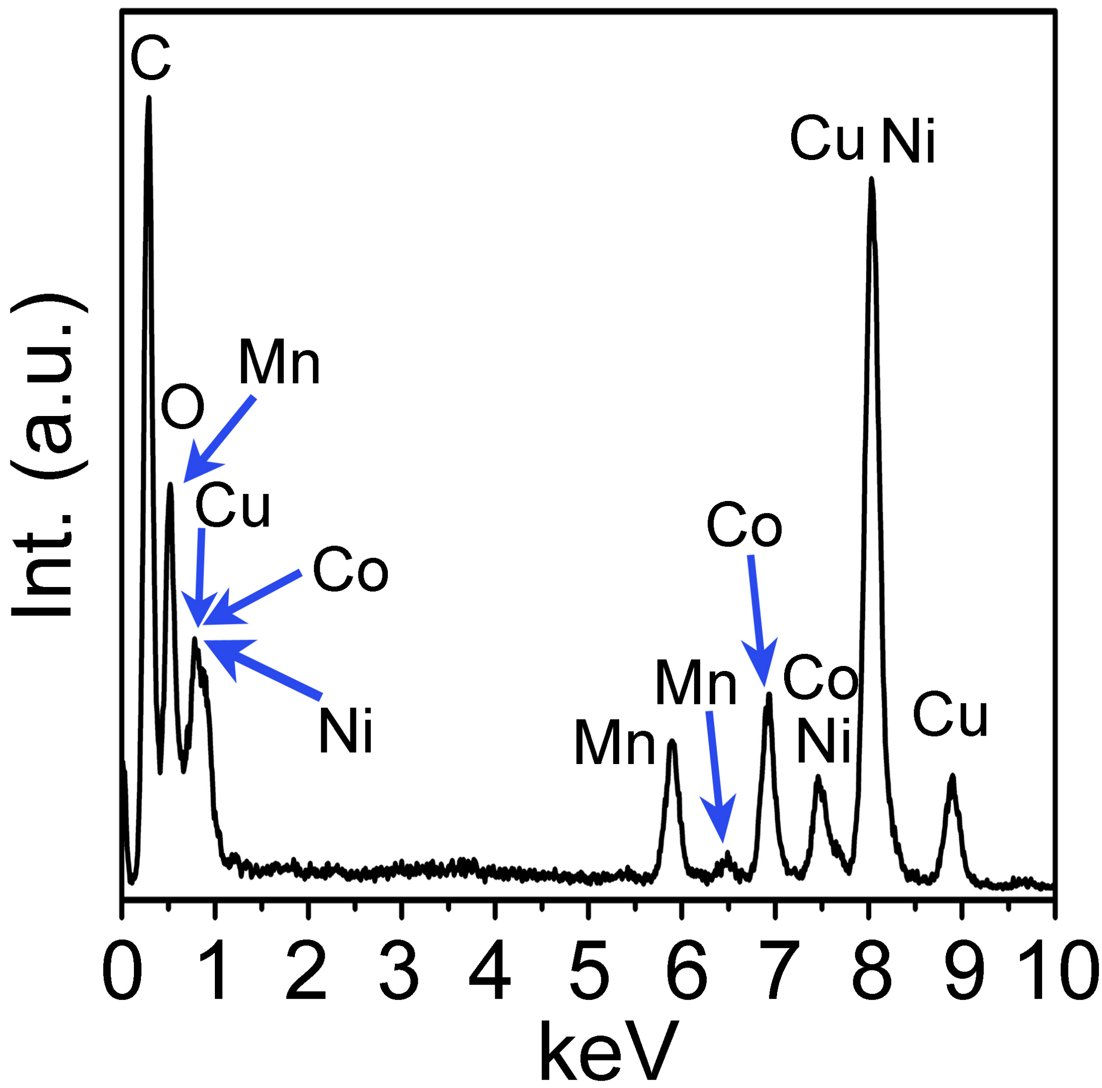

Figure S3. EDX spectrum of the hierarchical mesoporous $NiCo_2O_4@MnO_2$ core-shell nanowires.

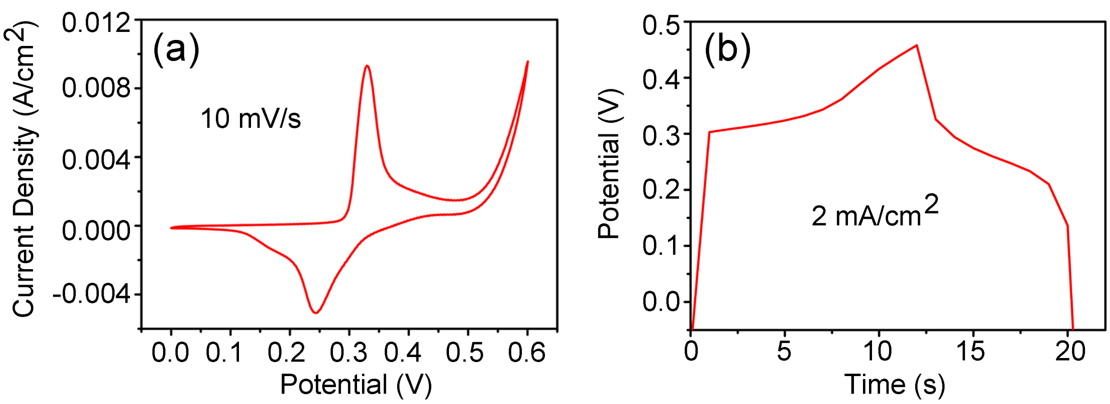

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Figure S4. (a) CV and (a) CD curves of pure Ni foam.

The pure Ni foam possesses areal capacitance only 0.032 F cm^{-2} at 2 mA cm^{-2}. However, the $NiCo_2O_4@MnO_2$ core-shell nanowires possess areal capacitance up to 2.244 F cm^{-2} at 2 mA cm^{-2}. Thus, in this case the contribution of nickel foam to the total areal capacitance of the hybrid $NiCo_2O_4@MnO_2$ core-shell nanowires is ~ 1.4 %.

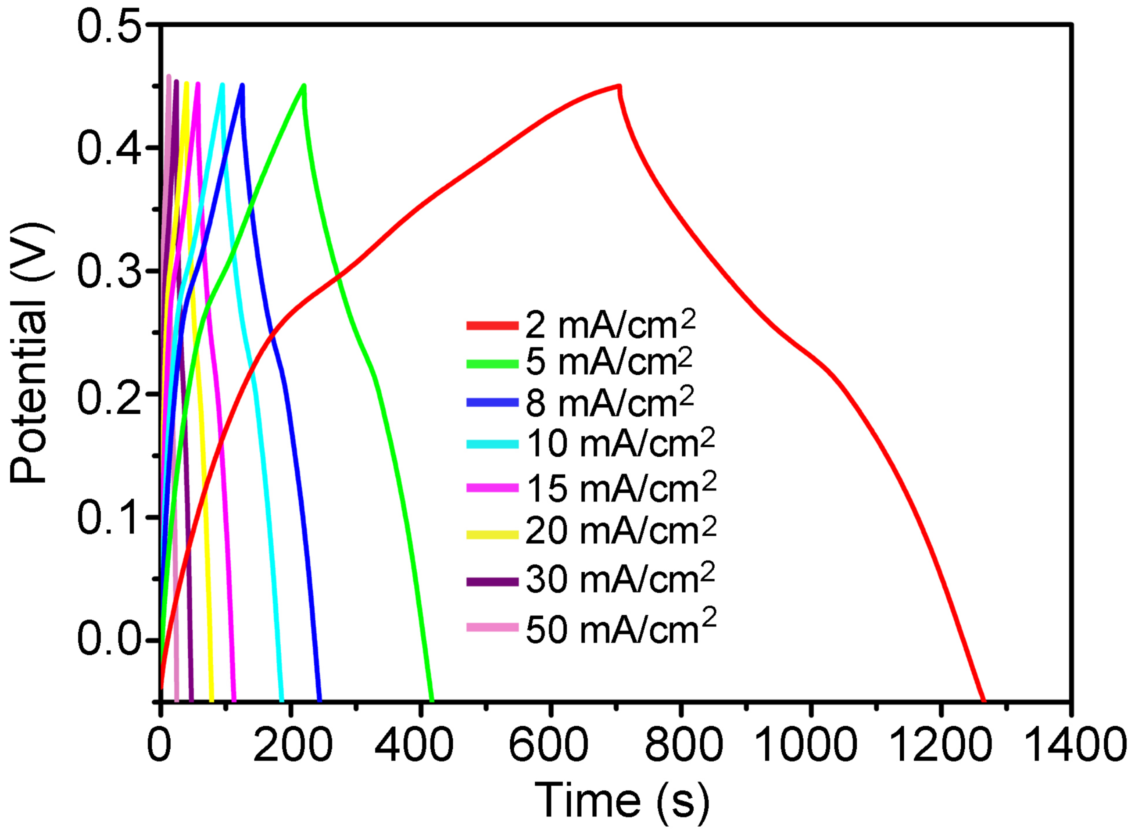

Figure S5. (a) CD curves of the $NiCo_2O_4@MnO_2$ electrode at different current densities.

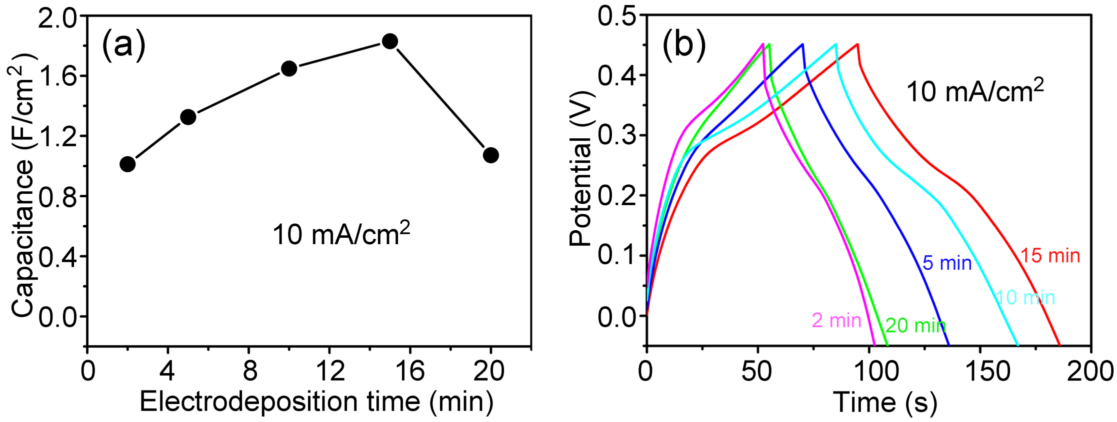

Figure S6. (a) Specific capacitance and (b) CD curves of the $NiCo_2O_4$@MnO_2 electrode as a function of the MnO_2 electrodeposition time.

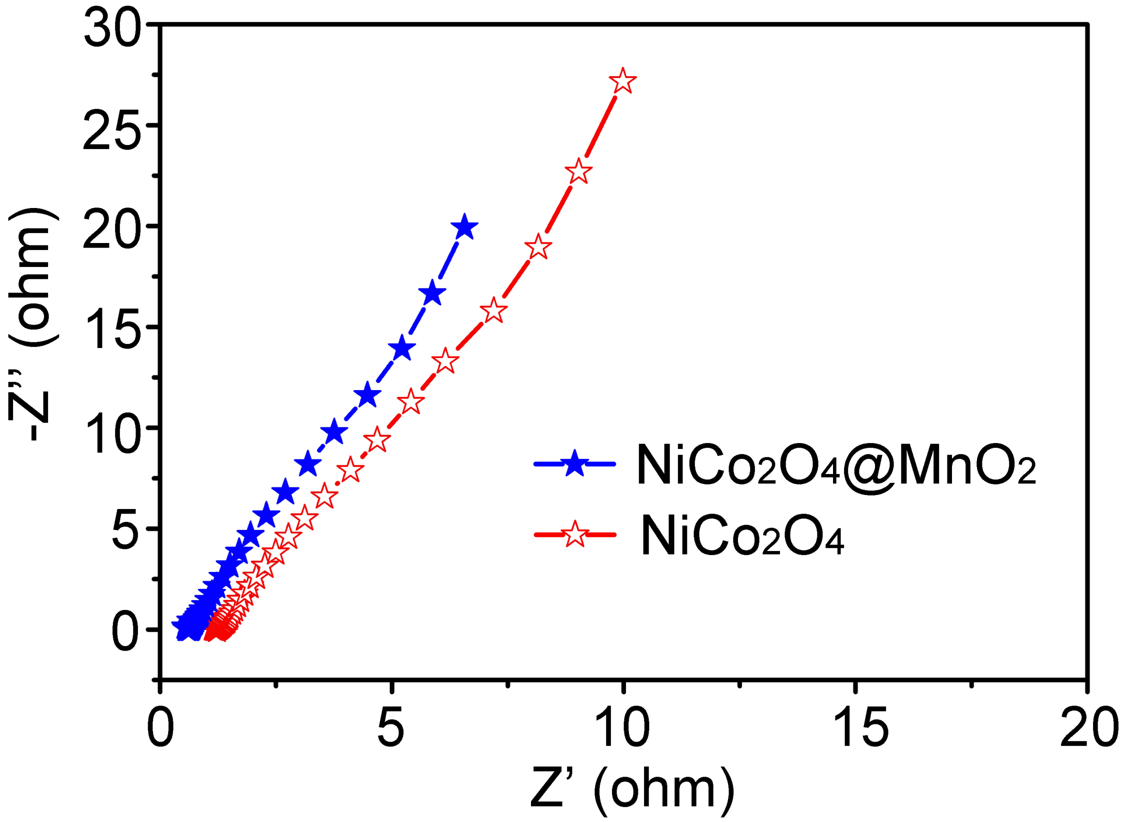

Figure S7. EIS spectra of the $NiCo_2O_4$@MnO_2 and $NiCo_2O_4$ electrode.

The EIS spectra are composed of three distinct regions.[6,7] First, the intercept on the real axis in the high frequency range provides the equivalent series resistance (ESR), which includes the inherent resistances of the electrode active material, bulk resistance of electrolyte, and contact resistance at the interface between electrolyte and electrode. Second, the charge transfer resistance (Rct), which results from diffusion of electrons, can be calculated from the diameter of semicircle in the high frequency range. Third, Warburg resistance, which describes the diffusion of redox species in the electrolyte, can be reflected from the slope of the EIS curve in the low frequency range. The equivalent series resistance (ESR) of the $NiCo_2O_4$@MnO_2 core-shell nanowires (0.9 Ω) is much smaller than that of the bare $NiCo_2O_4$ nanowires electrode (1.5 Ω), indicating a lower diffusion resistance.

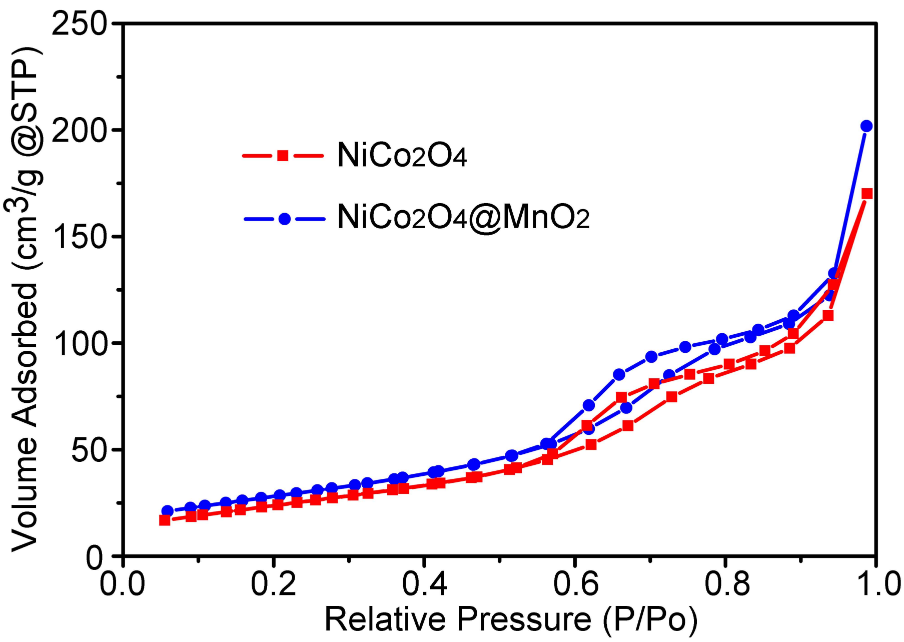

Figure S8. The BET surfaces of the $NiCo_2O_4$ and $NiCo_2O_4$@MnO_2.

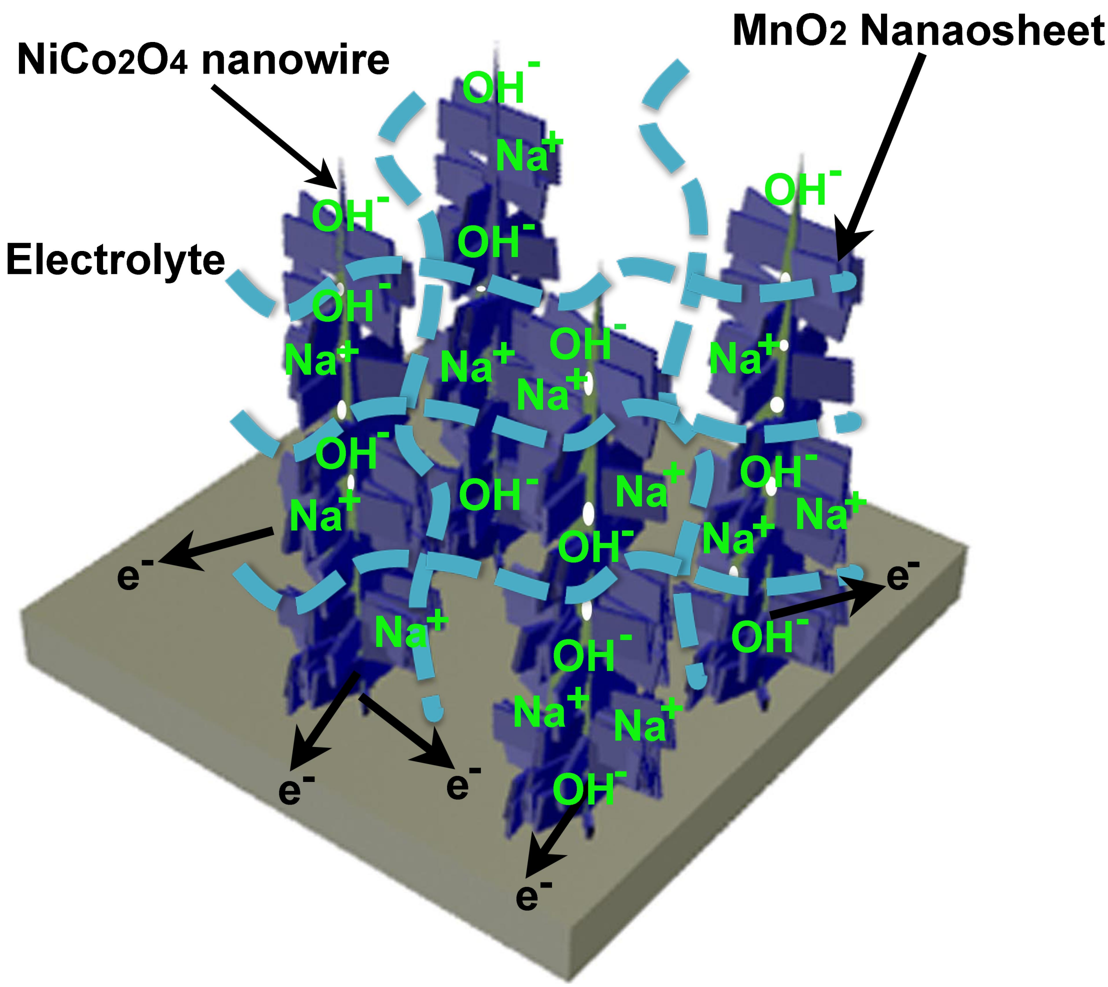

Figure S9. Schematic of the charge storage advantage of the hierarchical mesoporous $NiCo_2O_4$@MnO_2 core-shell nanowire arrays on Ni foam, in which both the $NiCo_2O_4$ core and MnO_2 shell materials contribute to the charge storage.

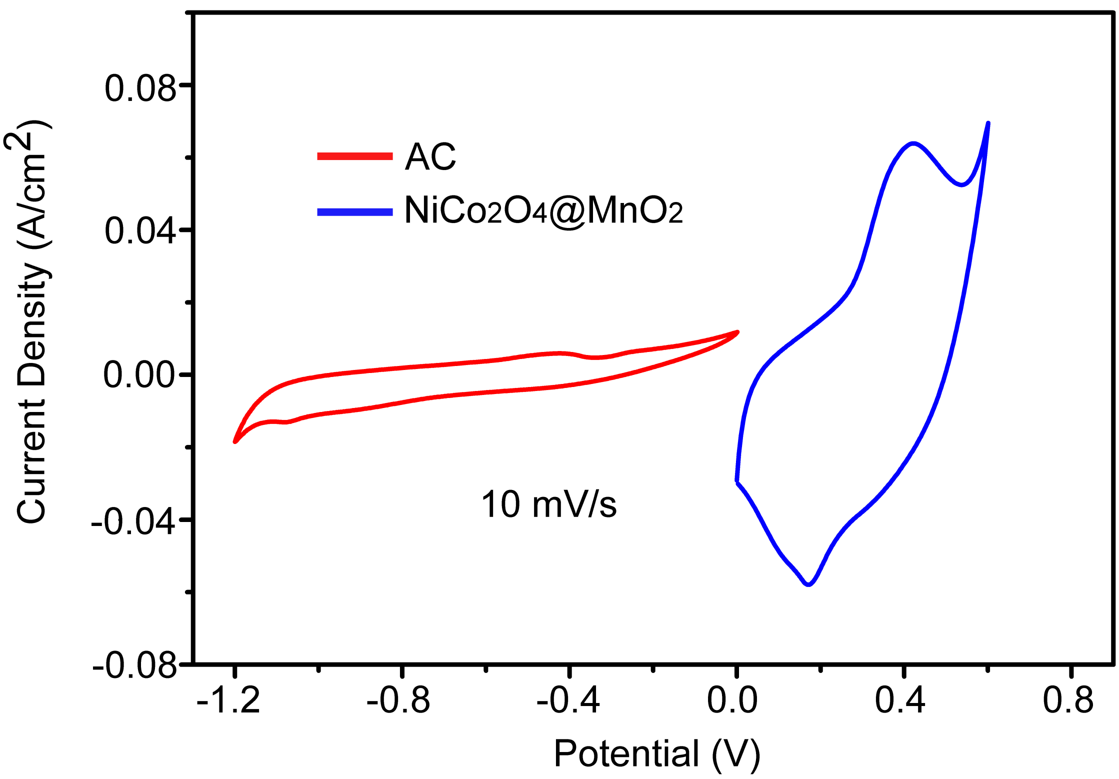

Figure S10. Comparative CV curves of the $NiCo_2O_4@MnO_2$ and activated carbon (AC) electrodes performed in a three-electrode cell at 10 mV/s.

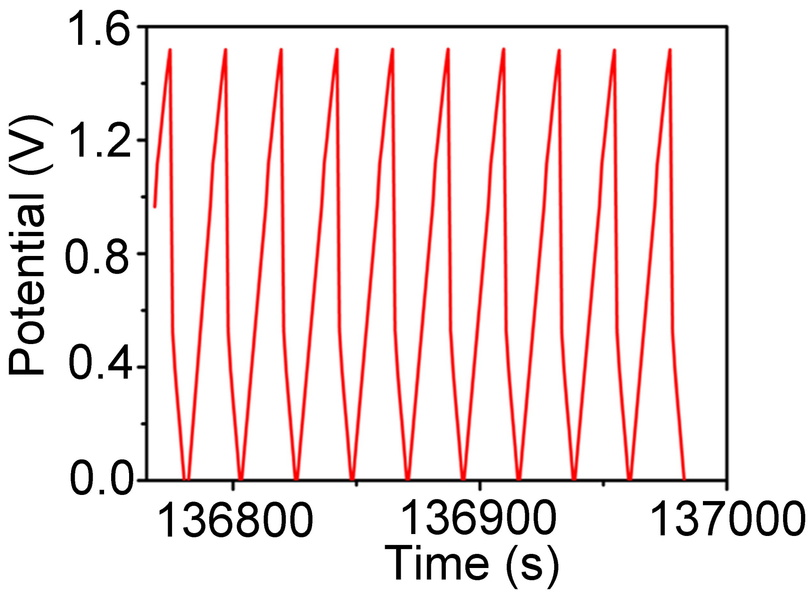

Figure S11. The CD curves of the last 10 cycles for the asymmetric supercapacitor.

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