Electronic supplementary information

High-performance supercapacitor and lithium-ion battery based on 3D hierarchical NH_4F-induced nickel cobaltate nanosheet-nanowire cluster arrays as self-supported electrodes

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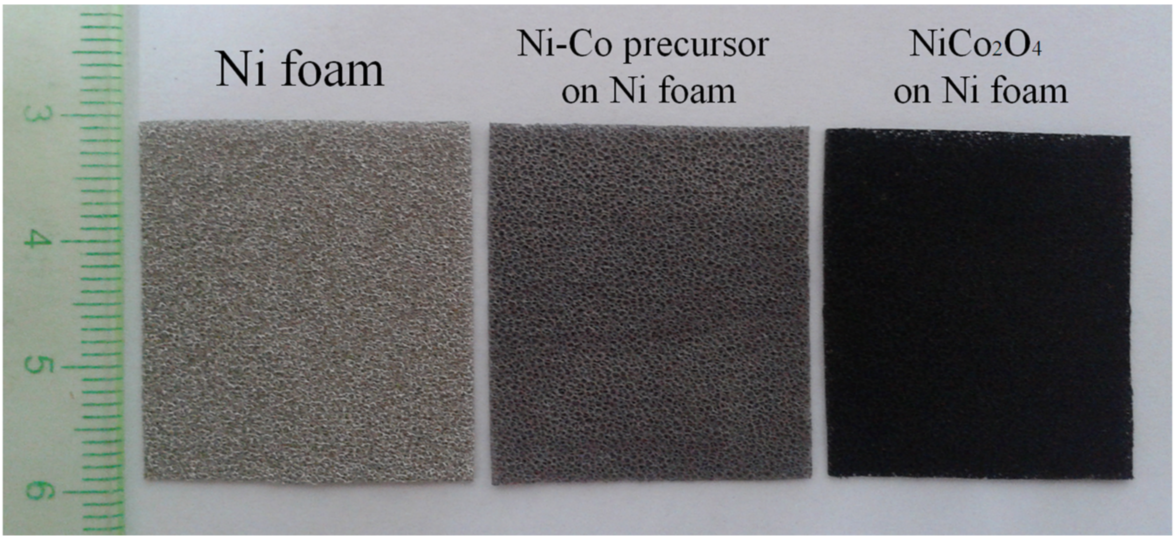

Figure S1. Photographs of Ni substrate, nickel cobalt hydroxide precursor on Ni foam and $NiCo_2O_4$ on Ni foam.

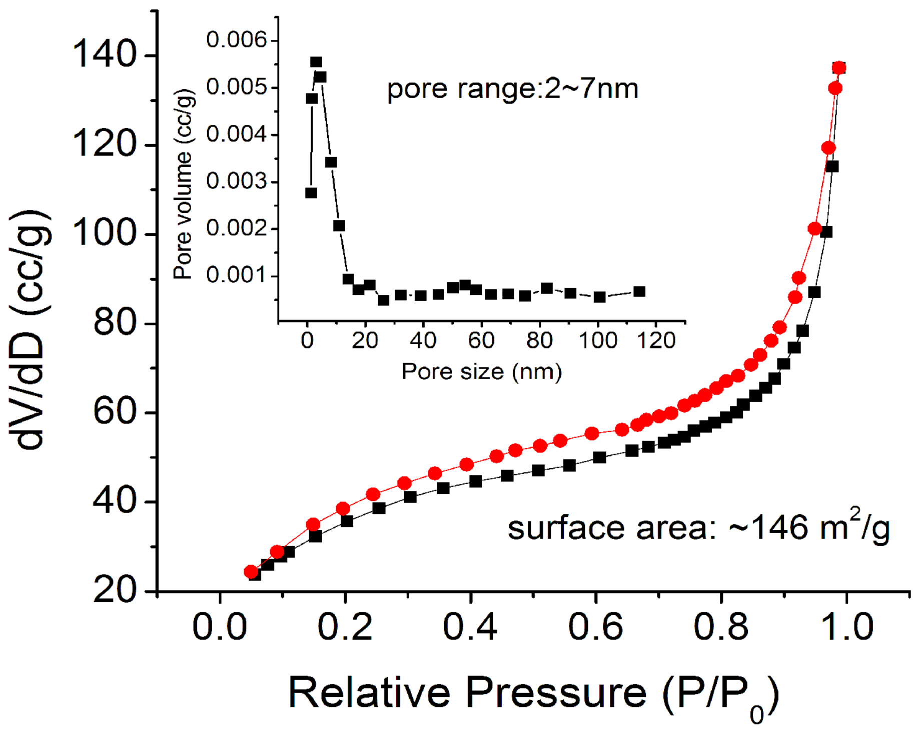

Figure S2. N_2 adsorption-desorption isotherm and pore size distribution curves of the $NiCo_2O_4$ NSWC scraped from the substrate.

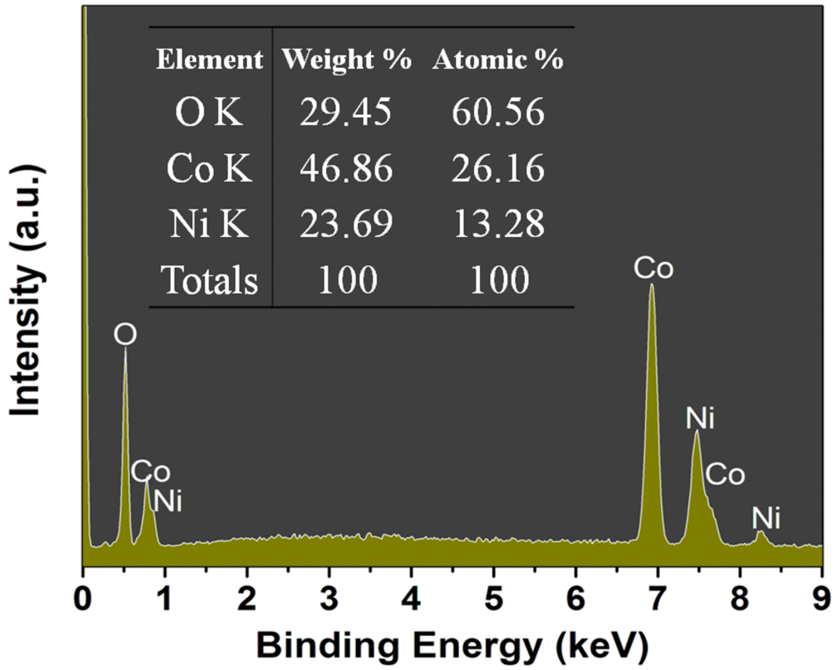

Figure S3. EDX pattern of the $NiCo_2O_4$ NSWC arrays.

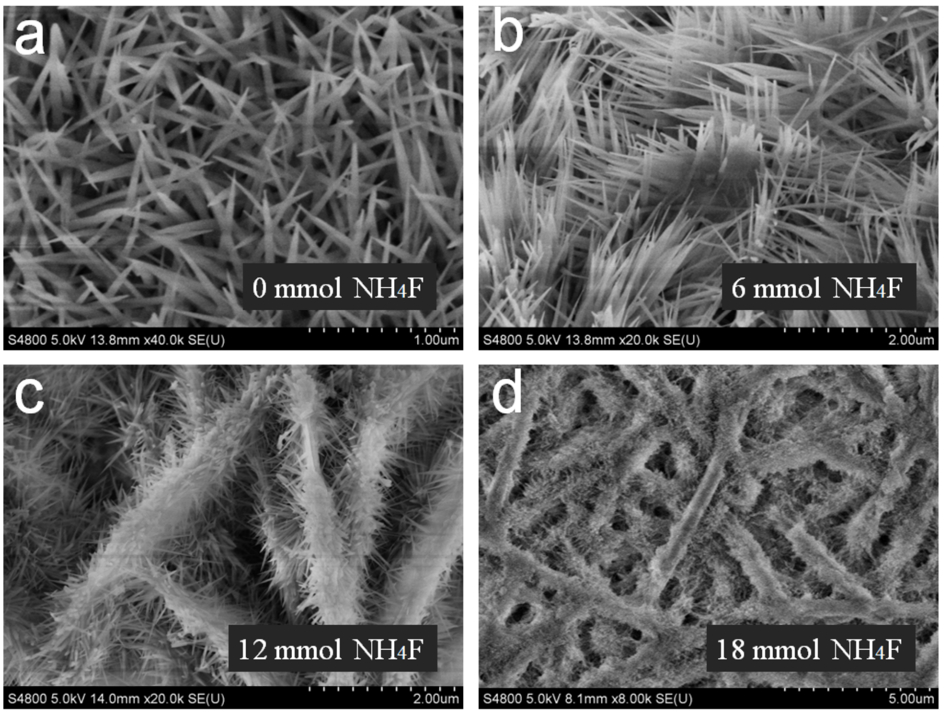

Figure S4. SEM images of the products grow on Ti foil obtained at different concentration of NH_4F.

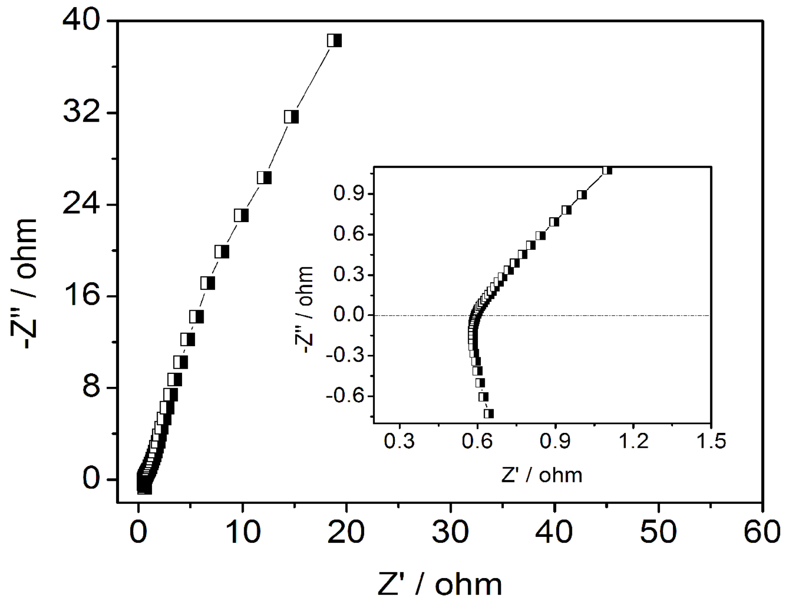

Figure S5. EIS plot of the $NiCo_2O_4$ NSWC/Ni foam electrode before cycling tests. The inset is an enlarged curve of the high frequency region.

The EIS data shows a solution resistance Rs (the intrinsic resistance of the electroactive materials, the contact resistance of material with substrate, the electrolyte resistance) and a charge-transfer resistance Rct. A vertical line leaning to imaginary axis in the low frequency range represents the solution resistance of about 0.59 Ω, indicating an ideal electronic conductivity and good electrochemical capacitance of the electrode. At high frequency region, it displays a negligible semicircle and a high slope, revealing the low charge transfer resistance (Rct) and fast ion diffusion rate during the redox reaction.

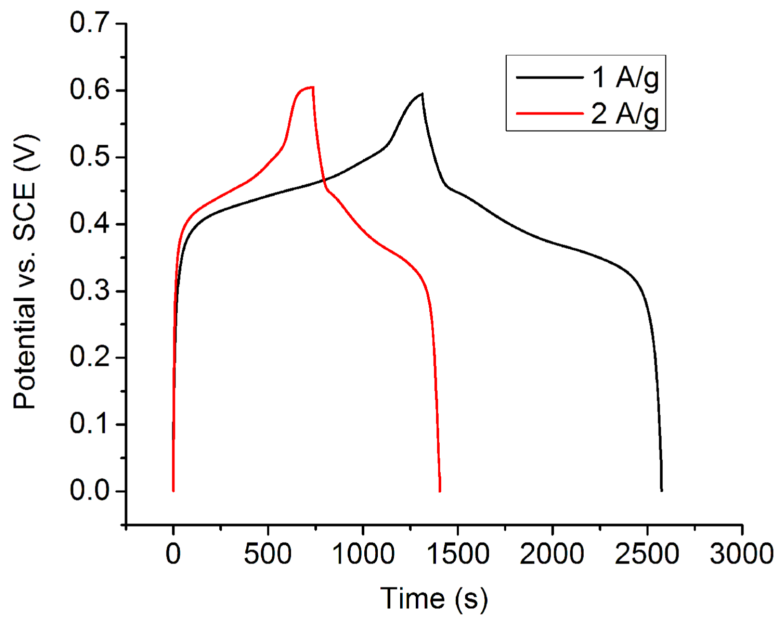

Figure S6. The capacitive performance of $NiCo_2O_4$ NSWC/Ni foam electrode at low current densities.

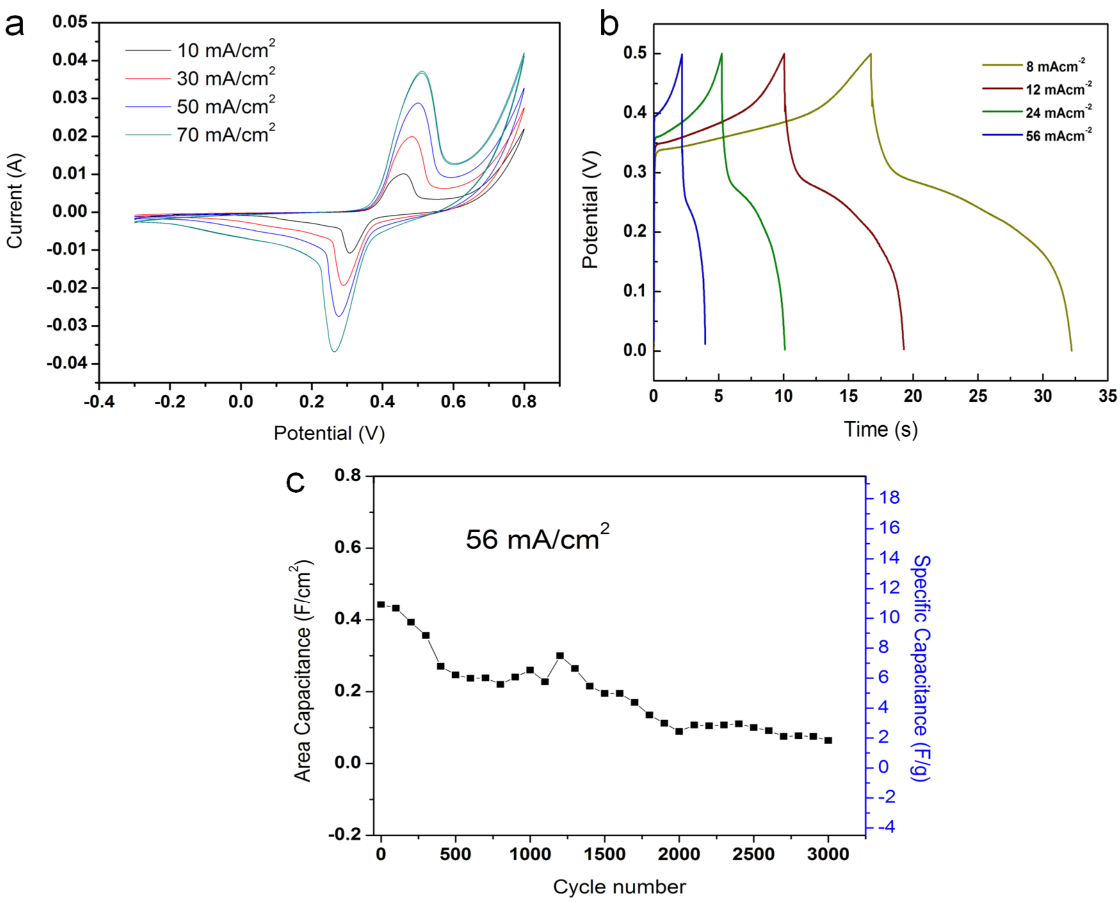

Figure S7. Electrochemical property of nickel foam (0.0402g/cm^2), obtained by hydrothermal treating at 100 °C for 5 h and subsequent calcination at 300 °C in purity argon for 2 h, was tested independently (a) at different scan rates; (b) at different charge-discharge rates; (c) Cycling performance of discharge electric quantity at the current density of 56 mA cm^{-2} (corresponding to 1.4 A/g).

Discussion on the contribution of nickel foam

It is clearly shown that the nickel foam shows a redox process which is attributed to the reversible reaction of Ni(II)/Ni(III) formed on the nickel surface. For a typical charge-discharge process of the active material on nickel foam (for example, current density is 56 mA/cm^2), the area capacitance is calculated to be 0.443 F/cm^2 (11 F/g for specific capacitance). And according to Fig. 5d, it is about 2.79 F/cm^2 (1550 F/g). After enduring about 3000 cycles at 56 mA/cm^2, the capacitance decreased by 80%. Obviously, the mass capacitance contribution from the nickel foam can be absolutely neglectable. And the area capacitance contribution from the nickel foam can also be neglectable after thousands of cycles.

Table S1. Comparison of area capacitance before and after removing the contributed part of Ni foam

Current density (mA cm^{-2})	Total capacitance (F cm^{-2})	Capacitance of Ni foam (F cm^{-2})	Real capacitance of $NiCo_2O_4$ (F cm^{-2})	Contribution of Ni foam
18	3.83	0.492	3.338	12.84%
27	3.39	0.473	2.917	13.95%
36	3.15	0.461	2.692	14.54%
54	2.79	0.443	2.347	15.87%
90	2.38	0.413	1.967	17.35%
144	2.09	0.376	1.714	17.99%

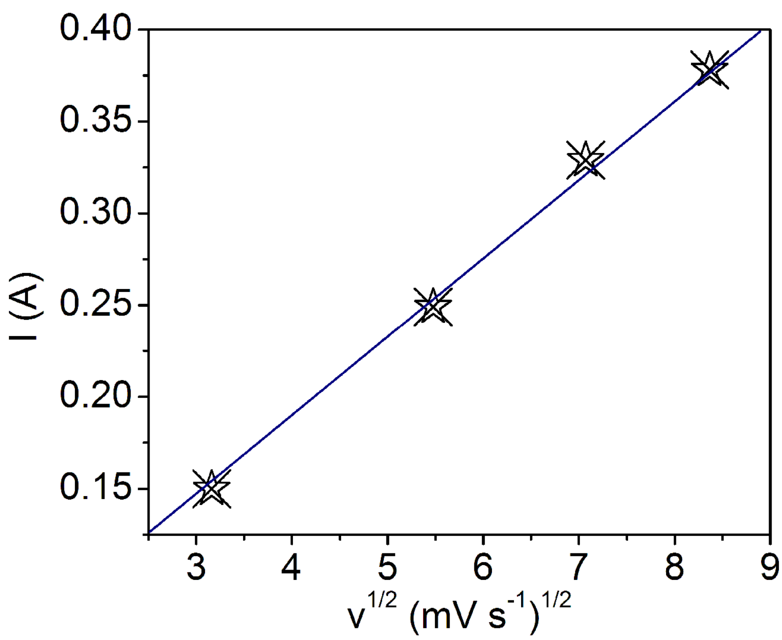

Figure S8. Dependence of the current density on $v^{1/2}$ for the $NiCo_2O_4$ nanosheets/Ni foam electrode.

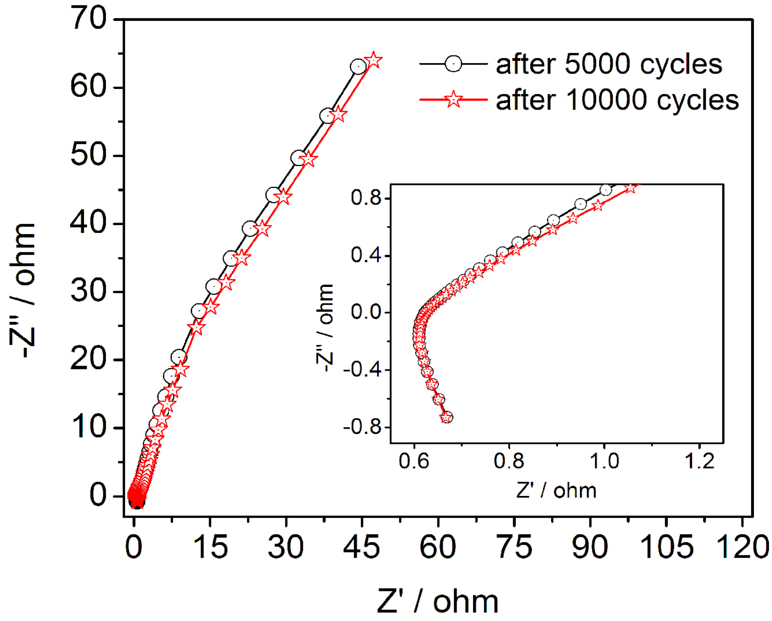

Figure S9. Nyquist plots of the EIS spectra for the $NiCo_2O_4$ NSWC/Ni foam electrode after 5000 and 10000 cycles, respectively

Table S2. Comparison of electrochemical performance

Nanostructures	Capacitance ($F\ g^{-1}$)	Capacitance ($F\ cm^{-2}$)	Current density	Capacitance loss	Reference
Single crystal $NiCo_2O_4$ nanoneedle arrays	1118.6	1.01	5.56 mA /cm^2	10.6 % after 2000 cycles	1
Ultrathin Mesoporous $NiCo_2O_4$ Nanosheets	1450	1.16	20 A/g (16 mA/cm^2)	6 % after 2300 cycles	2
Mesoporous $NiCo_2O_4$ Nanosheets	1708	2.05	19.8 mA /cm^2 (16.5 A/g)	6.7% after 3000 cycles	3
Hierarchical Co_3O_4@Ni–Co–O	1525	18.13	2.5 A/g (30 mA/cm^2)	4% after 1000 cycles	4
urchin-like $NiCo_2O_4$ nanostructures	1348	/	15 A/g	9.2 % after 2000 cycles	5
Hierarchical porous $NiCo_2O_4$ nanowires	743	/	1 A/g	6.2 % after 3000 cycles	6
$NiCo_2O_4$–reduced graphene oxide	615	/	20 A/g	/	7

composites					
$NiCo_2O_4$ NSWC arrays	1752	3.15	36 mA/cm^2 (20 A/g)	6.2% after 10200 cycles	This work

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