Electronic Supplementary Material (ESI) for Energy & Environmental Science

Electronic Supplementary Information

Single-crystalline $NiCo_2O_4$ Nanoneedle Arrays Grown on Conductive Substrates as Binder-free Electrodes for High-performance Supercapacitors

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Experimental Section

Synthesis of $NiCo_2O_4$ nanoneedle arrays on Ni foam and Ti foil. All the chemicals are directly used after purchase without further purification. In a typical synthesis, 2 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ and 4 mmol of $Co(NO_3)_2 \cdot 6H_2O$ are dissolved into a mixed solution of 40 mL of ethanol and 40 mL of H_2O at room temperature to form a clear pink solution, followed by the addition of 24 mmol of urea. The solution is then transferred to a 100 mL bottle with a blue cap. The Ni foam or Ti foil (2 cm x 4 cm in rectangular shape) is immersed in a 3 M HCl solution for 15 min to get rid of the possible surface oxide layer before it is put into the bottle for reaction. The bottle is then capped and heated to 85 ^{o}C in an electric oven. After reaction for 8 h, the sample is taken out after the solution is

cooled down to room temperature naturally, and cleaned by ultrasonication to remove the loosely attached products on the surface. After that, the Ni foam or Ti foil with grown products is dried at 60 ^{o}C for characterization. In order to get crystallized $NiCo_2O_4$ nanowires, the Ni foam or Ti foil with the as-grown precursor nanoneedles is annealed at a relatively low temperature of 250 ^{o}C for 90 min. This annealing will not cause oxidation of Ni foam.

Material characterization. The morphology of the samples is characterized by field-emission scanning electron microscopy (FESEM; JEOL-6700) and transmission electron microscopy (TEM; JEOL, JEM-2010). The high-resolution TEM (HRTEM) images are recorded by a JEOL-2100 microscope. The crystal phase of the products is examined by X-ray diffraction (XRD; Bruker, D8-Advance X-ray Diffractometer, Cu K*a*, λ = 1.5406 Å). The Brunauer-Emmett-Teller (BET) surface area of the $NiCo_2O_4$ nanoneedles is determined through nitrogen sorption measurement on Autosorb 6B at 77K.

Electrochemical measurements. The electrochemical tests were conducted with a CHI 660D electrochemical workstation in an aqueous KOH electrolyte (2.0 M) with a three-electrode cell where Pt foil serves as the counter electrode and a standard calomel electrode (SCE) as the reference electrode. The nominal area of the $NiCo_2O_4$-Ni foam immersed into the electrolyte is controlled to be around 1 cm x 1.8 cm. The mass loading of the $NiCo_2O_4$ nanowires on Ni foam is around 0.9 mg cm^{-2}.

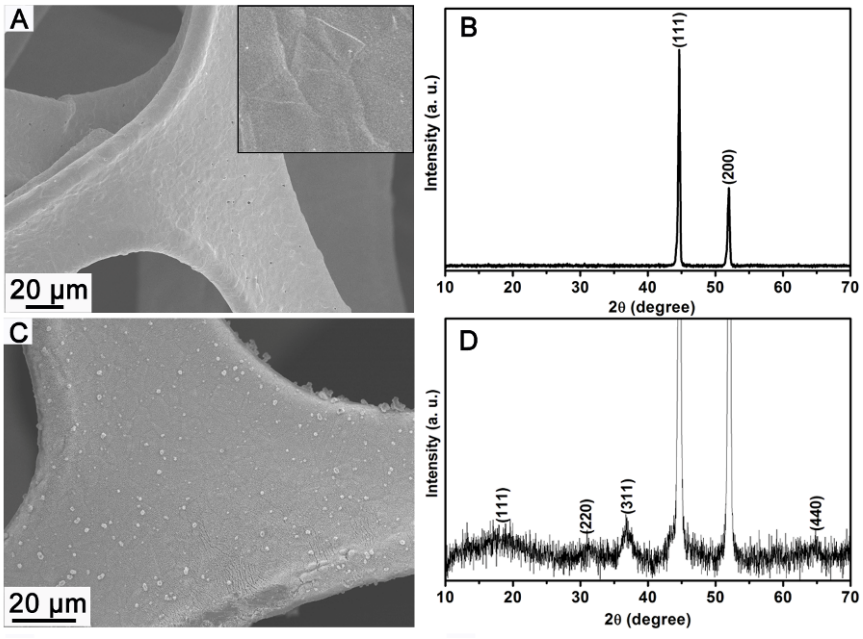

Figure S1. Typical FESEM images and corresponding XRD patterns of bare Ni foam and $NiCo_2O_4$ nanoneedle arrays/Ni foam hybrid structure: (A) FESEM image of bare Ni foam after the acid etching treatment, and (B) corresponding XRD pattern. (C) FESEM image of Ni foam after growing $NiCo_2O_4$ nanoneedles, and (D) corresponding XRD pattern.

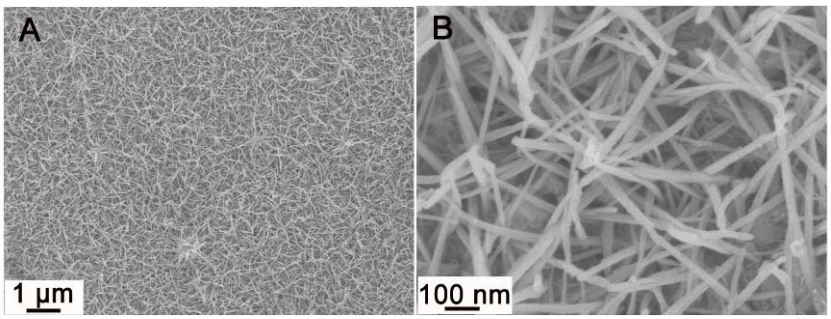

Figure S2. Typical FESEM images of the precursor nanowires by adding 48 mmol of urea in the reaction, which is double of the amount used for the product shown in Figure 1 in the maintext.

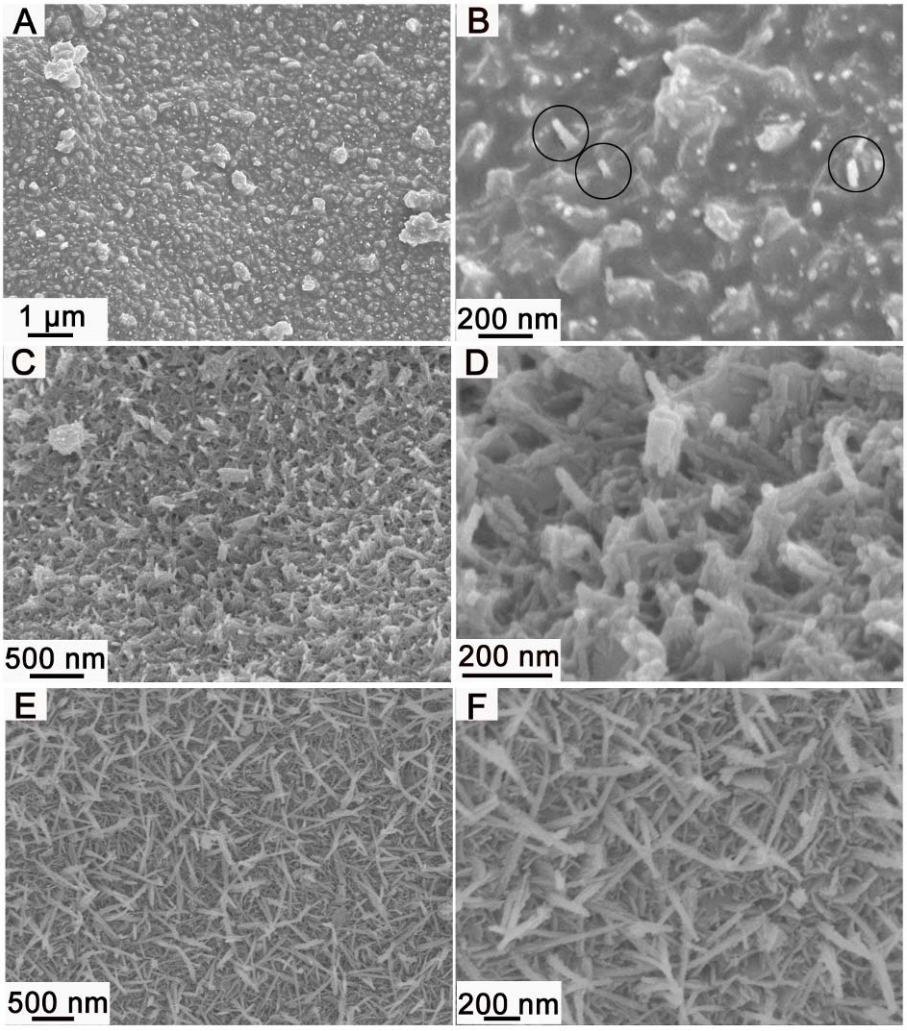

Figure S3. FESEM images of precursor nanowires on Ni foam with different reaction durations: (A, B) 30 min; (C, D) 2 h; and (E, F) 3 h.

Table S1. Comparison of electrochemical performance

Nanostructures	Capacitance ($F\ g^{-1}$)	Capacitance ($F\ cm^{-2}$)	Capacitance loss (%)	Current density
Single crystal nanoneedle arrays	1118.6	1.01	10.6 after 2000 cycles	5.56 mA/cm^2
Porous nanowires	743	/	6.2 after 3000 cycles	1 $A\ g^{-1}$
Ni-Co-O-n nanowires	760	/	19 after 3000 cycles	1 $A\ g^{-1}$
NiO-TiO_2 nanotube arrays	40-100	~3	Zero loss after 500 cycles	0.4 $mA\ cm^{-2}$
Co_3O_4@MnO_2 hybrid nanowires	/	0.56	2.7 after 5000 cycles	11.25 $mA\ cm^{-2}$
Co_3O_4@MnO_2 hybrid nanowires	480	/	/	2.67 $A\ g^{-1}$

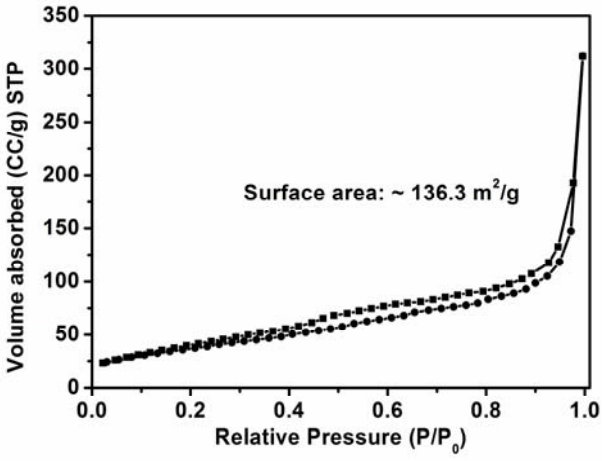

Figure S4. N_2 adsorption-desorption isotherm of the $NiCo_2O_4$ nanoneedles.

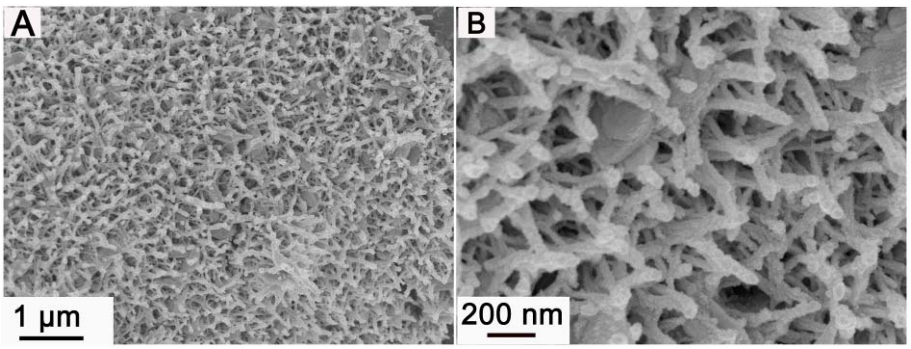

Figure S5. FESEM images of the $NiCo_2O_4$ nanowire arrays on Ni foam after charged/discharged for 2000 cycles at a current density of 5.56 mA cm^{-2}.