Electronic Supplementary Information

FeCo$_2$O$_4$ submicron-tube arrays grown on Ni foam as high rate-capability and cycling-stability electrodes allowing superior energy and power densities with symmetric supercapacitors

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Fig. S2. XPS spectra of the FeCo$_2$O$_4$ on Ni foam.

Fig. S3. SEM images of the FeCo$_2$O$_4$ grown on Ni foam obtained with different $C_{Fe^{3+}}$ of (a) 1.3 mM (b) 5.0 mM (c) 12.5 mM (d) 17.5 mM.

Fig. S4. TGA curve of a typical sample before thermal conversion, which was recorded from room temperature to 600$^\circ$C.

Fig. S5. SEM image (a) and CV curves (b) of typical FeCo$_2$O$_4$ tube arrays on Ni foam after ultrasound.

Table S1. Comparison of the optimal FeCo$_2$O$_4$ submicron tubes on Ni foam and previously reported ternary metal oxides of cobalt.
1. Experimental section

Synthesis. All reagents were analytical grade and used without further purification. 0.71 g of Fe(NO$_3$)$_3$•9H$_2$O and 1.02 g of Co (NO$_3$)$_2$•6H$_2$O were dispersed in 50 mL of deionized water. This solution was transferred into a 250 mL three-necked flask with cleaned nickel foam and heated to 80 °C. Then, 2.65 g of oxalic acid was dissolved in 50 mL of deionized water and then slowly injected into the flask. The thus resulting concentrations of Fe$^{3+}$, Co$^{2+}$, and oxalic acid were 17.5, 35, and 210 mM, respectively. The concentration of all reactants was changed together by diluting all solutions ($C_{Fe^{3+}}$ values are 12.5, 10, 5 and 1.25 mM). This ensures the desired stoicheometric ratios and provides one single parameter (the size of the three coupled concentrations) that can be systematically changed. The reaction system was kept at 80 °C for 2 h under mechanical agitation and then cooled to room temperature naturally. The product was collected, washed with deionized water, freeze-dried, and annealed in air at 400 °C for 2 h.

Materials characterizations. Powder X-ray diffraction (XRD) with a D/Max-RA X-ray diffractometer (Cu Ka =1.5418 A radiation) at 5° min$^{-1}$ characterized crystal structure and chemical compositions. Scanning electron microscopy (SEM) images were obtained on a field emission scanning electron microscopy (FE-SEM) on S-4800 (Hitachi) at 10 kV. Transmission electron microscopy (TEM), HRTEM, and selected area electron diffraction (SAED) were analyzed on a JEM-2100 (JEOL) at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) examined the valence states of elements in a Thermo VG Scientific MultiLab ESCA2000 system with a CLAM4 hemispherical analyzer at a base pressure below 3×10$^{-10}$ mbar. Thermogravimetric
analysis (TGA) was performed on a TGA/SDTA thermogravimetric analyzer from room temperature to 600°C in air at a heating rate of 20 °C min⁻¹.

**Electrochemical measurements.** The electrochemical performance was evaluated with a typical three-electrode system on a Metrohm Autolab 302N electrochemical workstation at room temperature in 3 M KOH aqueous solution. The FeCo₂O₄ on Ni foam (2 cm × 1 cm) was used as the working electrode; a platinum plate served as counter electrode and a Ag/AgCl reference electrode was used. Cyclic voltammetry (CV) scans were measured between -0.2 and 0.6 V at various scan rates. Galvanostatic charge–discharge (CD) cycle tests were investigated in the range of zero to 0.6 V at various current densities. Specific capacitances were calculated from the galvanostatic CD curves. Specific areal capacitances \( C_a \) were calculated using \( C_a = I \Delta t/(S \Delta V) \), where \( I \) is the applied current, \( \Delta V \) is the selected, linear voltage drop, \( \Delta t \) is the corresponding discharge time, and \( S \) is the area of the electrode \( (S = \text{length} \times \text{width}) \). \( I/S \) is the current density and \( \Delta V/\Delta t \) is the slope of the discharge along the selected linear region. For the electrode obtained at \( C_{Fe^{3+}} = 10 \text{ mM} \) observed with a current density of 2 mA/cm² (see blue line in Fig. 3b), the most linear discharge voltage drop range extends from 0.55 to 0.4 V with the corresponding \( \Delta t \) being from 415 s to 556 s. Therefore, \( C_a = 2 \text{ mA/cm}^2 \times 141 \text{ s}/0.15 \text{ V} = 1.88 \text{ F/cm}^2 \). In the same way, at 4, 10, 20, 40 and 100 mA/cm² (Fig. 4b), the \( C_a \) are 1.78, 1.64, 1.56, 1.46 and 1.38 F/cm², respectively. The corresponding gravimetric capacitances are \( C_g = I \Delta t/(m \Delta V) \), where \( m \) is the mass of the active material, and other parameters are the same as above, thus \( C_g = S \times C_g/m \). For example, at 4 mA /cm², the mass density \( m/S = 1.5 \text{ mg/cm}^2 \) (obtained from TGA) leads to \( C_g = 1186 \text{ F/g} \).
The electrical impedance spectroscopy (EIS) was tested in the range from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV. Cycling life was investigated on a Land Battery Test System (Wuhan Kingnuo Electronic Company, China). The anode was the FeCo$_2$O$_4$/Ni foam electrode, and the cathode was blank nickel foam.

All-solid-state symmetric supercapacitors were assembled with PVA/KOH as separator and electrolyte between two FeCo$_2$O$_4$ electrodes. PVA/KOH composite gel electrolyte was prepared by mixing PVA powder (1.5 g), KOH (1 g), and deionized water (18 mL) under a vigorous stir at 95 ℃ until the solution became homogeneous. The CV scans were investigated between 0-1 V at various scan rates. CD testing was performed from 0-0.7 V at various current densities. Energy density ($E$) was calculated using $0.5 C_s \Delta V^2$. Power density ($P$) was calculated via $P = E/\Delta t$. 
2. Figures and figure captions

Fig. S1. The tubes before thermal treatment: (a) SEM images, (b) low- and (c) high-magnification TEM, and (e) HRTEM images
Fig. S2. XPS spectra of the FeCo$_2$O$_4$ on Ni foam: In the high-resolution Fe2$p$ XPS spectrum (a), three peaks are observed at 709.9, 714.1 and 722.6 eV, indicating the presence of Fe$^{2+}$. In the Co2$p$ XPS spectrum (b), five peaks reside at 779.2, 780.7, 785.1, 794.6 and 801.7 eV, which indicates that Co$^{2+}$ and Co$^{3+}$ exist together.$^{1,2}$

References:
Fig. S3. SEM images of the FeCo$_2$O$_4$ grown on Ni foam obtained with different $C_{Fe^{3+}}$ of (a) 1.3 mM (b) 5.0 mM (c) 12.5 mM (d) 17.5 mM.
Fig. S4. TGA curve of a typical sample before thermal conversion, which was recorded from room temperature to 600°C.

The TGA curve of a typical sample ($C_{Fe^{3+}} = 10$ mM) before thermal conversion shows an initial mass loss due to the evaporation of water. The loss between 190°C to 350 °C (stage II) results from the decomposition. The FeCo$_2$O$_4$ content in this sample is thus 12.77 wt.%, and its mass density in the electrode 1.5 mg cm$^{-2}$. 
**Fig. S5.** SEM image (a) and CV curves (b) of typical FeCo$_2$O$_4$ tube arrays on Ni foam after ultrasound.

**Table S1.** Comparison of the optimal FeCo$_2$O$_4$ submicron tubes on Ni foam and previously reported ternary metal oxides of cobalt

<table>
<thead>
<tr>
<th>Composites</th>
<th>Specific capacitance</th>
<th>Rate capability</th>
<th>Cycling stability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCo$_2$O$_4$ submicron tubes</td>
<td>1254 F/g at 2 mA/cm$^2$</td>
<td>73% from 2 to 100 mA/cm$^2$</td>
<td>91% after 5000</td>
<td>This work</td>
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<td>MnCo$_2$O$_4$ nanoparticles</td>
<td>405 F/g at 5 mA/cm$^2$</td>
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<td>CuCo$_2$O$_4$ particles</td>
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<td>26% from 1 to 50 A/g</td>
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<td>ZnCo$_2$O$_4$ nanotubes</td>
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<td>NiCo$_2$O$_4$ nanoparticles</td>
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<td>NiCo$_2$O$_4$ nanosheets</td>
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<td>52% from 1 to 20 A/g</td>
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<td>84.4% after 3000</td>
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<tr>
<td>NiCo$_2$O$_4$ nanoparticles</td>
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<td>54.1% from 1 to 20 A/g</td>
<td>70.4% after 1000</td>
<td>26</td>
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</tbody>
</table>