Supporting Information

Nickel foam supported mesoporous NiCo$_2$O$_4$ arrays with excellent methanol electro-oxidation performance

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Fig. S1 TGA plots for the precursors of (A) NCO-NS and (B) NCO-NC
**Fig. S2** XRD patterns of NCO-NS (black line) and NCO-NC (red line) scratched down from nickel foam
Fig. S3 High-resolution XPS spectra of (A) Co 2p and (B) Ni 2p of NCO-NS
Fig. S4 EDS analysis of (A) NCO-NS and (B) NCO-NC
Fig. S5 The high-magnification images of NCO-NC grown on nickel foam.
Fig. S6 CV plots of Co$_3$O$_4$ and NiO electrodes in 1 M KOH with 0.5 M methanol at a scan rate of 10 mV s$^{-1}$. 
**Fig. S7** XRD patterns of NiO (black line) and Co$_3$O$_4$ (red line) scratched down from nickel foam.
Fig. S8 SEM images of (A-C) NiO and (D-E) Co$_3$O$_4$ grown on nickel foam
**Fig. S9** Raman spectra of 1 M KOH electrolytes with 0.5 M methanol after 500 cycles.

The peaks around 1017 cm\(^{-1}\) and 1461 cm\(^{-1}\) are C-O stretching mode and CH\(_3\) bending mode of CH\(_3\)OH (J. Phys. Chem., 1980, 84, 3130). In addition, it can be clearly see that the additional peaks around 910, 1066, 1353 and 1461 cm\(^{-1}\) (overlapping peaks), which maybe belong to the symmetric C-O stretching mode, antisymmetric C-O stretching mode, C-H wagging motion and C=O in plane of HCOH (J. Phys. Chem. B, 2005, 109, 432). The involvement of OH and CHO species as intermediates in the electro-oxidation of methanol has been proposed in elsewhere (Electrochim. Acta, 1998, 44, 1135. Journal of Power Sources, 2008, 185, 776). Therefore, Raman spectra of electrolytes can prove that CH\(_3\)OH has been oxidized to other intermediate products.
**Fig. S10** CV plot of blank nickel foam in 1 M KOH with 0.5 M methanol at a scan rate of 10 mV s$^{-1}$
Table 1

The fitting values of impedimetric parameters for both NiCo$_2$O$_4$ electrodes in 1 M KOH electrolytes with and without 0.5 M methanol.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Impedimetric parameters</th>
<th>L (Ω cm$^{-2}$)</th>
<th>$R_s$ (Ω cm$^{-2}$)</th>
<th>$Q_1$, $Y_0$ (Ω$^{-1}$ S$^n$ cm$^{-2}$)</th>
<th>$R_{ct}$ (Ω cm$^{-2}$)</th>
<th>$W$, $Y_0$ (Ω$^{-1}$ S$^{0.5}$ cm$^{-2}$)</th>
<th>$Q_2$, $Y_0$ (Ω$^{-1}$ S$^n$ cm$^{-2}$)</th>
<th>n1</th>
<th>n2</th>
<th>$f_{knee}$ (Hz)</th>
<th>C (F cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO-NCO-NS</td>
<td></td>
<td>7.4E$^{-7}$</td>
<td>1.59</td>
<td>2.6E$^{-3}$</td>
<td>4.27</td>
<td>0.67</td>
<td>0.6</td>
<td>0.18</td>
<td>0.96</td>
<td>6.8</td>
<td>-</td>
</tr>
<tr>
<td>WO-NCO-NC</td>
<td></td>
<td>9.5E$^{-7}$</td>
<td>0.87</td>
<td>3.7E$^{-3}$</td>
<td>0.89</td>
<td>0.55</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>31.6</td>
<td>0.3</td>
</tr>
<tr>
<td>W-NCO-NS</td>
<td></td>
<td>6.4E$^{-7}$</td>
<td>1.75</td>
<td>7.5E$^{-3}$</td>
<td>5.02</td>
<td>0.24</td>
<td>0.34</td>
<td>0.6</td>
<td>0.98</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>W-NCO-NC</td>
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<td>7.4E$^{-7}$</td>
<td>1.33</td>
<td>7.1E$^{-3}$</td>
<td>0.86</td>
<td>0.97</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
<td>26.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Note: The symbols “W” and “WO” represent the 1 M KOH electrolytes with and without 0.5 M methanol respectively.