

## Supporting Information

### **Nickel foam supported mesoporous NiCo<sub>2</sub>O<sub>4</sub> arrays with excellent methanol electro-oxidation performance**

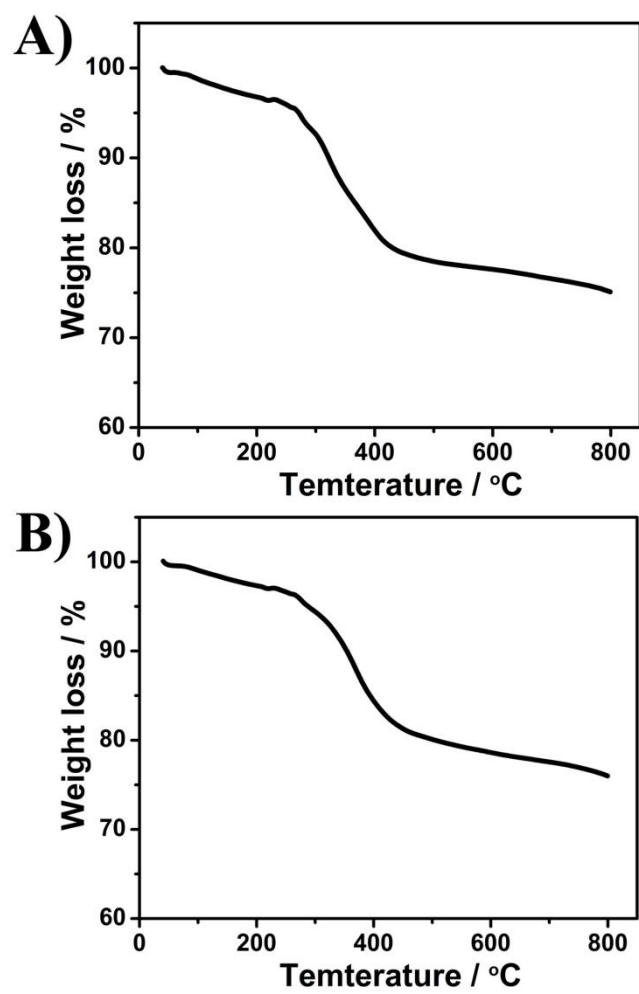
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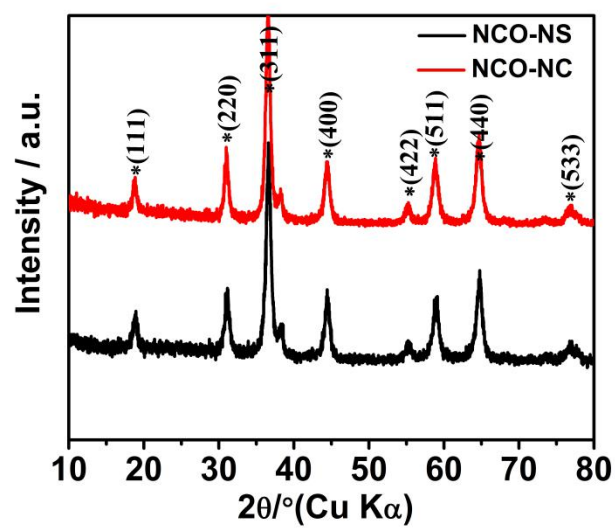
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E-mail:liuxy@jlu.edu.cn

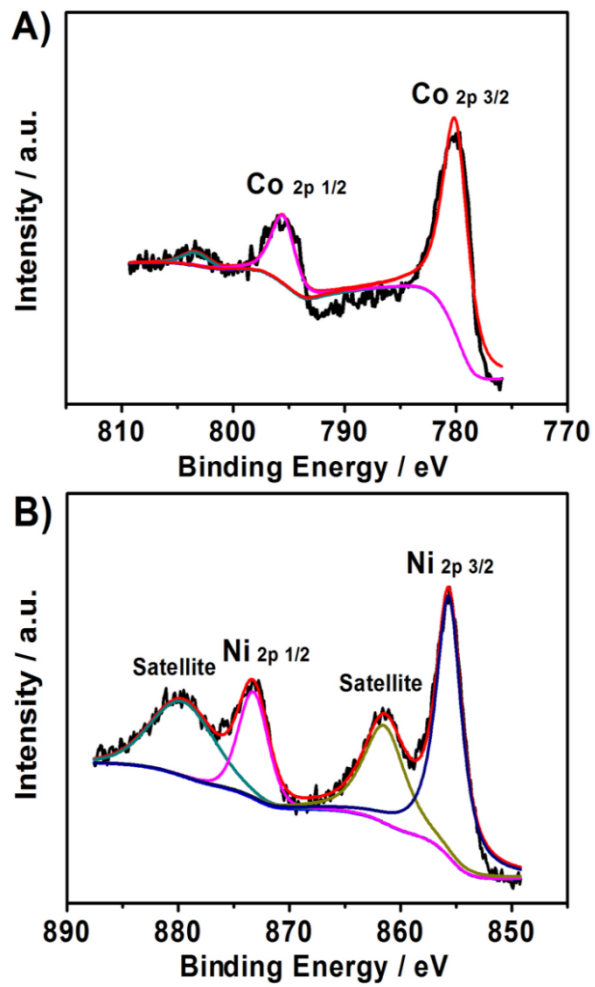
<sup>b</sup>Center for High Pressure Science and Technology Advanced Research, Changchun 130012, China.



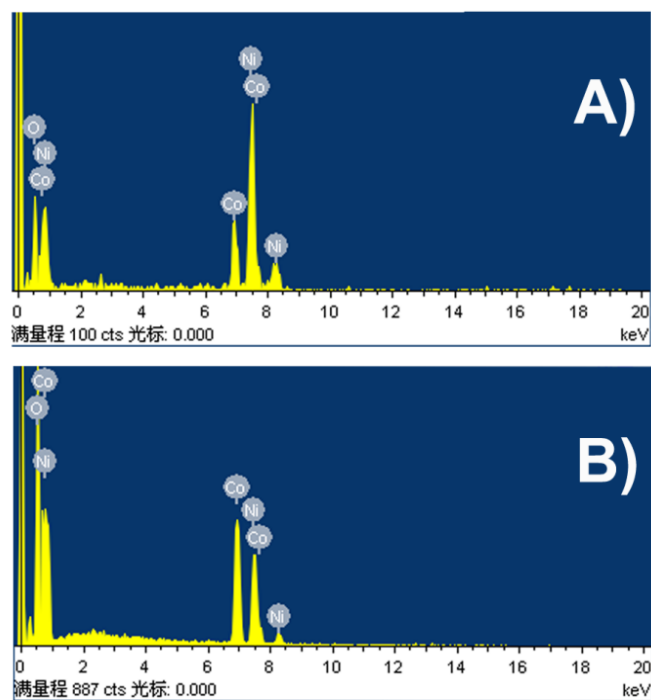
**Fig. S1** TGA plots for the precursors of (A) NCO-NS and (B) NCO-NC



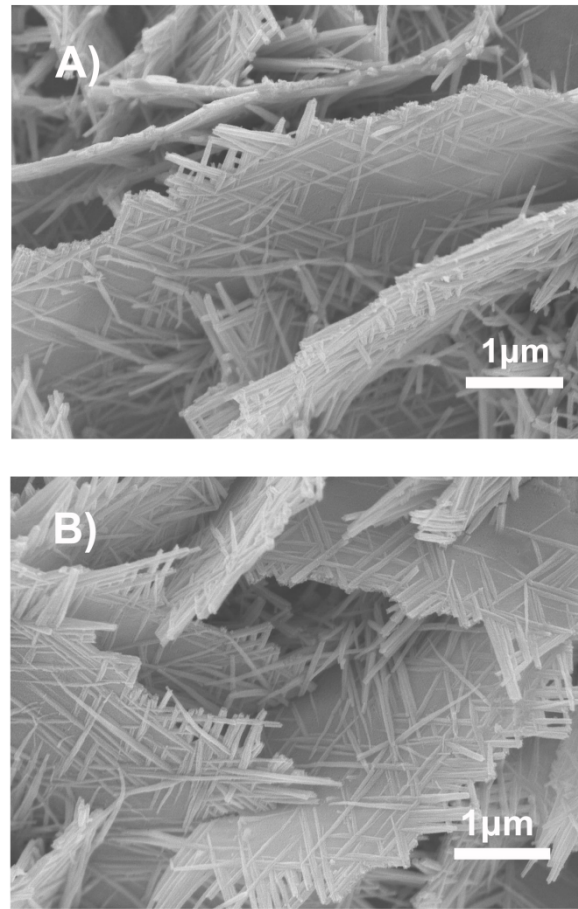
**Fig. S2** XRD patterns of NCO-NS (black line) and NCO-NC (red line) scratched down from nickel foam



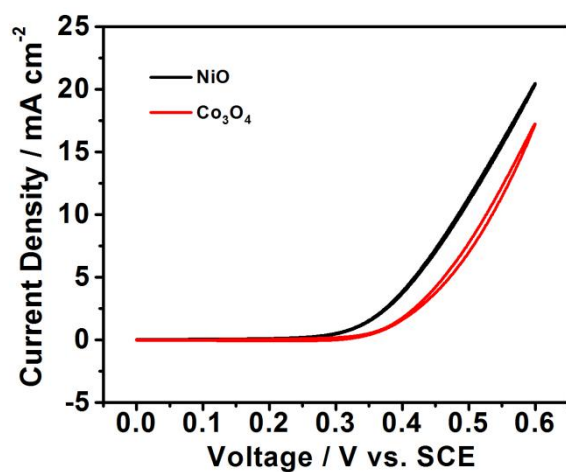
**Fig. S3** High-resolution XPS spectra of (A) Co 2p and (B) Ni 2p of NCO-NS



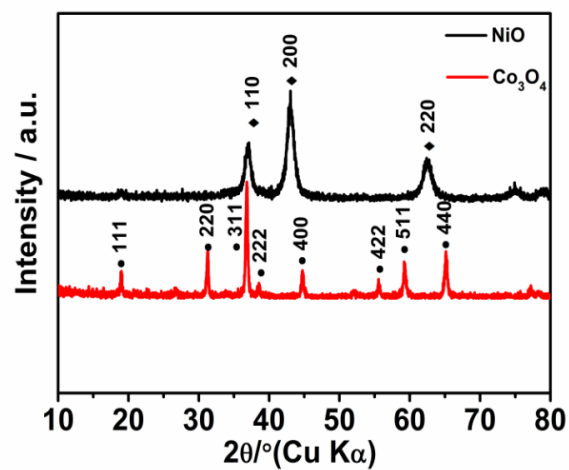
**Fig. S4** EDS analysis of (A) NCO-NS and (B) NCO-NC



**Fig. S5** The high-magnification images of NCO-NC grown on nickel foam.

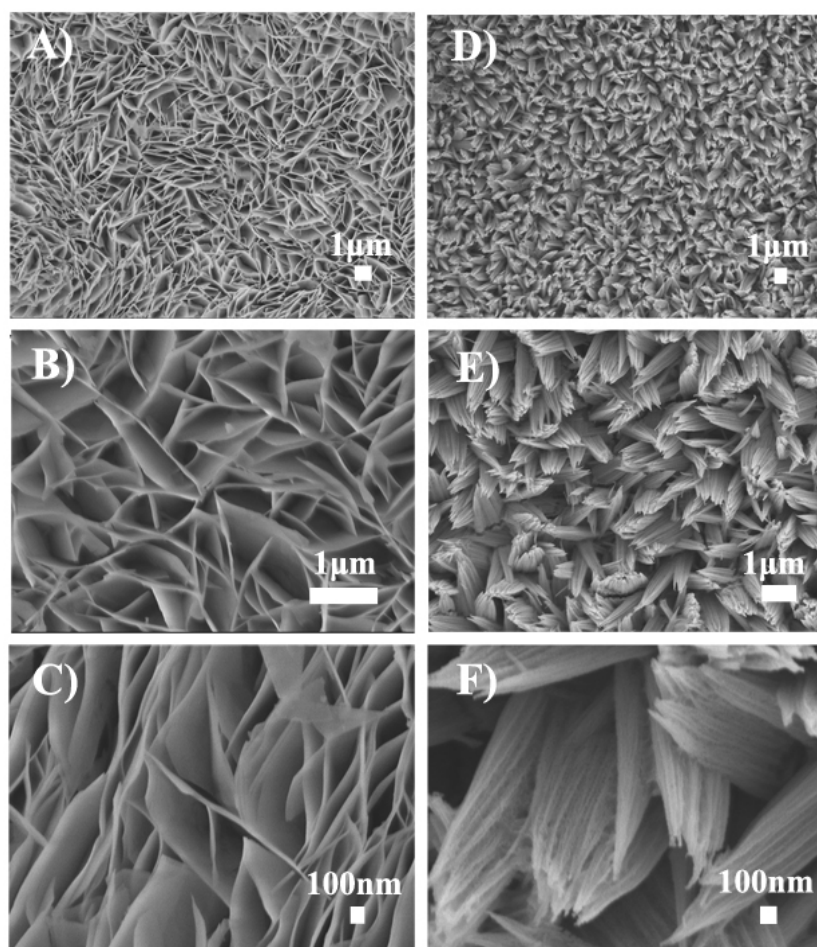


**Fig. S6** CV plots of Co<sub>3</sub>O<sub>4</sub> and NiO electrodes in 1 M KOH with 0.5 M methanol at a scan rate of 10 mV s<sup>-1</sup>

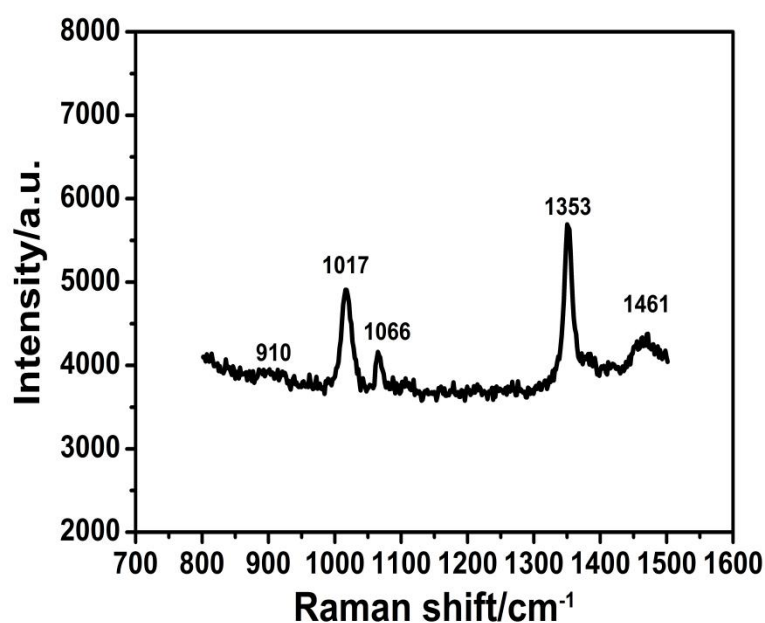


**Fig. S7** XRD patterns of NiO (black line) and Co<sub>3</sub>O<sub>4</sub> (red line) scratched down from nickel foam

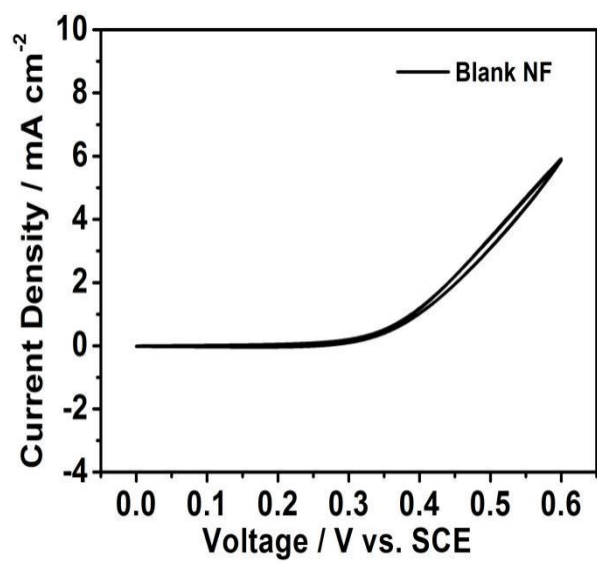




**Fig. S8** SEM images of (A-C) NiO and (D-E) Co<sub>3</sub>O<sub>4</sub> grown on nickel foam



**Fig. S9** Raman spectra of 1 M KOH electrolytes with 0.5 M methanol after 500 cycles. The peaks around  $1017\text{ cm}^{-1}$  and  $1461\text{ cm}^{-1}$  are C-O stretching mode and  $\text{CH}_3$  bending mode of  $\text{CH}_3\text{OH}$  (J. Phys. Chem., 1980, 84, 3130). In addition, it can be clearly see that the additional peaks around 910, 1066, 1353 and  $1461\text{ cm}^{-1}$ ( 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  $\text{CH}_3\text{OH}$  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<sup>-1</sup>

**Table 1**

The fitting values of impedimetric parameters for both NiCo<sub>2</sub>O<sub>4</sub> electrodes in 1 M KOH electrolytes with and without 0.5 M methanol.

Electrode	Impedimetric parameters									
	L	R <sub>e</sub>	Q <sub>1</sub> , Y <sub>0</sub>	R <sub>ct</sub>	W, Y <sub>0</sub>	Q <sub>2</sub> , Y <sub>0</sub>	n1	n2	f <sub>knee</sub>	C
	(Ω cm <sup>2</sup> )	(Ω cm <sup>2</sup> )	(Ω <sup>-1</sup> S <sup>n</sup> cm <sup>-2</sup> )	(Ω cm <sup>2</sup> )	(Ω <sup>-1</sup> S <sup>0.5</sup> cm <sup>-2</sup> )	(Ω <sup>-1</sup> S <sup>n</sup> cm <sup>-2</sup> )			(Hz)	(F cm <sup>-2</sup> )
WO-NCO-NS	7.4E <sup>-7</sup>	1.59	2.6E <sup>-3</sup>	4.27	0.67	0.18	0.6	0.96	6.8	-
WO-NCO-NC	9.5E <sup>-7</sup>	0.87	3.7E <sup>-3</sup>	0.89	0.55	-	0.7	-	31.6	0.3
W-NCO-NS	6.4E <sup>-7</sup>	1.75	7.5E <sup>-3</sup>	5.02	0.24	0.34	0.6	0.98	2.2	-
W-NCO-NC	7.4E <sup>-7</sup>	1.33	7.1E <sup>-3</sup>	0.86	0.97	-	0.6	-	26.1	0.3

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