Electronic Supplementary Information for

Free standing growth of $MnCo_2O_4$ nanoflakes as an electrocatalyst for methanol electro-oxidation

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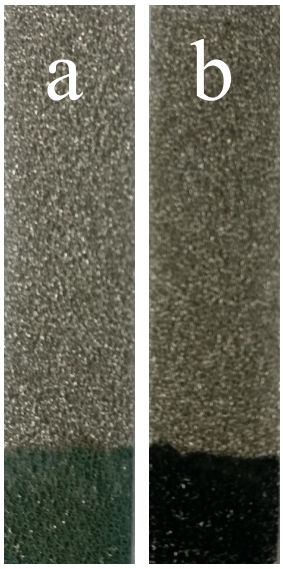


Figure S1: Photographs of (a) MnCo-hydroxide (b) $MnCo_2O_4$ grown on nickel foam.

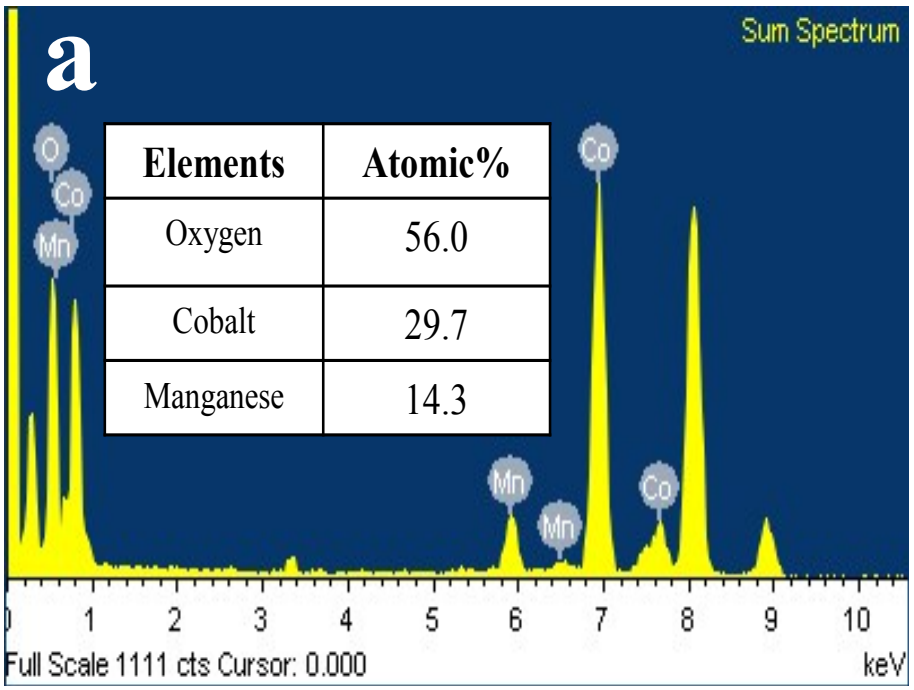


Figure S2. EDX spectrum of the $MnCo_2O_4$ sample.

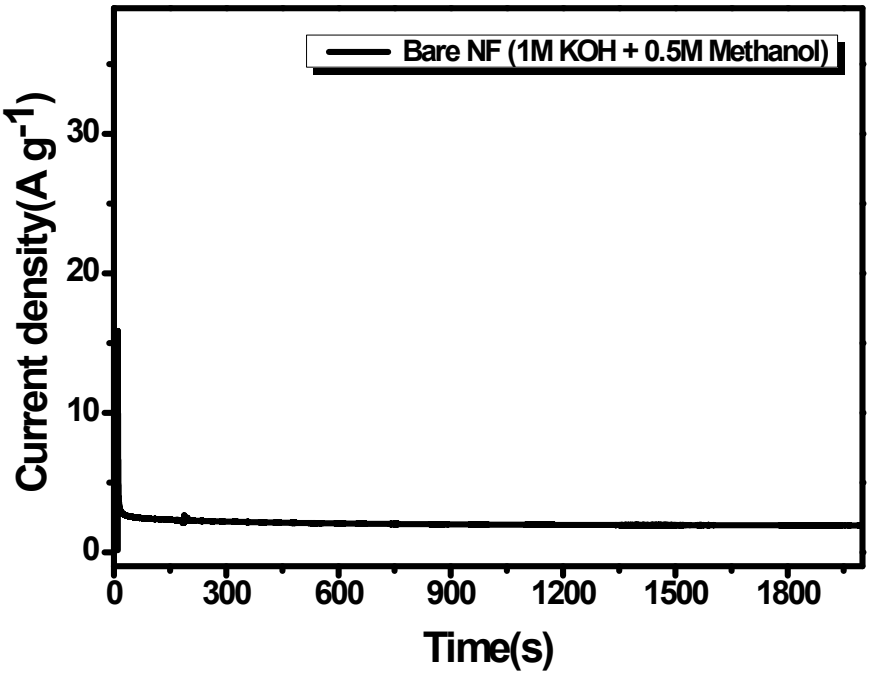


Fig. S3 CA curves of bare NF in 1M KOH with 0.5M methanol.

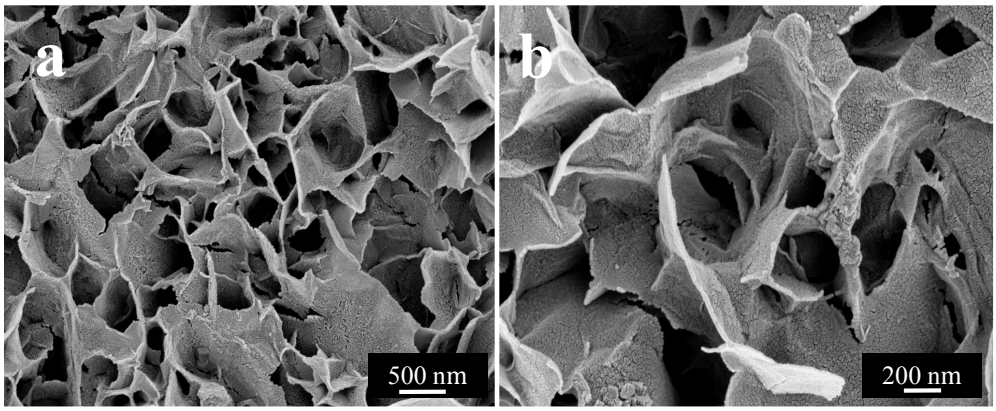
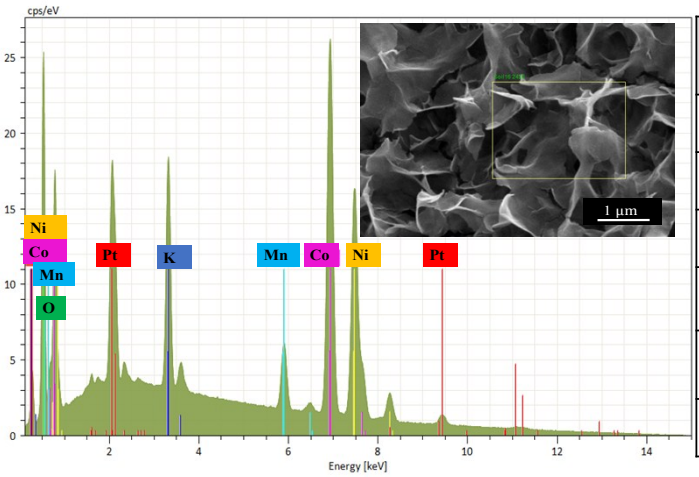


Fig. S4 (a-b) Low and high magnification FE-SEM images of $MnCo_2O_4$ electrode after 1000 cycles at scan rate of 10 mV s^{-1}.



Element	Atom(%)
Oxygen	29.50
Potassium	7.10
Manganese	13.05
cobalt	27.01
Nickel	23.34
	100

Fig. S5 (a) EDS mapping carried out after long cycling for methanol oxidation.

The elemental analysis of $MnCo_2O_4$ electrode was carried out after long-term cycling as shown in **Figure S5**. The elemental analysis shows the presence of Oxygen (O), Potassium (K), Manganese (Mn), Cobalt (Co), Nickel (Ni) elements. The Mn, Co, O elements observed due to $MnCo_2O_4$ electro-catalyst material. Nickel (Ni) and Potassium (K) was detected due to nickel foam substrate and KOH used as electrolyte, respectively.

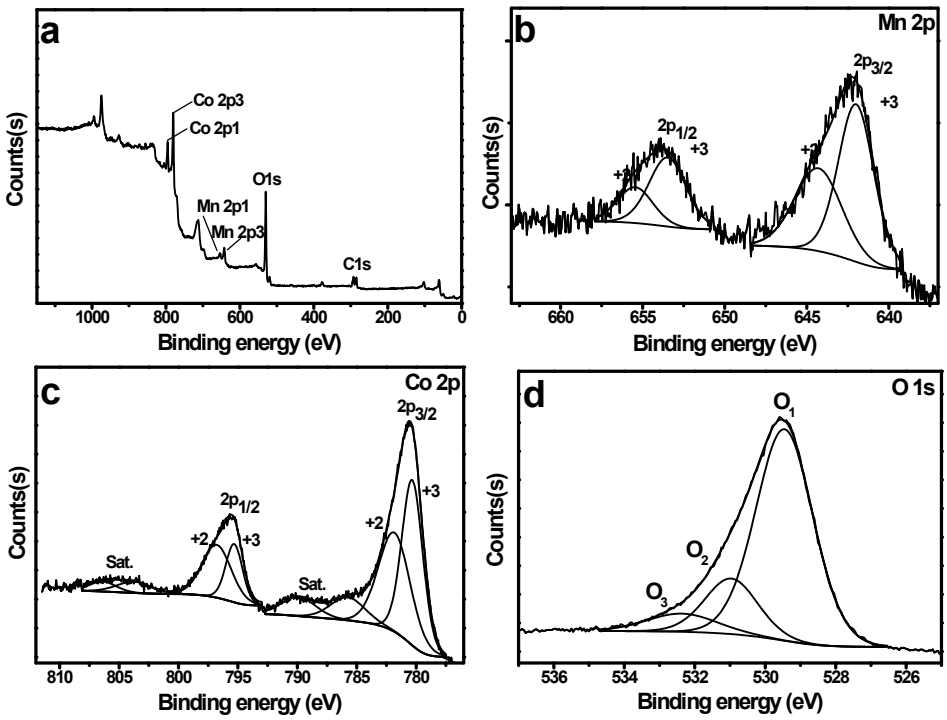


Fig. S6 XPS spectra of the $MnCo_2O_4$ sample: (a) full survey, (b) Mn 2p, (c) Co 2p and (d) O 1s taken after long term cycling for methanol electro-oxidation.

Figure S6 shows the XPS analysis of $MnCo_2O_4$ electro-catalyst after ling cycling. Full spectrum of $MnCo_2O_4$ shows the presence of Mn, Co and O elements. The deconvoluted spectra of Mn 2p shows the binding energies of 2p 3/2 and 2p 1/2 in $MnCo_2O_4$ are 642.2 and 653.9 eV, respectively. Similarly for Co the peaks observed at 780.6 and 795.6 eV observed corresponds to the 2p 3/2 and 2p 1/2, respectively. Furthermore, peaks at about 529.5(O1), 531.2(O2) and 532.5(O3) eV in the O 1s spectrum are ascribed to metal-oxygen bond, number of defects sites with low oxygen coordination and physisorbed or chemisorbed water, respectively.

This results reveals, no major change in binding energies of Mn, Co, and O elements after long –term cycling. In short, the $MnCo_2O_4$ spinel structure was maintained even after long-term cycling.

Table S1: The performance of different spinel oxides used as electro-catalyst for methanol oxidation.

No.	Catalyst	Method	Electrolyte (M)	Potential window (V)	Current density	Scan rate (mV s^{-1})	Stability	Ref
1	$MnCo_2O_4$	Co-precipitation	1M KOH +0.5M methanol	0-0.7	80 A g^{-1}	10	92% retention after 500 cycles	13
2	$ZnCo_2O_4$	Hydrothermal	1M KOH +0.5M methanol	0-0.8	105 A g^{-1}	10	92% retention after 500 cycles	16
3	$NiCo_2O_4$ /MWCNT	Grinding followed by calcination	1M KOH +6.0M methanol	0-0.8	400 mA cm^{-2}	100	76% retention after 500 cycles	28
4	Co_3O_4 /NiO	Hydrothermal	1M KOH +0.5M methanol	0-0.75	140 mA cm^{-2}	25	100% retention after 500 cycles	29
5	$NiCo_2O_4$	Electrodeposition	1M KOH +0.5M methanol	0-0.6	50 A g^{-1}	10	91% retention after 1000 cycles	30
6	$CuCo_2O_4$	Hydrothermal	1M KOH +0.5M methanol	0-0.6	51 A g^{-1}	NA	NA	31
7	$NiCo_2O_4$ /rGO	Hydrothermal	0.1M KOH +0.5M methanol	0-0.8	0.035 mA cm^{-2}	50	79.3% retention after 500 cycles	32
8	$NiCo_2O_4$	Hydrothermal	1M KOH +0.5M methanol	0-0.7	51 A g^{-1}	10	92% retention after 500 cycles	33
9	$NiCo_2O_4$	Hydrothermal	1M KOH +0.5M methanol	0-0.6	134 mA cm^{-2}	10	88% retention after 500 cycles	34
10	$MnCo_2O_4$	Electrodeposition	1M KOH +0.5M methanol	0-0.5	96 A g^{-1}	10	90% retention after 1000 cycles	This work