Supporting Information

$MnO_2/MnCo_2O_4/Ni$ Heterostructure with Quadruple Hierarchy: A Bifunctional Electrode Architecture for Overall Urea Oxidation

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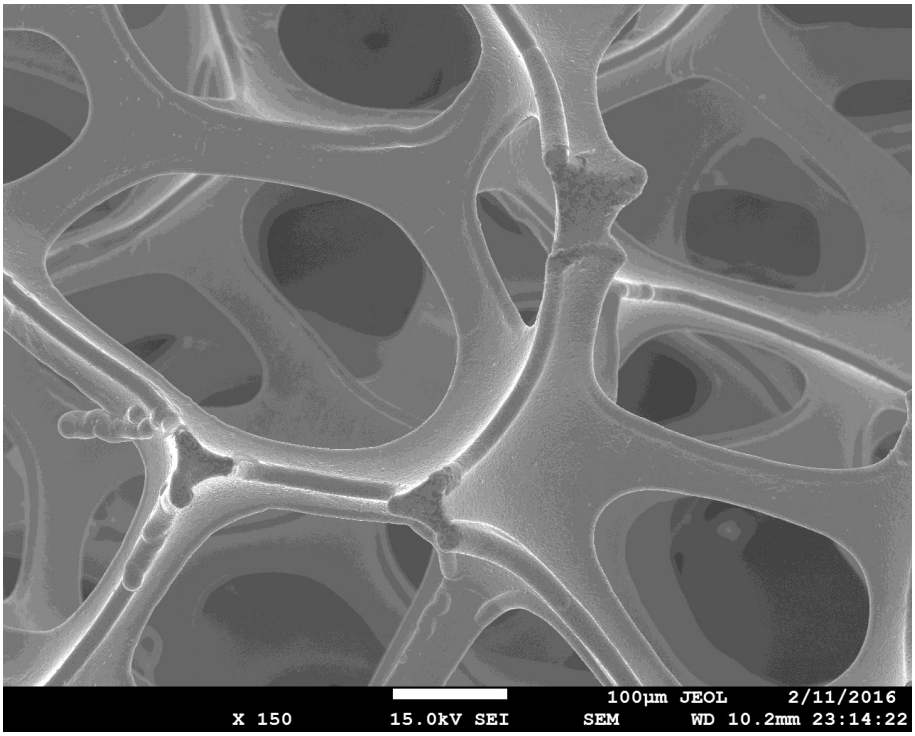

Figure S1. SEM image of bare Ni foam scaffold.

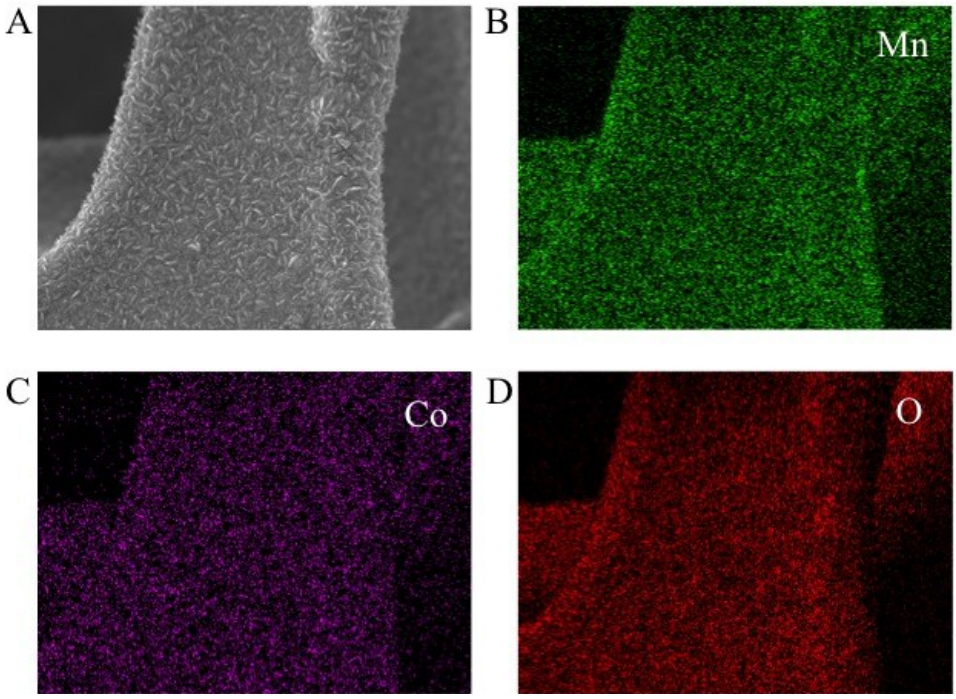

Figure S2. (A) SEM image and (B)-(D) elemental mapping images of $MnCo_2O_4$/Ni foam composites.

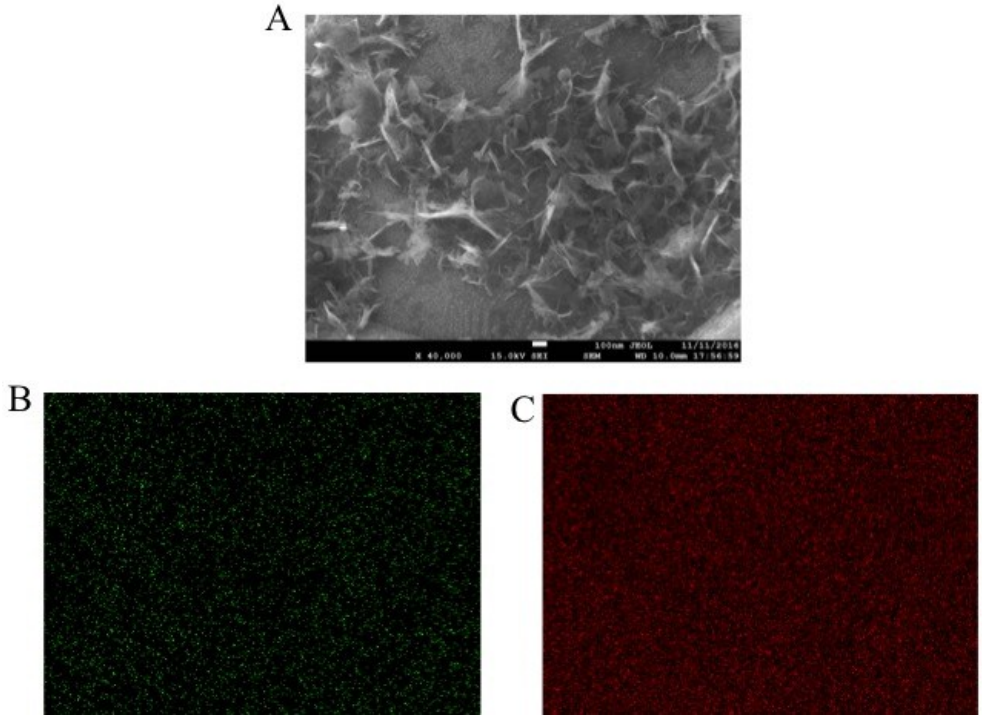

Figure S3. (A) SEM image and (B)-(C) elemental mapping images of MnO_2/Ni foam composites.

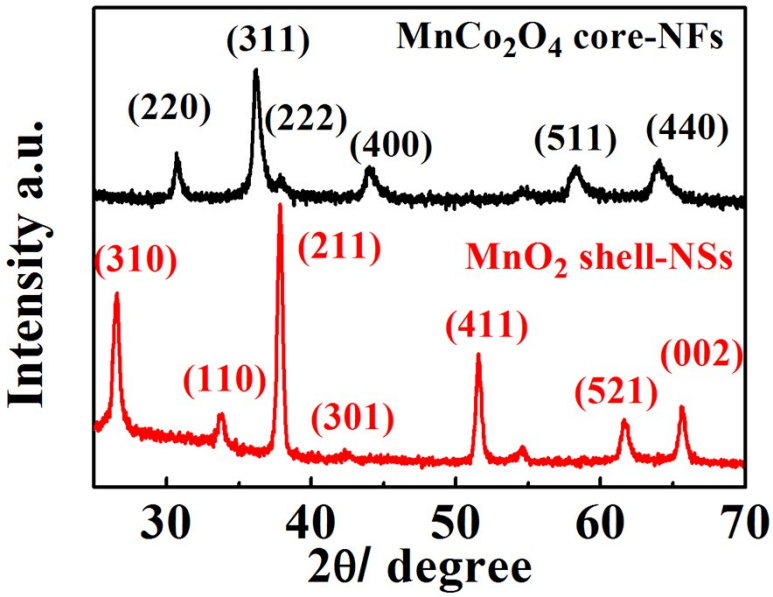

Figure S4. XRD patterns of MnO_2 Shell-NSs electrodeposited on ITO glass (red) and $MnCo_2O_4$ core-NFs (black) .

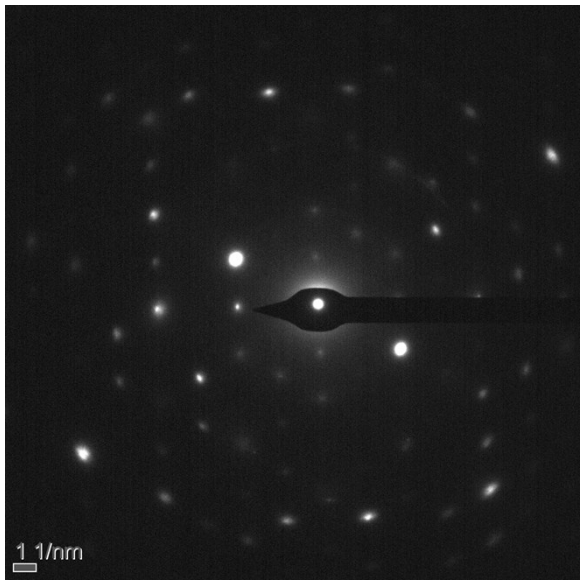

Figure S5. SAED pattern of electrodeposited MnO_2 shell-NSs.

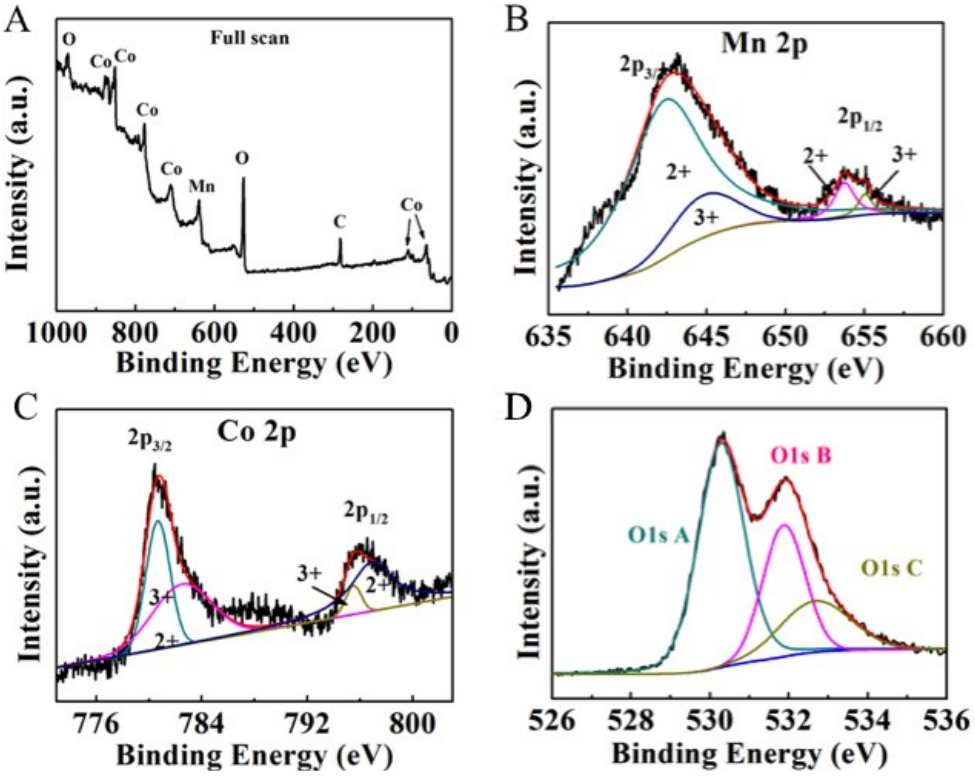

Figure S6. (A)XPS spectrum of MMCN, High-resolution XPS spectrum of (B) Mn 2p, (C) Co 2p and (D) O 1s.

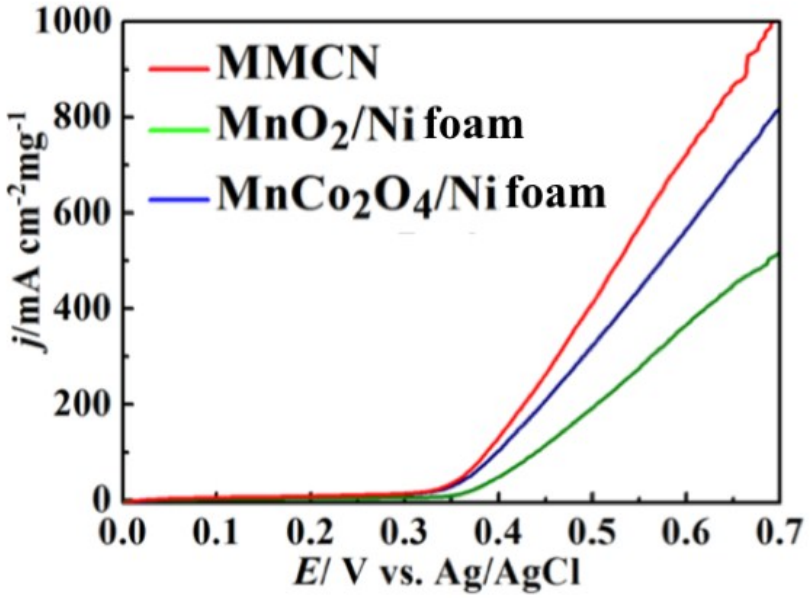

Figure S7. UOR polarization curves of MMCN, $MnCo_2O_4$/Ni foam and MnO_2/Ni foam electrodes in 0.5 urea/1 M KOH at a scan rate of 5 mV s^{-1}.

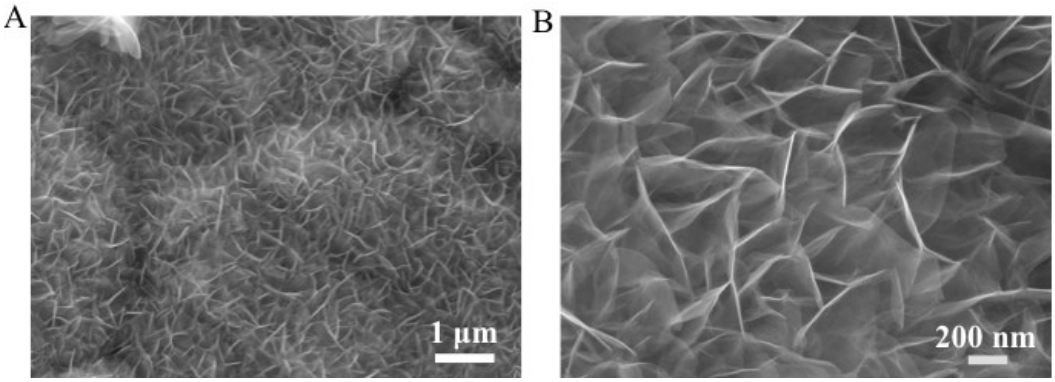

Figure S8. SEM images of MnO_2/Ni foam electrode at different magnifications.

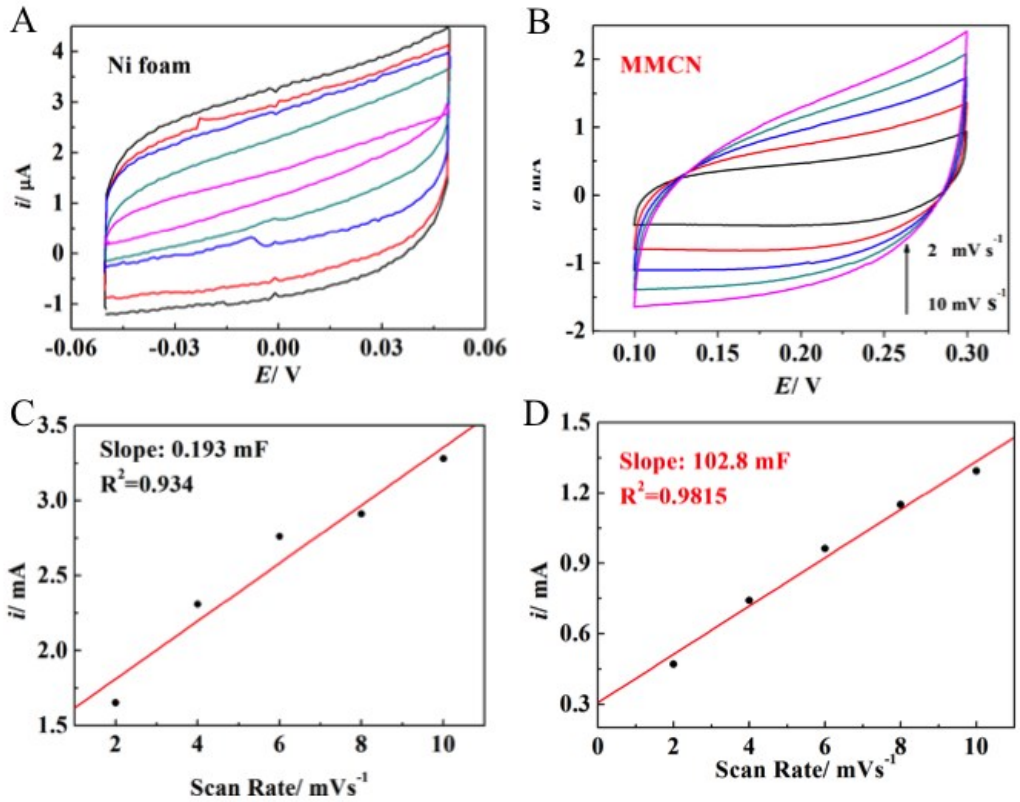

Figure S9. CV curves measured at different scan rates from 2 mV/s to 10 mV/s of (A) Ni foam, (B) MMCN, current densities recoreded at 0.2 V ploted vs. scan rates of (C) Ni foam and (D) MMCN.

The calculation of the electrochemical surface area (ECSA) is based on the measured double-layer capacitance of the obtained MMCN, MnO_2/Ni foam, $MnCo_2O_4$/Ni foam and Ni foam electrodes in 1 M KOH according to previously established methods. The calculated capacitance and corresponding roughness factors for each synthesized electrode are listed in Table S2.

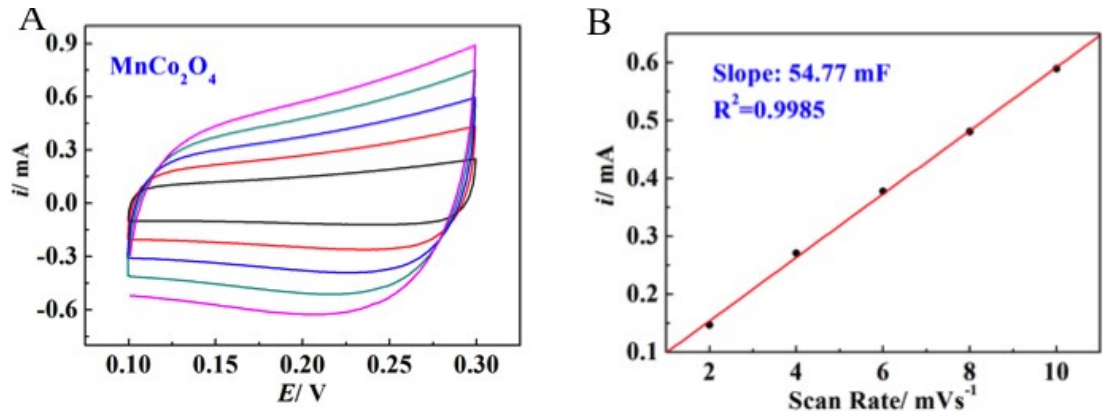

Figure S10. CV curves of $MnCo_2O_4$/Ni foam electrode measured at different scan rates from 2 mV/s to 10 mV/s and (B) current densities at 0.2 V ploted vs. scan rates.

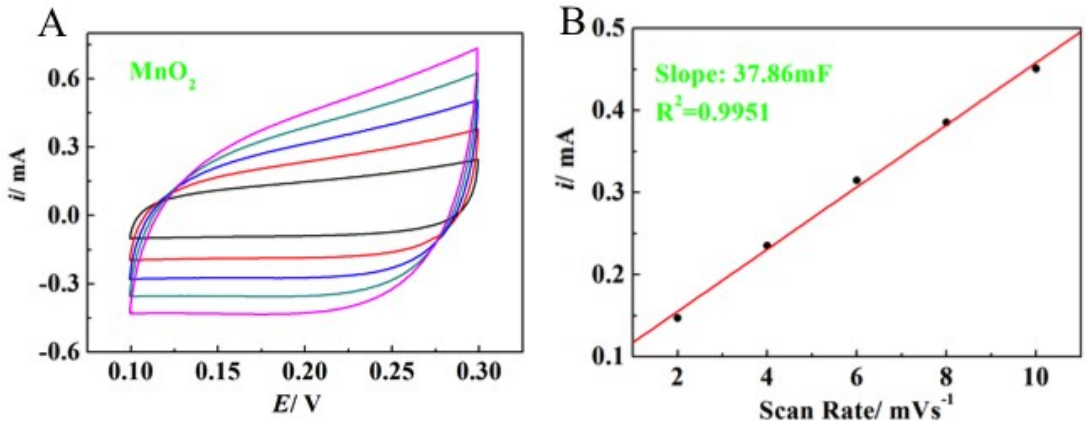

Figure S11. CV curves of MnO_2/Ni foam electrode measured at different scan rates from 2 mV/s to 10 mV/s and (B) current densities at 0.2 V ploted vs. scan rates.

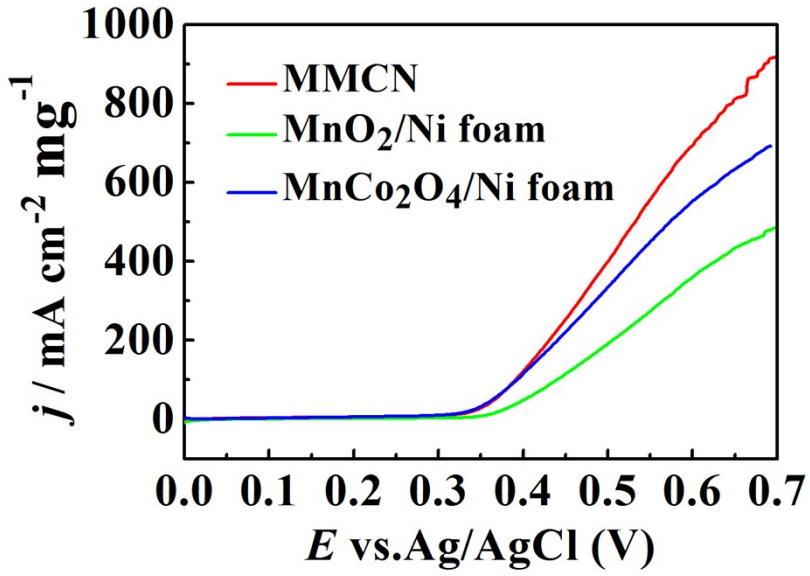

Figure S12. Absolute UOR polarization curves of MMCN, $MnCo_2O_4$/Ni foam and MnO_2/Ni foam electrodes in 0.5 urea/1 M KOH at a scan rate of 5 mV s^{-1}. The current is nomalized by catalyst mass loading and subtracted off the current from OER.

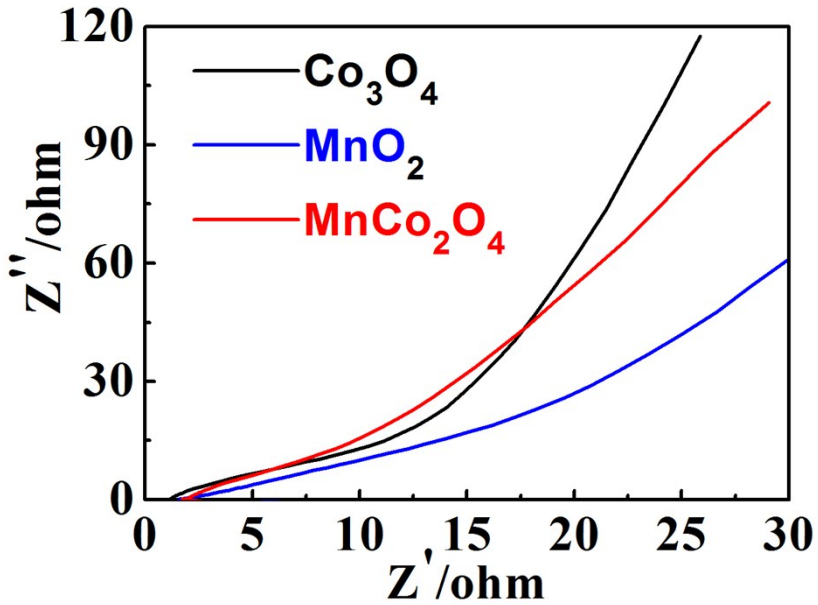

Figure S13. Nyquist plots Co_3O_4/Ni foam, $MnCo_2O_4$/Ni foam and MMCN electrodes.

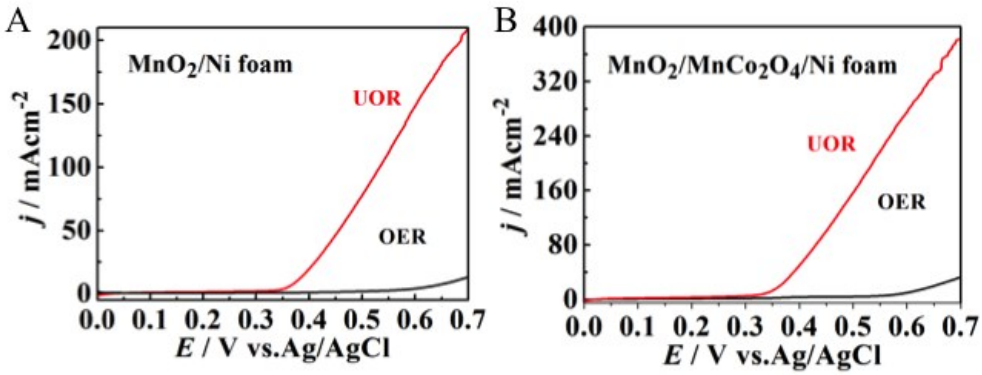

Figure S14. Comparison of UOR and OER polarization curves of (A) MnO_2/Ni foam and (B) $MnCo_2O_4$ electrodes.

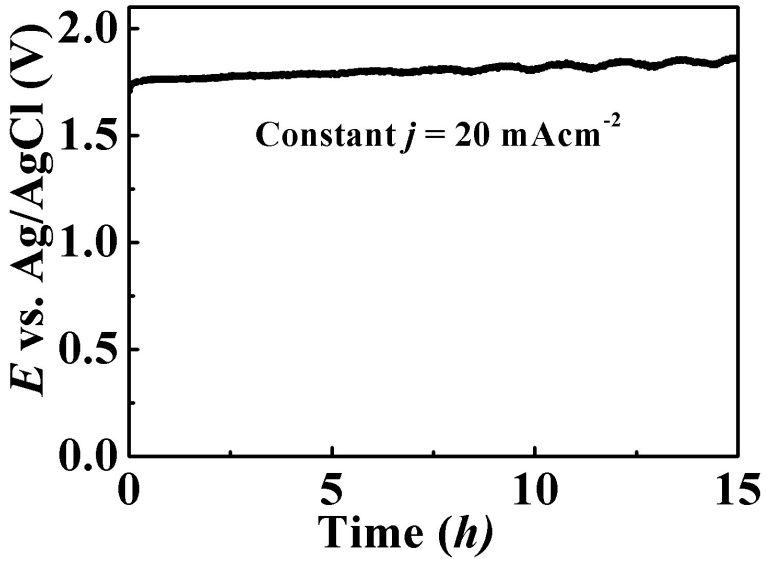

Figure S15. Chronopotentiometric curves at constant current density of 10 mA cm^{-2} for in two-electrode configuration in 0.5 M urea/1 M KOH.

The voltage is quite stable during the experiment, suggesting long-term stability of the electrodes.
In order to clarify any possible contribution of metal oxide to the reduction current of the electrode, the quantity of charge consumed by metal oxide reduction during 15 hours has been calculated as follows:

The total charge passed, Q_{total}
Q_{total}=i*t=0.02 A cm^{-2} * 0.3 cm-2*15 h*3600=324 C

MnO_2 is the main component of the metal oxide. The mass of MnO_2 is ~1.35 mg. The maximum possible charge that could be consumed in reduction of MnO2 can be calculated as follow:
Q_{MnO2} =1.35x10^{-3} * 4 * 96450 / 70.9=7.34 C
Q_{MnO2} reduction/Q_{total} *100%=2.25%

The calculation confirms that the cathodic current are substantially from hydrogen generation and the MMCN electrode can act as stable hydrogen catalyst.

Table S1. Comparison of the UOR catalytic activity between recently reported electrode materias .

Catalysts	Onset potential (at 10 mA cm^{-2})	*j*@1.7V vs. RHE ($mA\ cm^{-2}$)	Mass Activity (1.7 V vs. RHE)	Mass Loading	Reference
$MnO_2/MnCo_2O_4$	1.33	384	1020 mA cm^{-2} mg^{-1}	1.27	This work
$MnCo_2O_4$	1.37	240	840	0.97	This work
MnO_2	1.38	210	550	1.35	This work
S- MnO_2	1.33	~340	---	1.5	22
Pt	1.50	110	---	2.5	4
Graphene-$Ni(OH)_2$	1.52	35	---	0.25	49
$Ni(OH)_2$ nanocube array	1.55	---	400	0.3	18
$LaNiO_3$	~1.39	---	371	---	2
NiO nanosheet	1.38	---	670	0.27	23

Table S2. Roughness factors of the synthesized electrode materials

Electrode Materials	$MnO_2/MnCo_2O_4$	MnO_2	$MnCo_2O_4$	Ni foam
Specific Capacitance	102.8	37.9	54.8	0.193
Roughness Factor	533	196	284	1