Supporting Information

Biomass willow catkins-derived Co_3O_4/N-doped hollow hierarchical porous carbon microtubes as the effective tri-functional electrocatalyst

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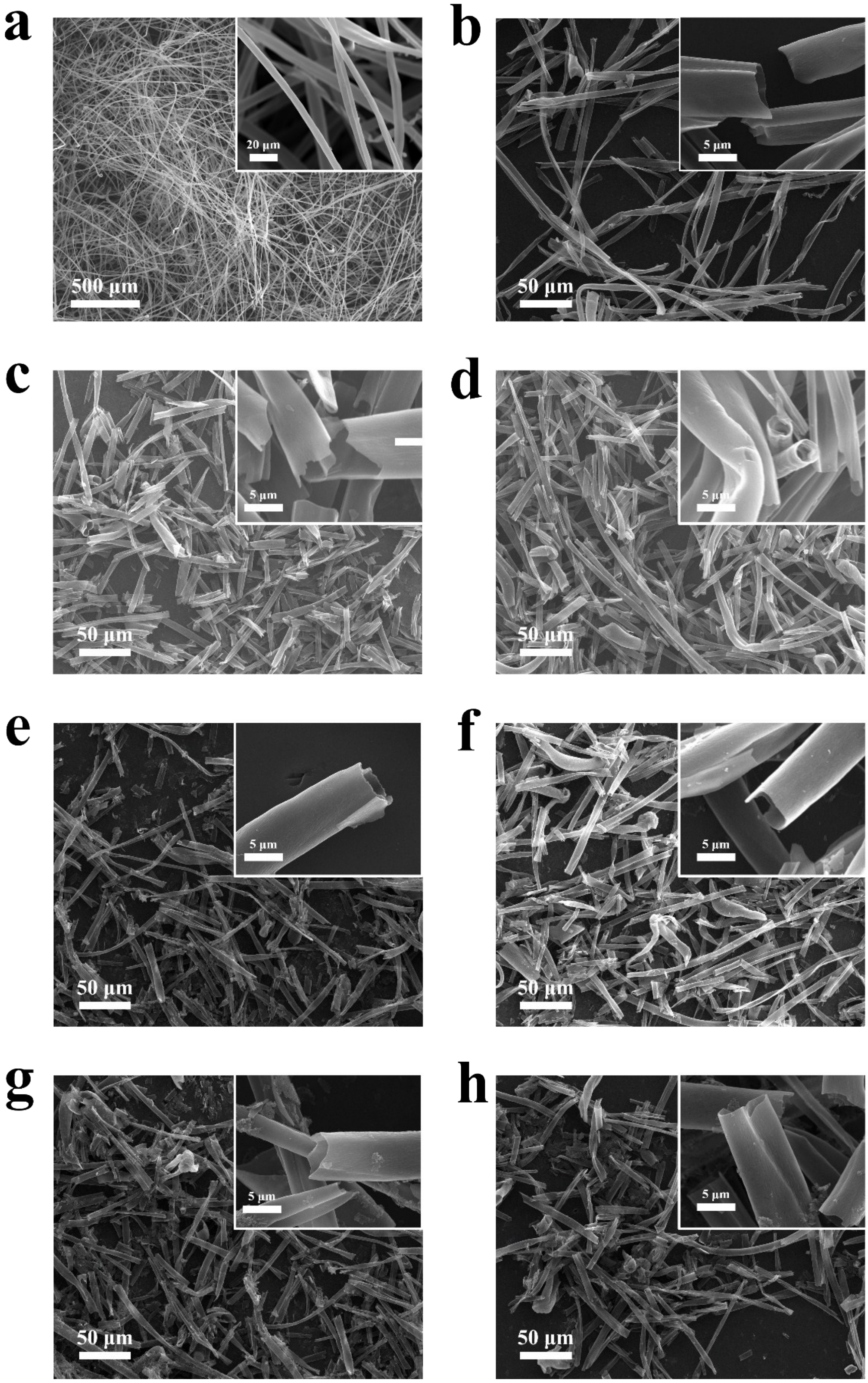

Fig. S1 SEM images of (a) pristine catkin, (b) CMTs-600, (c) CMTs-800, (d) NCMTs-800, (e) Co_3O_4/CMTs-800, (f) Co_3O_4/NCMTs-700, (g) Co_3O_4/NCMTs-800, (h) Co_3O_4/NCMTs-900.

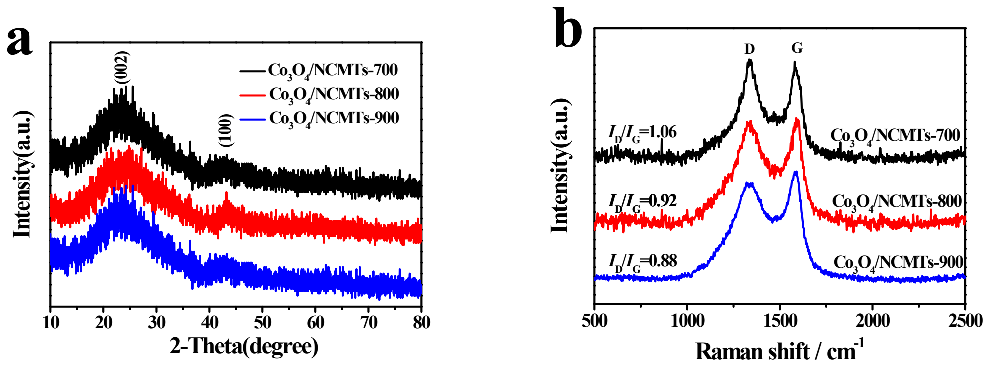

Fig. S2 (a) XRD survey and (b) Raman of the Co_3O_4/NCMTs-X (X = 700, 800, 900)

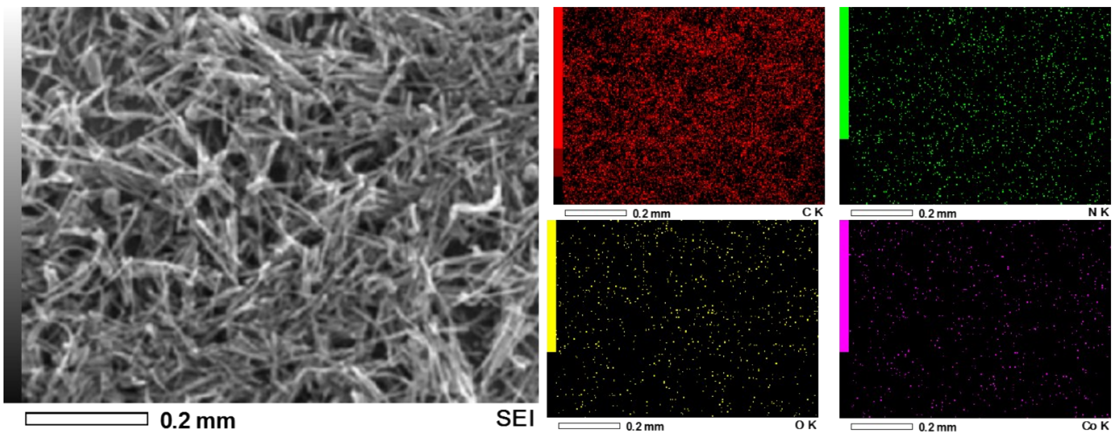

Fig. S3 Typical SEM images of Co_3O_4/NCMTs-800 materials and corresponding elemental mapping images of C, N, O and Co.

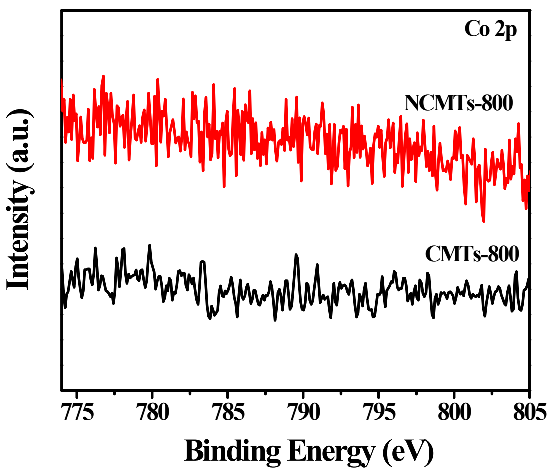

Fig. S4 the high-resolution Co 2p XPS spectrum of NCMTs-800 and CMTs-800.

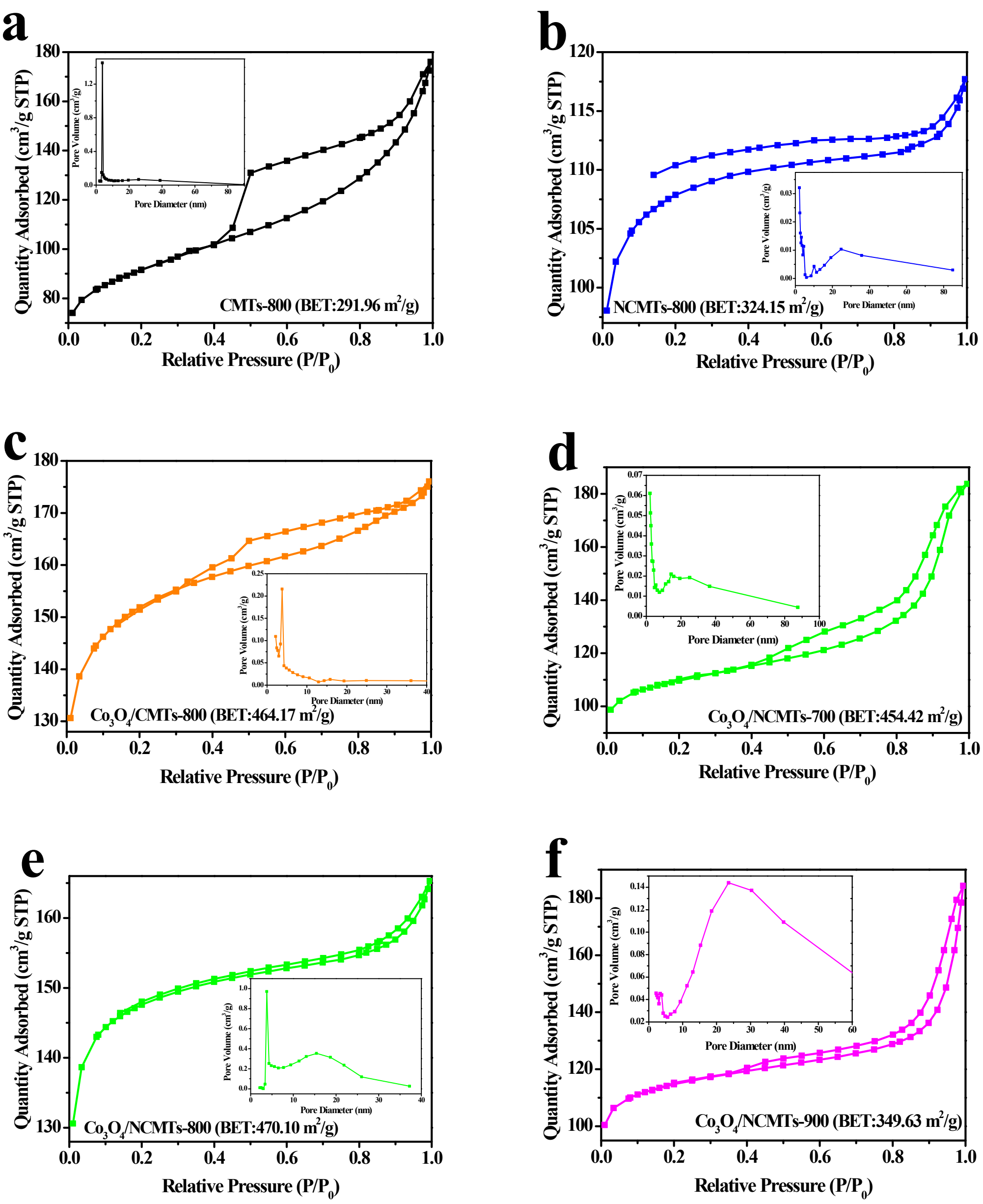

Fig. S5 The nitrogen adsorption-desorption isotherms and the corresponding pore-size distribution of the CMTs-800 (a), NCMTs-800 (b), Co_3O_4/CMTs-800 (c), Co_3O_4/NCMTs-700 (d), Co_3O_4/NCMTs-800 (e) and Co_3O_4/NCMTs-900 (f).

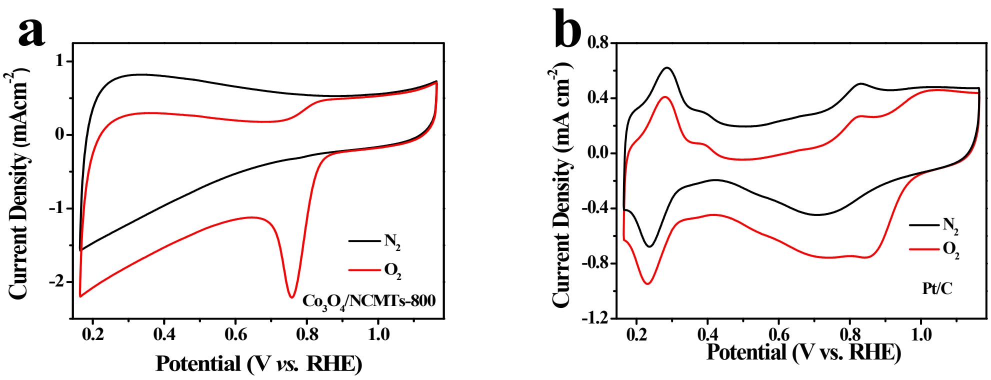

Fig. S6 CV curves of (a) Co_3O_4/NCMTs-800 and (b) Pt/C in N_2/O_2-saturated 0.1 M KOH solution at a scan rate of 50 mV/s.

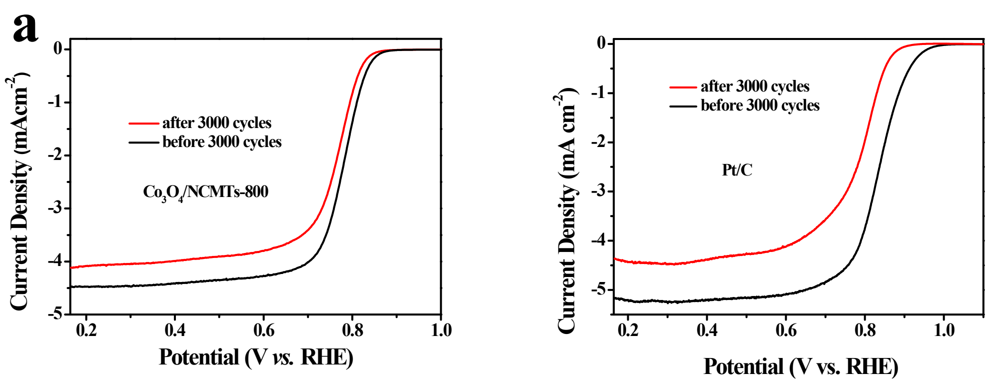

Fig. S7 Linear sweep voltammetric (LSV) curves of (a) Co_3O_4/NCMTs-800 and (b) Pt/C for ORR in O_2-saturated 0.10 M KOH before and after 3000 cycles.

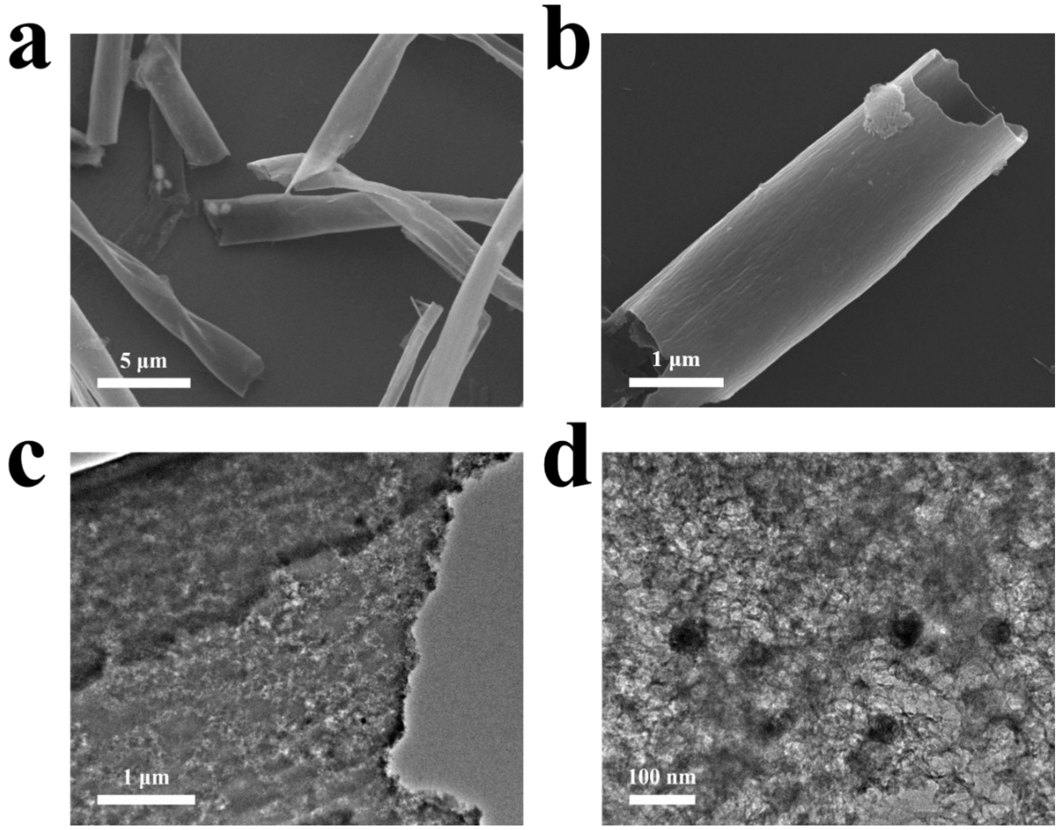

Fig. S8 SEM (a, b) and TEM (c, d) images of Co_3O_4/NCMTs-800 after 3000 cycles ORR stability test.

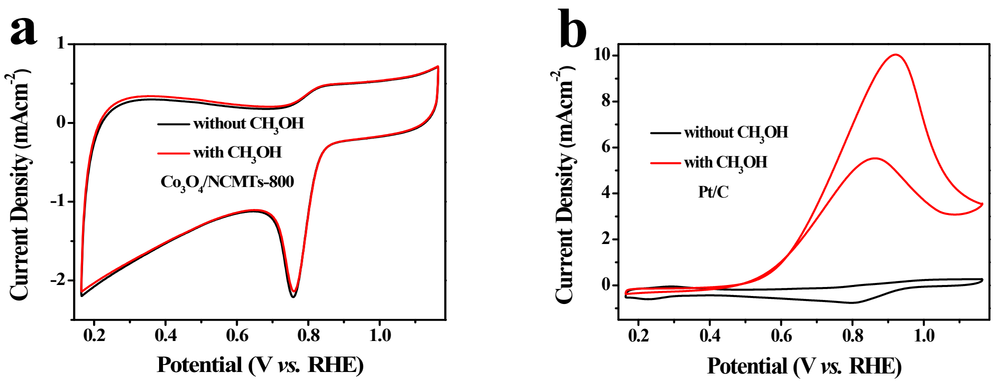

Fig. S9 The CVs of the (a) Co_3O_4/NCMTs-800 and (b) Pt/C in O_2-saturated 0.10 M KOH without and with 1.0 M CH_3OH.

Table S1 XPS results for CMTs-800, NCMTs-800, Co_3O_4/CMTs-800 and Co_3O_4/NCMTs-800

Sample	N content [at.%][a]	Pyridinic N [%][b]	Pyrrolic N [%][b]	graphitic N [%][b]	oxided N [%][b]
CMTs-800	0.43	32.53	8.43	48.19	10.85
NCMTs-800	3.87	52.06	10.80	27.95	9.19
Co_3O_4/CMTs-800	0.73	31.28	9.92	46.36	12.44
Co_3O_4/NCMTs-800	1.81	53.64	7.60	31.16	7.60

a: The total N content (at.%) in the CMTs-800, NCMTs-800, Co_3O_4/CMTs-800 and Co_3O_4/NCMTs-800 determined by XPS elemental analysis, respectively.

b: The percentage of pyridinic-, pyrrolic-, graphitic- and oxidied-type nitrogen for the doped N

Table S2 Textual parameters of the materials

Sample	BET surface area [m^2 g^{-1}]	Average pore diameter [nm]	Total pore volume [cm^3 g^{-1}]
CMTs-800	291.96	4.04	0.18
NCMTs-800	324.15	5.27	0.26
Co_3O_4/CMTs-800	464.17	5.47	0.26
Co_3O_4/NCMTs-700	454.42	5.48	0.27
Co_3O_4/NCMTs-800	470.10	7.39	0.29
Co_3O_4/NCMTs-900	349.63	11.32	0.35

Table S3. Comparison of electrochemical activity of Co_3O_4/NCMTs-800 to the other reported ORR catalysts in alkaline electrolyte

Catalysts	Mass loading /mg cm^{-2}	onset potential (V vs.RHE)	$E_{1/2}$ (V vs.RHE)	Biomass	Reference
Co_3O_4/NCMTs-800	0.28	0.906	0.778	Catkins	This work
BP350@C-1000	2.55	0.90	0.78	Pig blood	[S1]
N,P-carbon	0.31	~0.944	~0.754	Coconut shells	[S2]
N,S- carbon-800 (PHC)	0.66	~0.912	~0.77	Honeysuckles	[S3]
egg-CMS	0.136	~0.86	~0.69	Egg	[S4]
GLBS-1000	0.4	0.971	0.842	Keratin	[S5]
Ni/NiO/$NiCo_2O_4$/N-CNT-As	0.24	0.89	0.74	Seaweed	[S6]
Sewage sludge-derived porous carbon (SN-AW)	0.1	0.914	0.819	Sewage sludge	[S7]
NFe-NPCS-900-4	0.200	0. 955	0.836	Starch	[S8]
N and S comodified 3D porous graphene (NSG)	-	0.788	0.778	Horn	[S9]
NCS-800	0.05	~0.90	~0.76	Typha orientalis	[10]
WHC-700	0.16	0.98	~0.86	Eichhornia crassipes	[11]
N-CNAs	0.076	~0.884	0.774	Dried Grass	[12]
Fe/N/CNT@PCF	~0.23	0.866	0.770	catkin	[S13]
CMTs-750	0.20	~0.793	~0.523	catkin	[S14]
CMTs-950	0.20	~0.793	~0.523	catkin	

Table S4. Comparison of electrochemical activity of Co_3O_4/NCMTs-800 to the other reported OER catalysts in alkaline electrolyte

Catalysts	Mass loading /mg cm^{-2}	η_{10}/V (j=10 mA cm^{-2})	Biomass	Reference
Co_3O_4/NCMTs-800	1	0.35	biomass	This work
nitrogen-doped carbon hollow cubes (NCHCs)	0.401	~0.48	Lysine	[S15]
N and S comodified 3D porous graphene (NSG)	10	0.468	Horn	[S9]
Co_9S_8@NC	~0.41	0.400	Shrimp shell	[S16]
Sewage sludge-derived porous carbon (SN-AW)	0.1	0.384	Sewage sludge	[S7]
egg-CMS	2	0.3	Egg	[S4]
Ni/NiO/$NiCo_2O_4$/N-CNT-As	0.24	0.24	Seaweed	[S6]
$LiCoO_2$ NSs	0.1	0.530	-	[S17]
Delithiation $LiCoO_2$ NSs	0.1	0.500	-	
$LiCoO_2$ NPs	0.1	0.510	-	
Delithiation $LiCoO_2$ NPs	0.1	0.390	-	
NiCo LDH	0.17	0.474	-	[S18]
$MnCo_2Ox$	0.142	>0.410	-	[S19]
$NiMoO_4$ NW/CC	5	0.400	-	[S20]
$NiMoP_2$ NW/CC	5	0.330	-	
Co_2P	0.284	0.370	-	[S21]
Co-P films	2.52	0.345	-	[S22]
$Ni(OH)_2$ NSs	-	0.350	-	[S23]
NiMn HNSs	-	0.312		
Co_3O_4/rmGO	1	0.31	-	[S24]
CoOx@CN	1	0.260	-	[S25]

Table S5. Comparison of electrochemical activity of Co_3O_4/NCMTs-800 to the other reported HER catalysts in alkaline electrolyte

Catalysts	Mass loading /mg cm^{-2}	η_{10}/V (j=10 mA cm^{-2})	Biomass	Reference
Co_3O_4/NCMTs-800	1	0.21	biomass	This work
Co_9S_8@NC	~0.41	0.343	Shrimp shell	[S16]
Co_9S_8@NPC-10	~0.41	0.261	Shrimp shell	
human hair-derived porous carbons (HCP-800)	0.285	~0.26	human hair	[S26]
FeP NPs@NPC	1.4	0.22	Phytic acid	[S27]
Co-NRCNTs	0.28	0.370	-	[S28]
MoS_{2+x}/FTO	0.02	-0.310	-	[S29]
Co-P nanocube	0.286	0.280	-	[S30]
EG/$Co_{0.85}$Se/NiFe-LDH	4	0.260	-	[S31]
CoOx@CN	0.42	0.232	-	[S24]
CoP/CC	0.92	0.209	-	[S32]
Ni_2P	1.0	0.205	-	[S33]
Co-MoS_2	0.89	0.203	-	[S34]
NiFe LDH/Ni foam	-	0.200	-	[S35]
$CoSe_2$/carbon cloth	-	0.190	-	[S36]
NiCo HNSs	-	0.230	-	[S23]
NiMn HNSs	-	0.302	-	
$Ni(OH)_2$ NSs	-	0.374	-	
MoCx/C	0.80	0.151	-	[S37]

Table S6. Comparison of the electrocatalytic performance of the Co_3O_4/NCMTs-800|| Co_3O_4/NCMTs-800 electrode pair for two-electrode overall water splitting with that of reported non-precious metal electrocatalysts and precious metal electrocatalysts tested under similar conditions.

Catalysts	Mass loading /mg cm^{-2}	η_{10}/V (j=10 mA cm^{-2})	Reference
Co_3O_4/NCMTs-800	1	1.74	This work
NFPGNS	2.55	1.91	[S38]
Pristine NiFeOx/CFP	1.6	~1.88	[S39]
$Ni(OH)_2$/NiSe	-	1.78	[S40]
$Ni_{12}P_5$/$Ni_3(PO_4)_2$-HS	0.71	1.76	[S41]
Co-P film on Au foil	0.143	1.73	[S42]
$NiCo_2O_4$ | $Ni_{0.33}Co_{0.67}S_2$	0.3	1.72	[S43]
3.5 nm Pt /NF	-	1.71	[S35]
NiFe LDH/NF	-	1.70	
Ni_5P_4 on Ni foil	13.9	1.7	[S44]
Co-P/NC	0.283	1.7	[S45]
NiFe HNSs	-	1.67	[S23]
EG/$Co_{0.85}$Se/NiFe-LDH	4	1.67	[S31]
$NiMoP_2$/PE-$NiMoP_2$	5	1.67	[S46]
α-NiOOH/NF	0.8172	1.66 (η_1/V j=1 mA cm^{-2})	[S47]
2-cycle NiFeOx/CFP	1.6	1.61	[S40]

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