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electronic supplementary information for

Self-Supported Hierarchical CuO_x@Co_3O_4 Heterostructures as Efficient Bifunctional Electrocatalyst for Water Splitting

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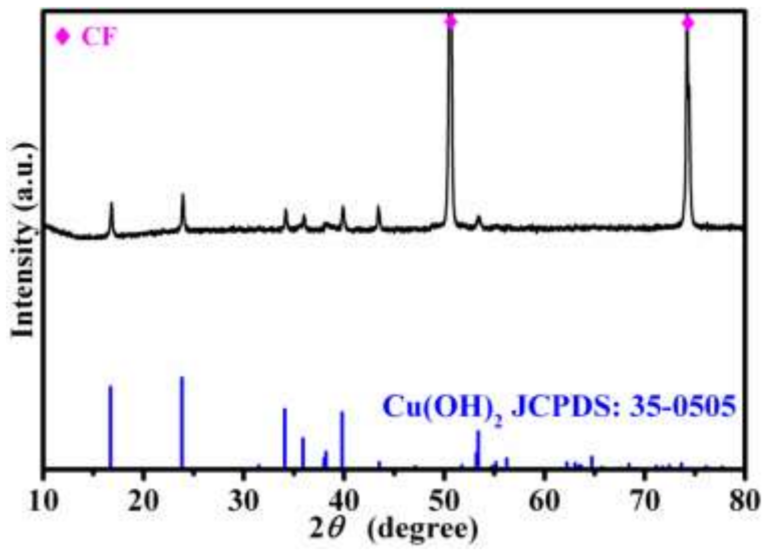

Fig. S1 XRD pattern of $Cu(OH)_2$ NRs/CF.

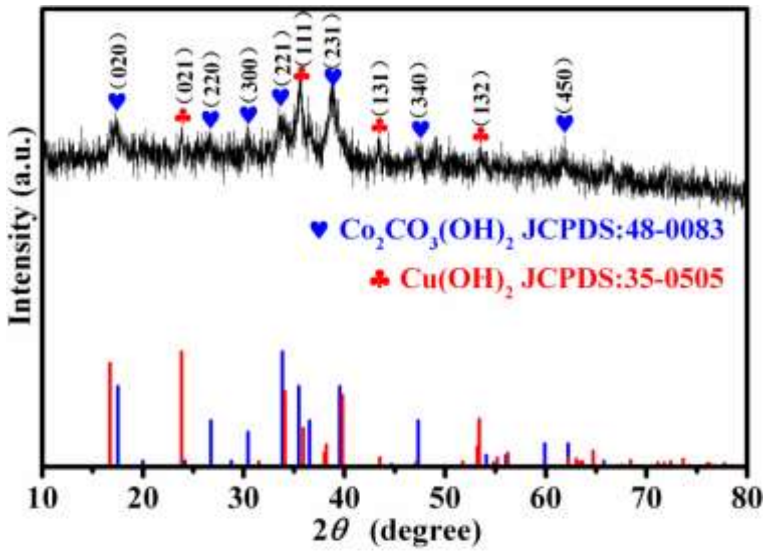

Fig. S2 XRD pattern of $Cu(OH)_2@Co_2CO_3(OH)_2$ NRs scraped off from the CF substrate.

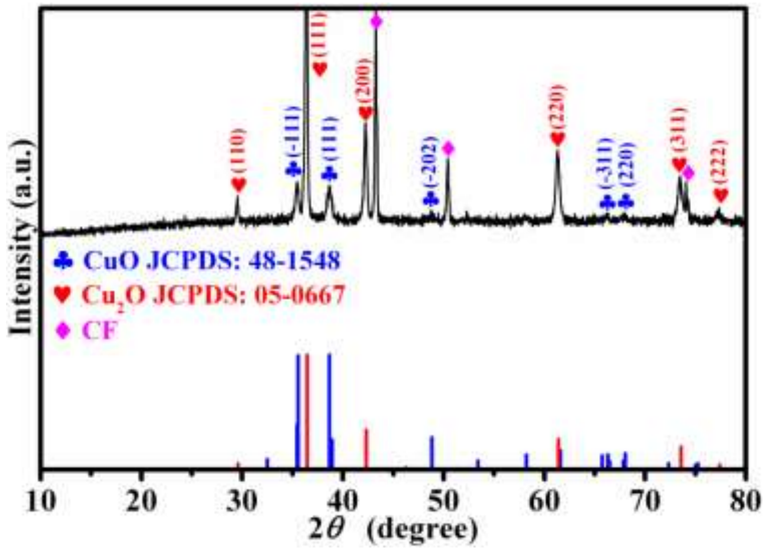

Fig. S3 XRD pattern of CuO_x NRs/CF.

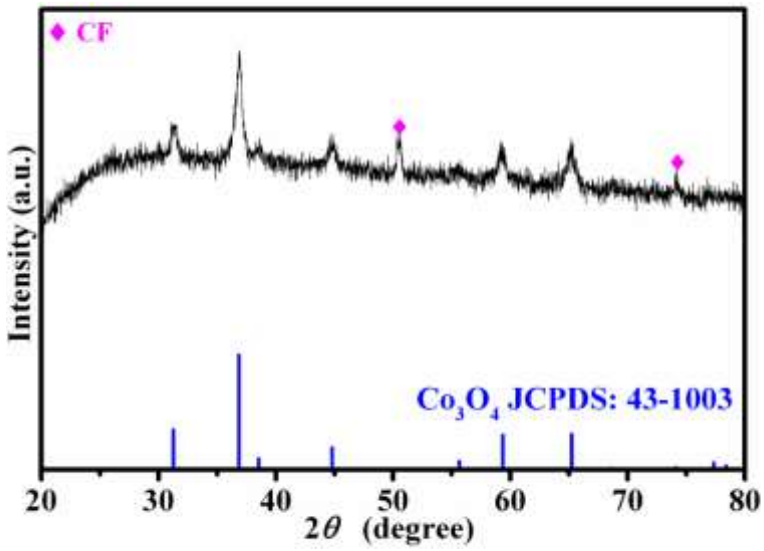

Fig. S4 The XRD pattern of Co_3O_4/CF.

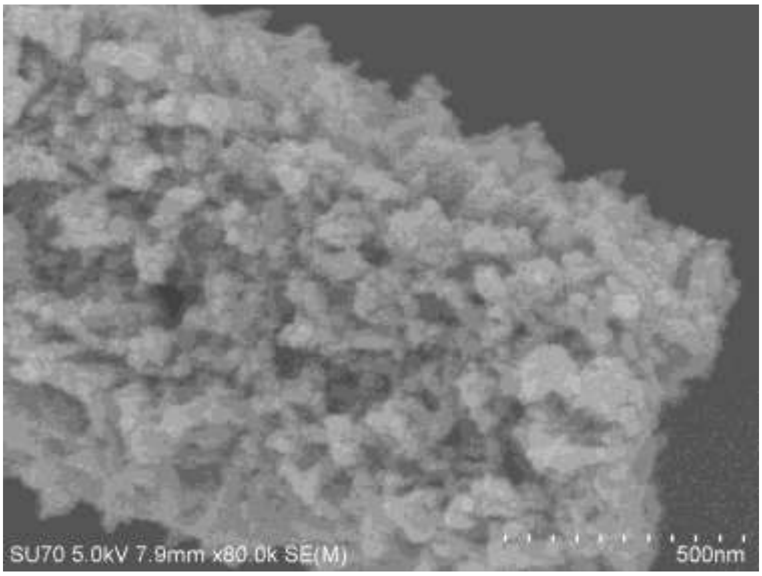

Fig. S5 Partial magnified SEM image of CuO_x@Co_3O_4 NRs.

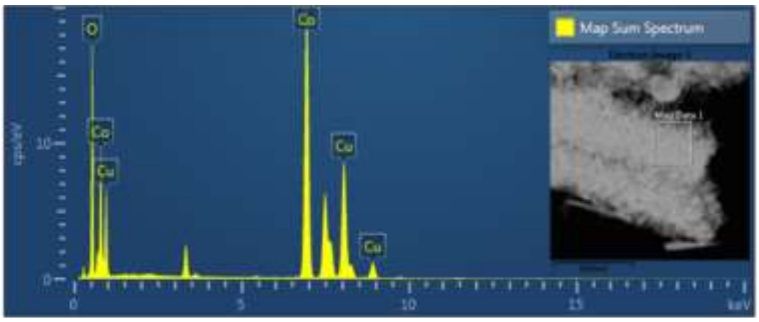

Fig. S6 The EDX spectrum of CuO_x@Co_3O_4 NRs.

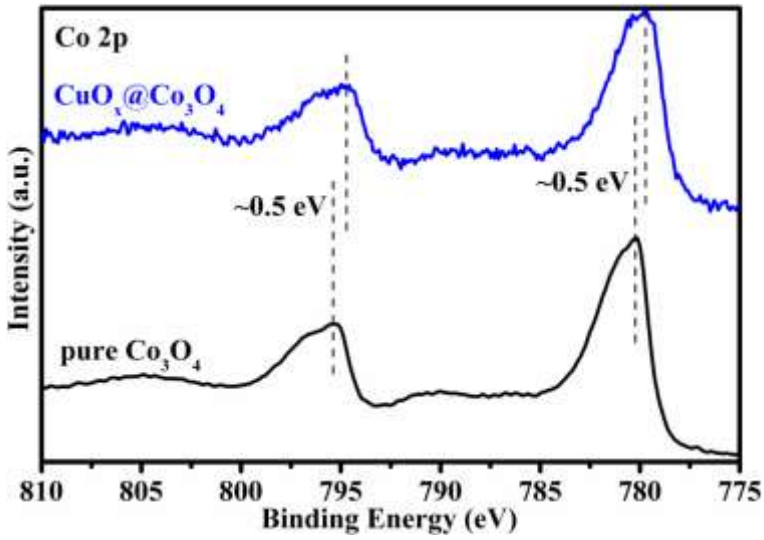

Fig. S7 High resolution XPS spectra for Co 2p regions in $CuO_x@Co_3O_4$ NRs/CF (blue line) and pure Co_3O_4 (black line).

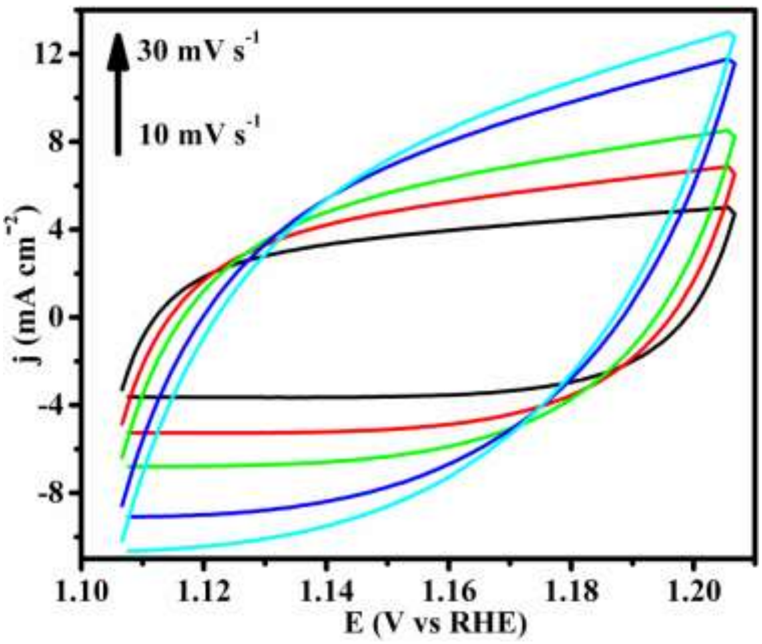

Fig. S8 CV scans for $CuO_x@Co_3O_4$ NRs/CF under various scan rates (10 to 30 mV s^{-1}) in the non-Faradaic potential range (0.10 ~ 0.20 V vs Ag/AgCl).

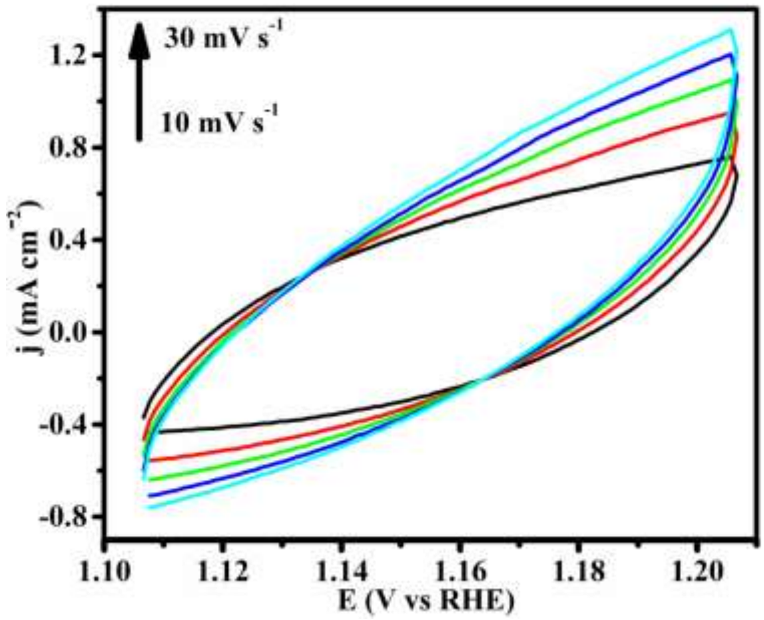

Fig. S9 CV scans for CuO_x NRs/CF under various scan rates (10 to 30 mV s^{-1}) in the non-Faradaic potential range (0.10 ~ 0.20 V vs Ag/AgCl).

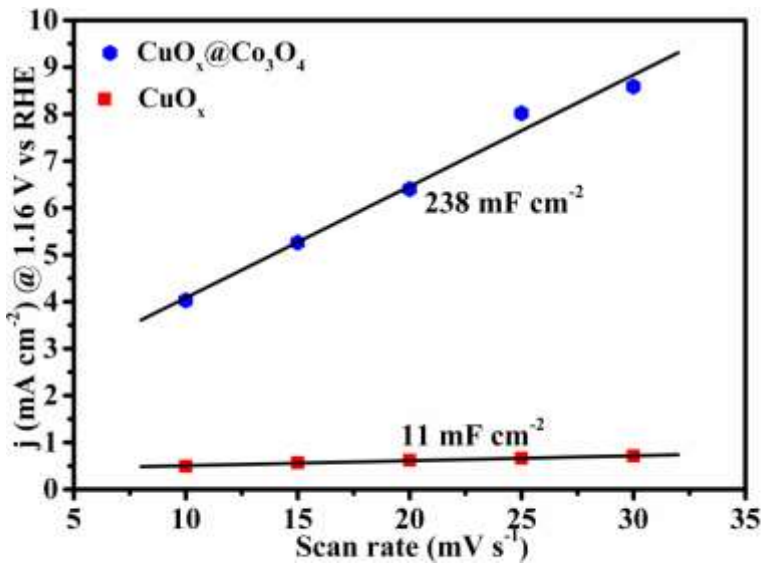

Fig. S10 C_{dl} plot for $CuO_x@Co_3O_4$ NRs/CF and CuO_x NRs/CF derived from current densities at 1.16 V vs RHE against the scan rates.

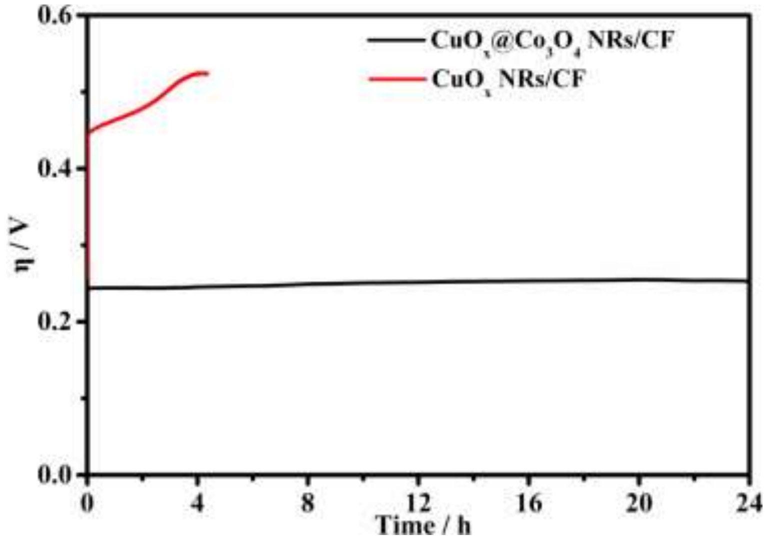

Fig. S11 Chronopotentiometry for CuO$_x$@Co$_3$O$_4$ NRs/CF and CuO$_x$ NRs/CF fixed at a current density of 50 mA cm^{-2} in 1.0 M KOH solution.

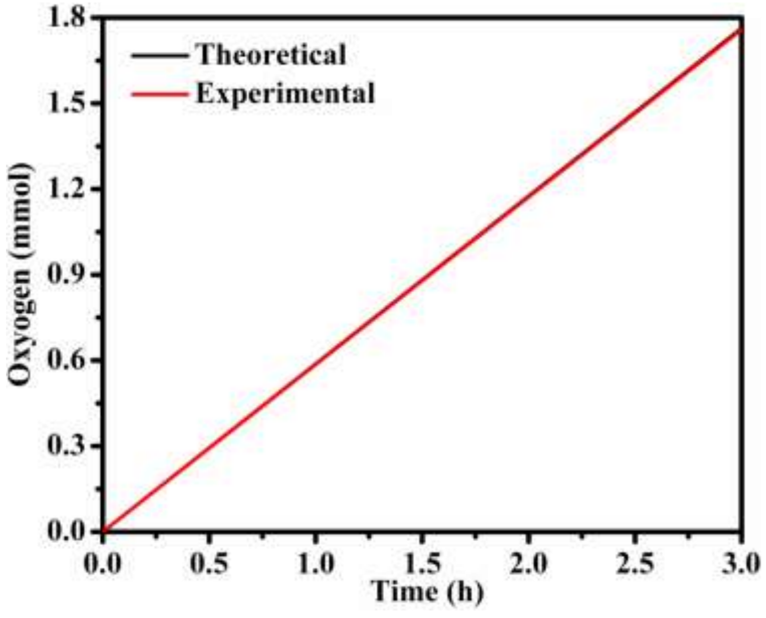

Fig. S12 The amount of theoretically calculated and experimentally measured O_2 versus the electrolysis time for CuO$_x$@Co$_3$O$_4$ NRs/CF.

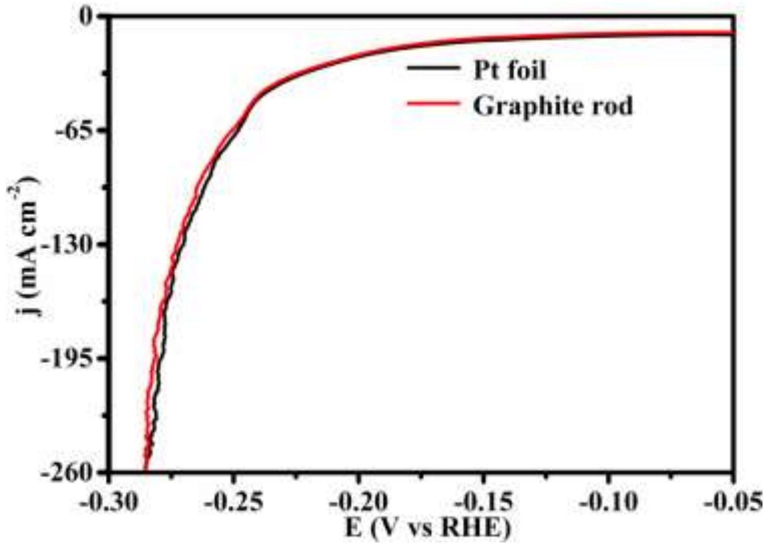

Fig. S13 Polarization plots of $CuO_x@Co_3O_4$ NRs/CF for HER by using Pt foil or graphite rod as the counter electrode, respectively.

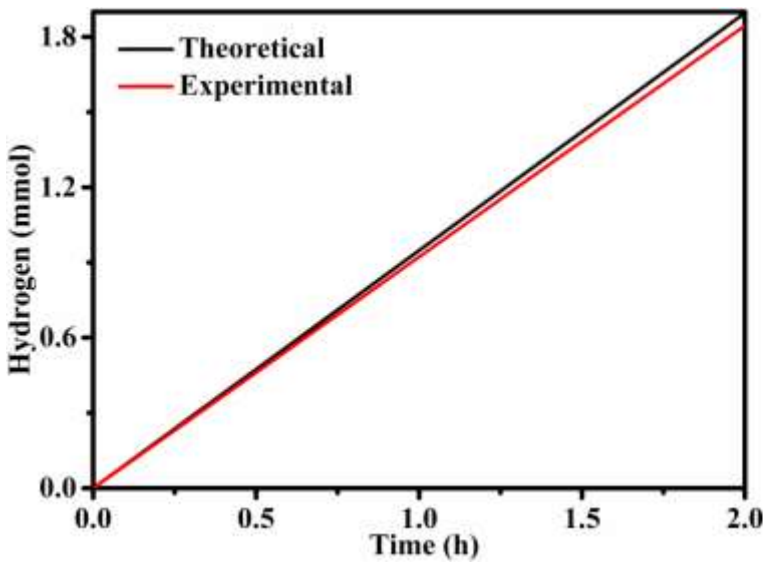

Fig. S14 The amount of theoretically calculated and experimentally measured H_2 versus the electrolysis time for $CuO_x@Co_3O_4$ NRs/CF.

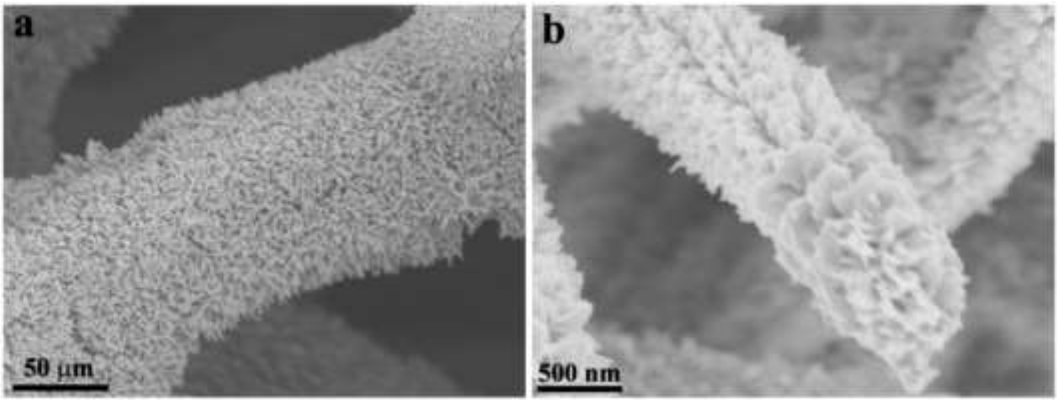

Fig. S15 The SEM images of $CuO_x@Co_3O_4$ NRs/CF after 24 h OER.

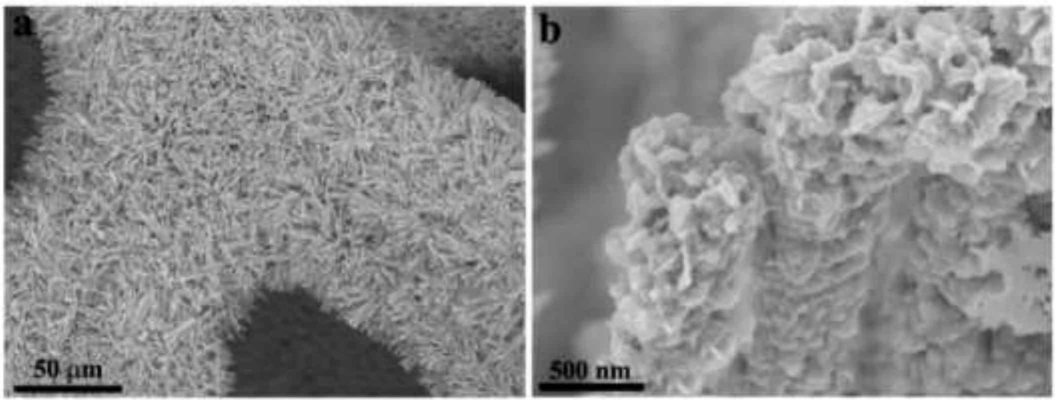

Fig. S16 The SEM images of $CuO_x@Co_3O_4$ NRs/CF after 24 h HER.

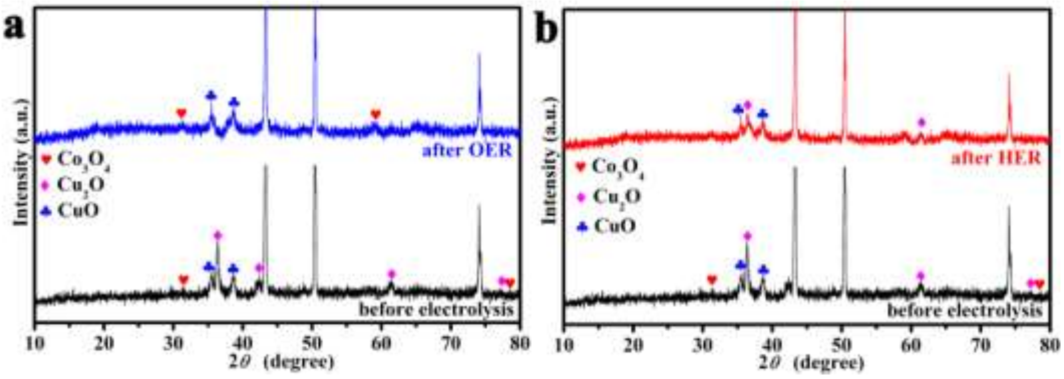

Fig. S17 The comparison of XRD patterns for $CuO_x@Co_3O_4$ NRs/CF before and after 24 h OER and HER.

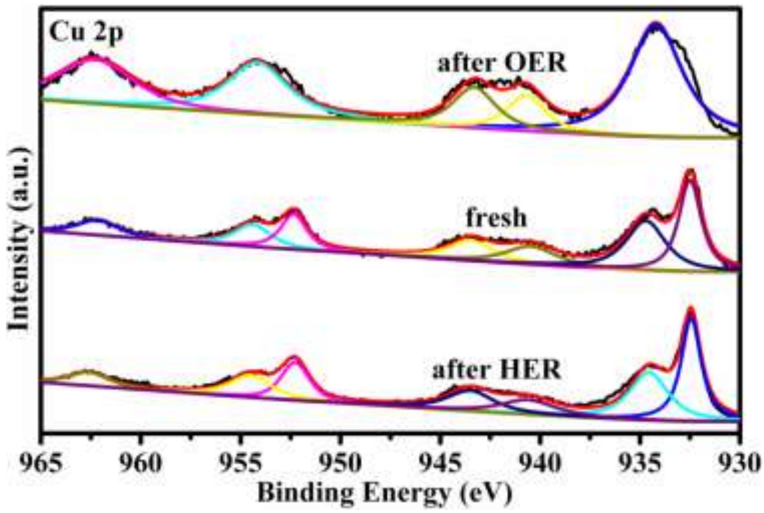

Fig. S18 The comparison of high resolution XPS spectra of Cu 2p before and after 24 h OER and HER.

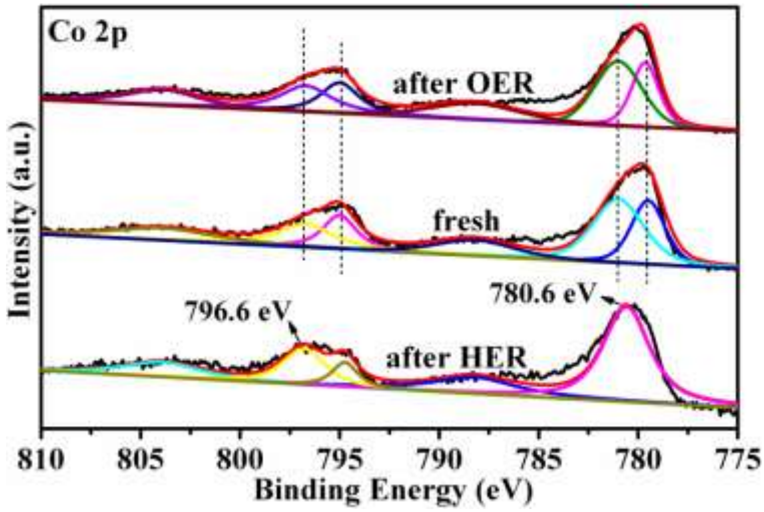

Fig. S19 The comparison of high resolution XPS spectra of Co 2p before and after 24 h OER and HER.

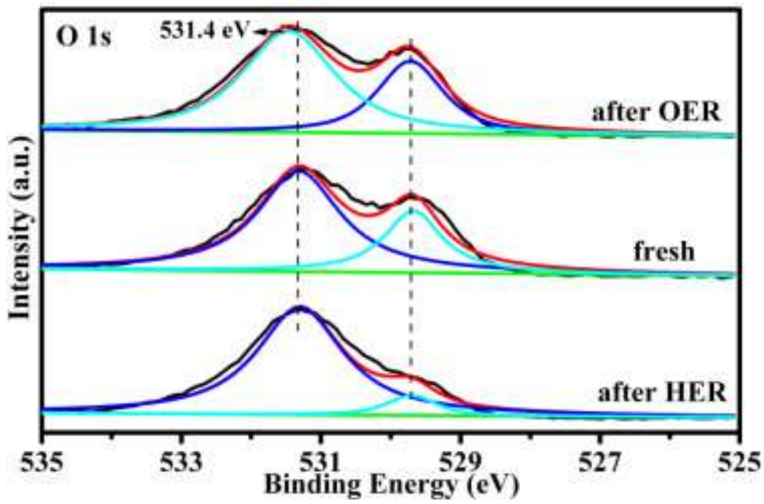

Fig. S20 The comparison of high resolution XPS spectra of O 1s before and after 24 h OER and HER.

Table S1. Comparison of OER activity from different catalysts.

Sample	electrolyte	j ($mA\ cm^{-2}$)	η (mV)	Tafel slope ($mV\ dec^{-1}$)	Reference
CuO_x@Co_3O_4 NRs/CF	1 M KOH	50	240	46	This work
CuO/Co_3O_4	1 M KOH	10	227	–	S1
CuO/Fe-Co_3O_4	1 M KOH	10	232	–	S2
$Cu/Cu_2O/CuO$	1 M NaOH	10	290	64	S3
$Fe(OH)_3$:$Cu(OH)_2$	1 M KOH	10	365	42	S4
CuO nanosheet bundles	1 M KOH	10	350	59	S5
$Cu(OH)_2$@NiFe-LDH	1 M KOH	10	283	88	S6
Annealed CuO	1 M KOH	1.0	430	61.4	S7
$NiFeO_x/CuO$	1 M KOH	100	300	36	S8
NiFe/Cu_2O NWs/CF	1 M KOH	10	215	42	S9
MWCNT-CuO-400	1 M KOH	10	420	59.9	S10
CuO-TCNQ/CF	1 M KOH	25	317	85	S11
CuO nanowire@Co_3O_4 nanosheet	1 M KOH	10	~258	72	S13
CuO NSDs/CF	1 M KOH	10	370	41	S14
NiFe-LDH/CuO NRs/CF	1 M KOH	50	290	60	S15

Table S2. Comparison of HER activity from different catalysts.

Sample	electrolyte	j ($mA\ cm^{-2}$)	η (mV)	Tafel slope ($mV\ dec^{-1}$)	Reference
CuO_x@Co_3O_4 NRs/CF	1 M KOH	50	242	69	This work
$Cu_{0.3}Co_{2.7}P$/NC	1 M KOH	10	220	122	S16
Cu_3P/CF	1 M KOH	20	447	124	S17
Cu NDs/Ni_3S_2 NTs-CFs	1 M KOH	10	128	76.2	S18
Cu@NC NT/CF	1 M KOH	10	123	63	S19
Cu@CoFe	1 M KOH	10	171	36.4	S20
$Co_2B/CoSe_2$	1 M KOH	10	300	76	S21
NiFe-NCs	1 M KOH	10	197	130	S22
NiFeOF	1 M NaOH	10	253	96	S23

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