Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Facile Synthesis of Nickel-Copper Hollow Spheres as Efficient Bifunctional Electrocatalysts for Overall Water Splitting

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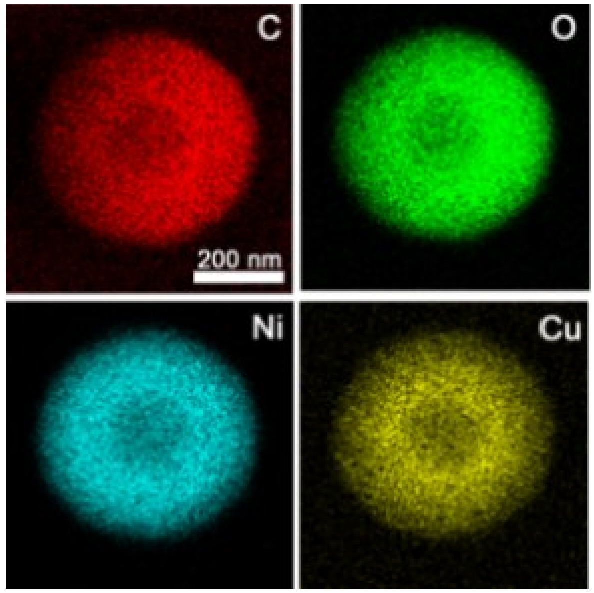

Fig. S1. Elemental mapping images of Ni_4Cu_2-G obtained after solvothermal reaction for 6h.

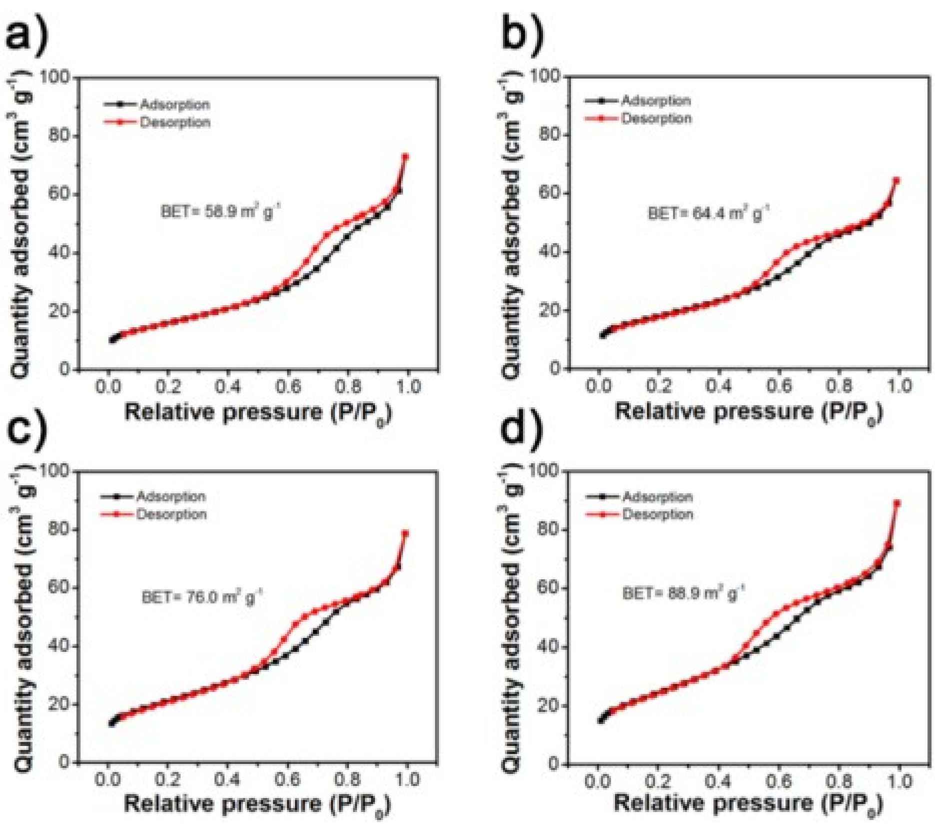

Fig. S2. N_2 sorption isotherms of a) Ni@C, b) Ni_4Cu_1@C, c) Ni_4Cu_2@C and d) Ni_4Cu_3@C.

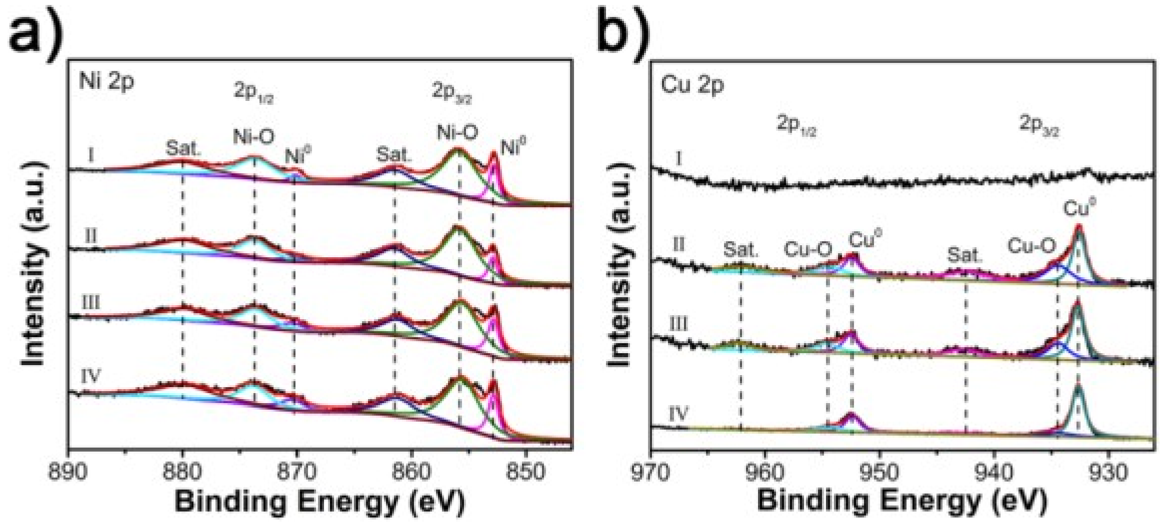

Fig. S3. High resolution XPS spectra of a) Ni 2p and b) Cu 2p of I) Ni@C, II) Ni_4Cu_1@C, III) Ni_4Cu_2@C and IV) Ni_4Cu_3@C.

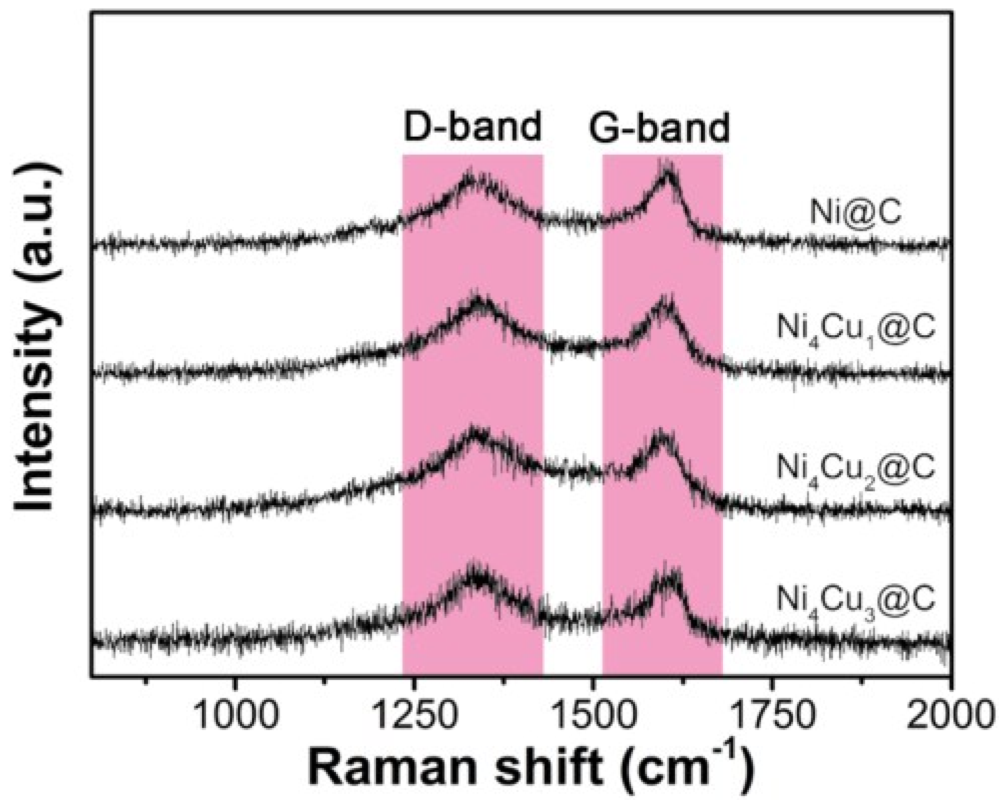

Fig. S4. Raman spectra of Ni_xCu_y@C hollow spheres with different molar ratios for Ni/Cu.

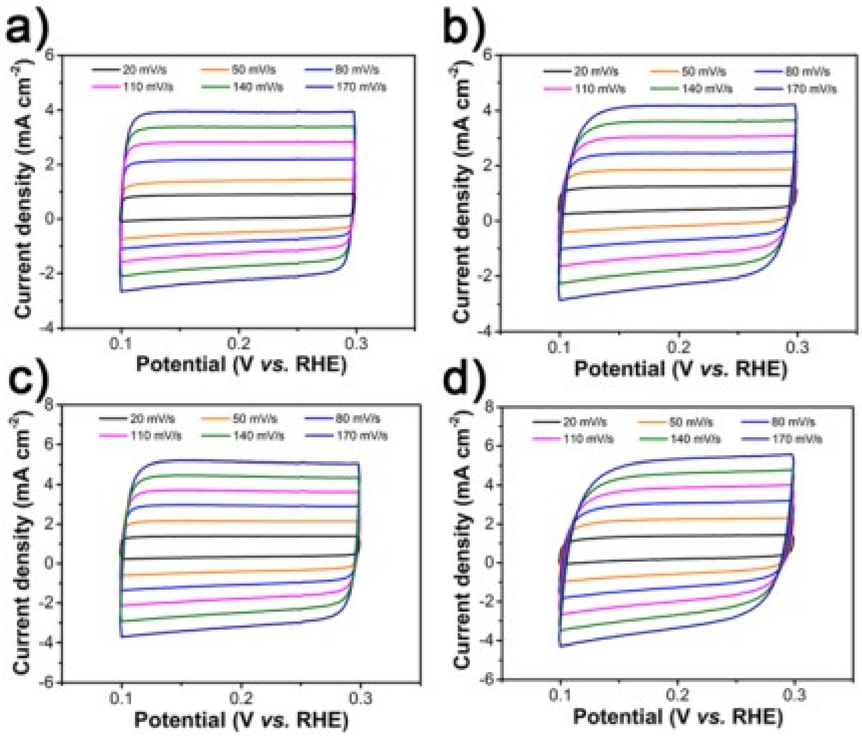

Fig. S5. Cyclic voltammograms of a) Ni@C, b) Ni_4Cu_1@C, c) Ni_4Cu_2@C and d) Ni_4Cu_3@C in 1 M KOH as HER catalysts.

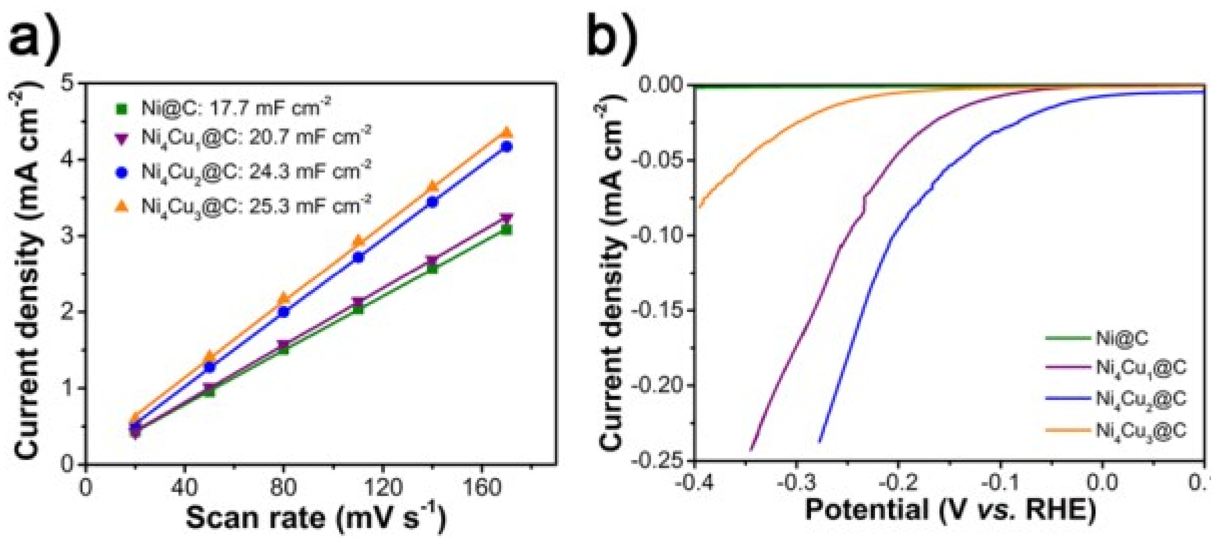

Fig. S6. a) Capacitive current at 0.2 V (*vs* RHE) as a function of scan rate obtained in 1 M KOH and b) normalized polarization curves by ECSA of Ni_xCu_y@C electrocatalysts.

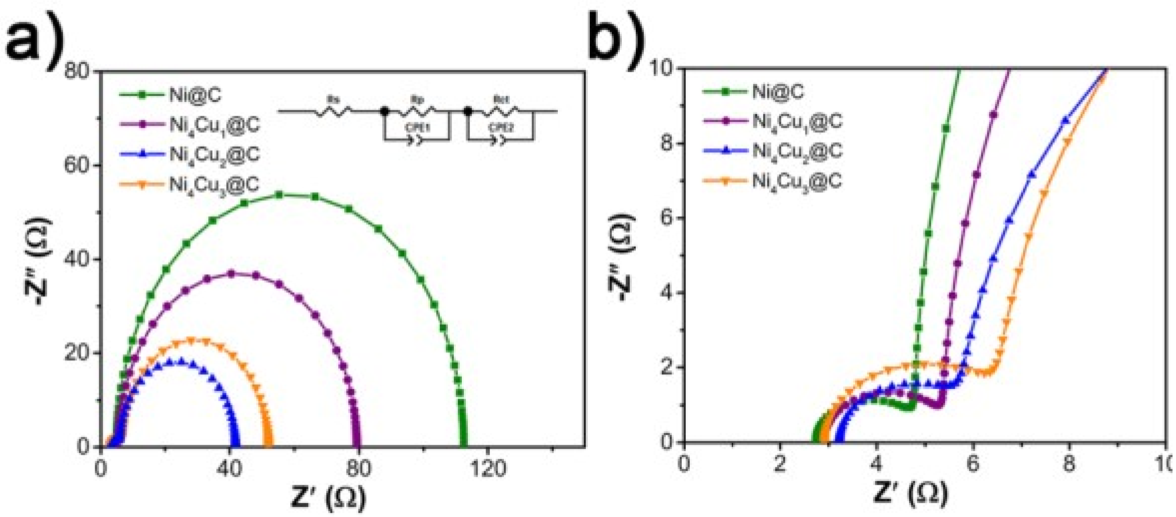

Fig. S7. a) Nyquist plots (at η=150 mV, -0.15 V *vs.* RHE) of Ni_xCu_y@C as HER electrocatalysts obtained in 1 M KOH and b) the corresponding zoom-in regions. R_s, R_p, R_{ct}, CPE1, and CPE2 represent the solution resistance, electrode texture and charge transfer resistances, and constant phase elements, respectively.

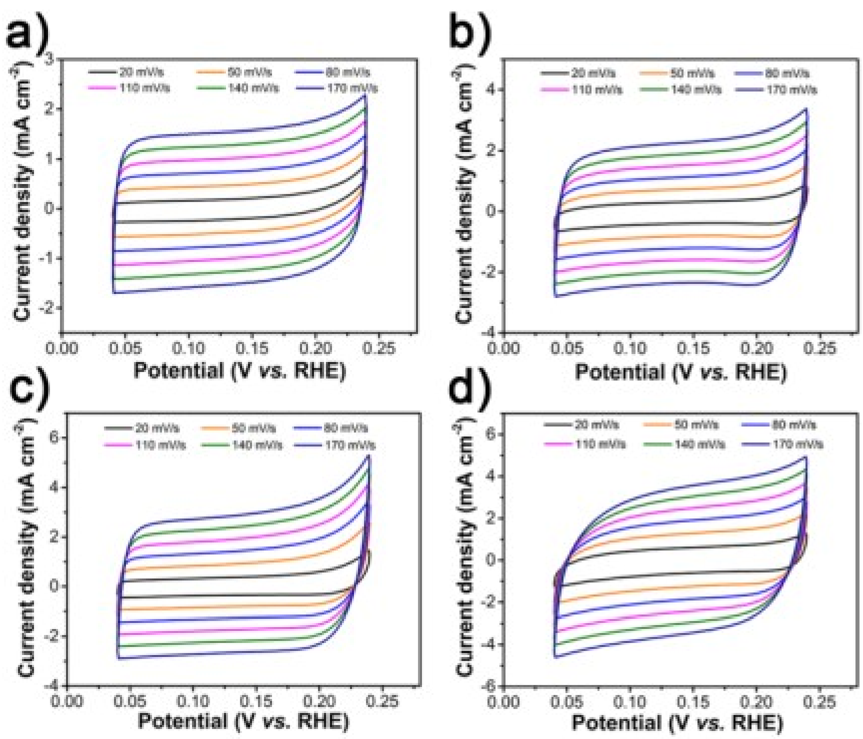

Fig. S8. Cyclic voltammograms of a) Ni@C, b) Ni_4Cu_1@C, c) Ni_4Cu_2@C and d) Ni_4Cu_3@C in 0.5 M H_2SO_4 as HER catalysts.

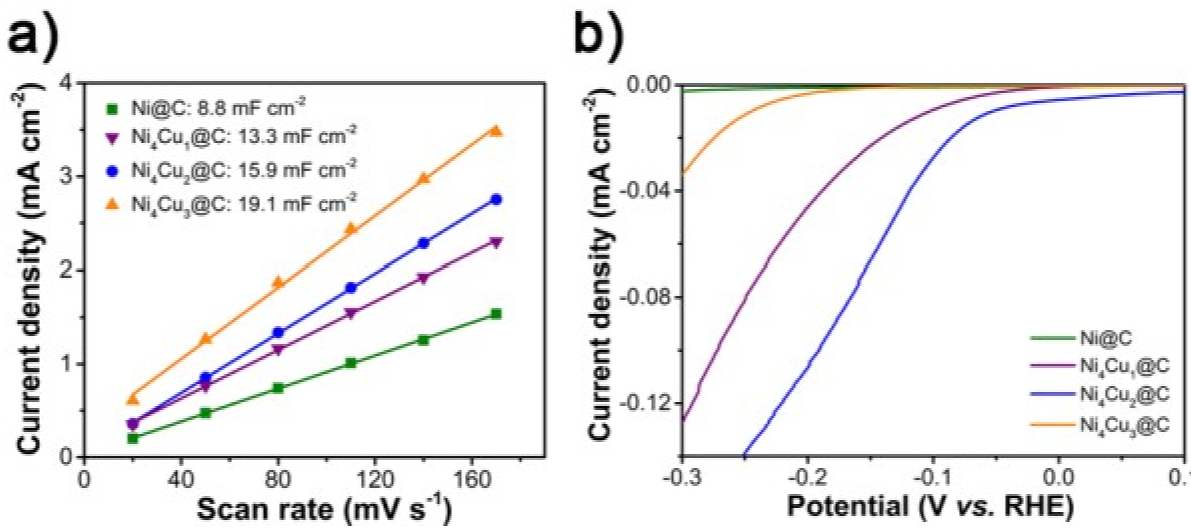

Fig. S9. a) Capacitive current at 0.13 V (*vs* RHE) as a function of scan rate obtained in 0.5 M H_2SO_4 and b) normalized polarization curves by ECSA of Ni_xCu_y@C electrocatalysts.

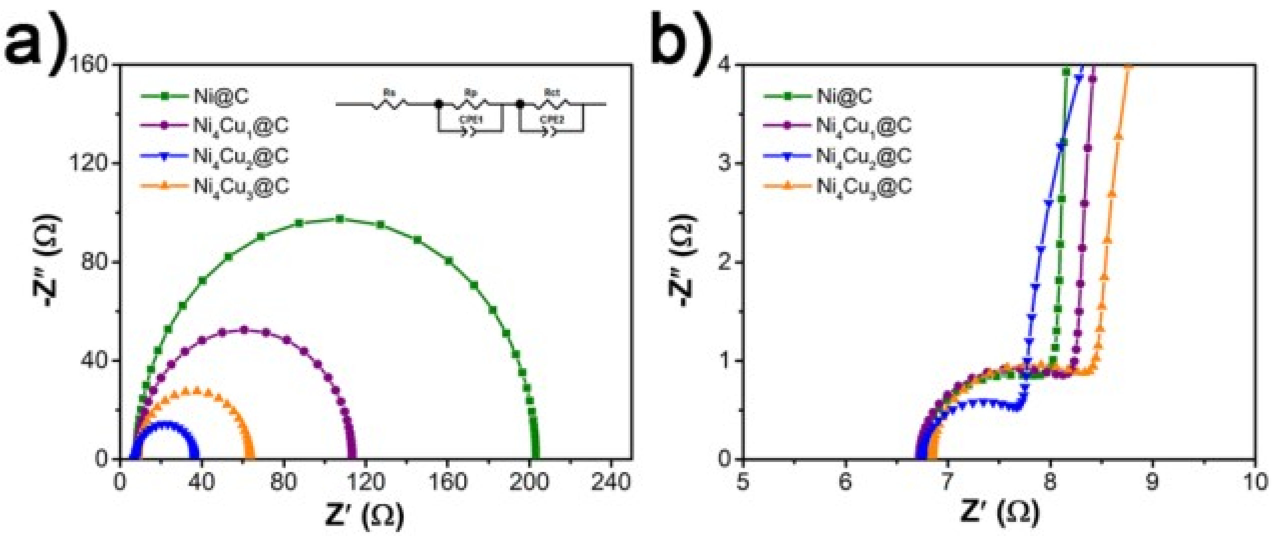

Fig. S10. a) Nyquist plots (at η=150 mV, -0.15 V *vs.* RHE) of Ni_xCu_y@C as HER electrocatalysts obtained in 0.5 M H_2SO_4 and b) the corresponding zoom-in regions. R_s, R_p, R_{ct}, CPE1, and CPE2 represent the solution resistance, electrode texture and charge transfer resistances, and constant phase elements, respectively.

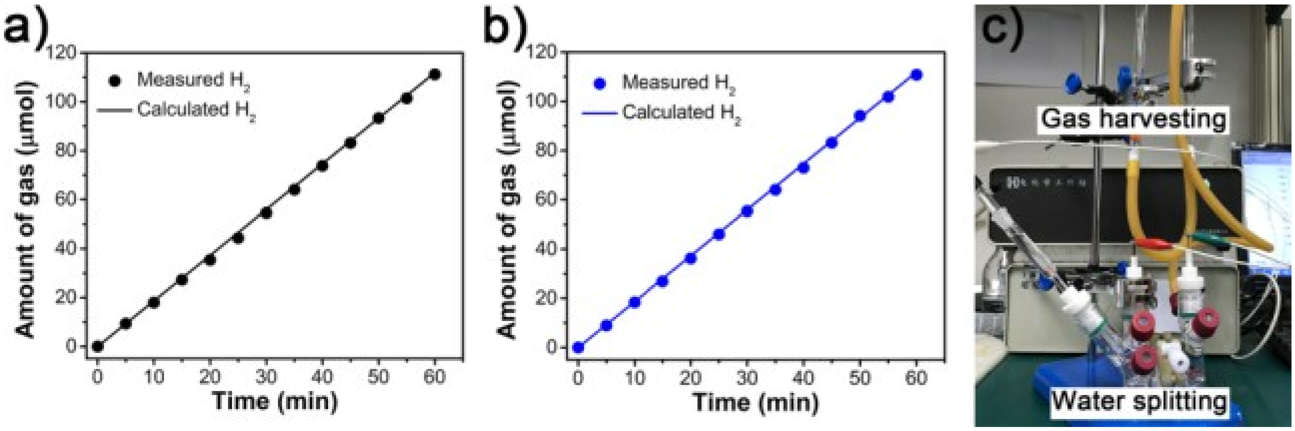

Fig. S11. The Faradaic efficiency of H_2 generation over Ni_4Cu_2@C electrode at a current of −6 mA in a) 1 M KOH and b) 0.5 M H_2SO_4 for 60 minutes, respectively. c) Gas collection device of water splitting.

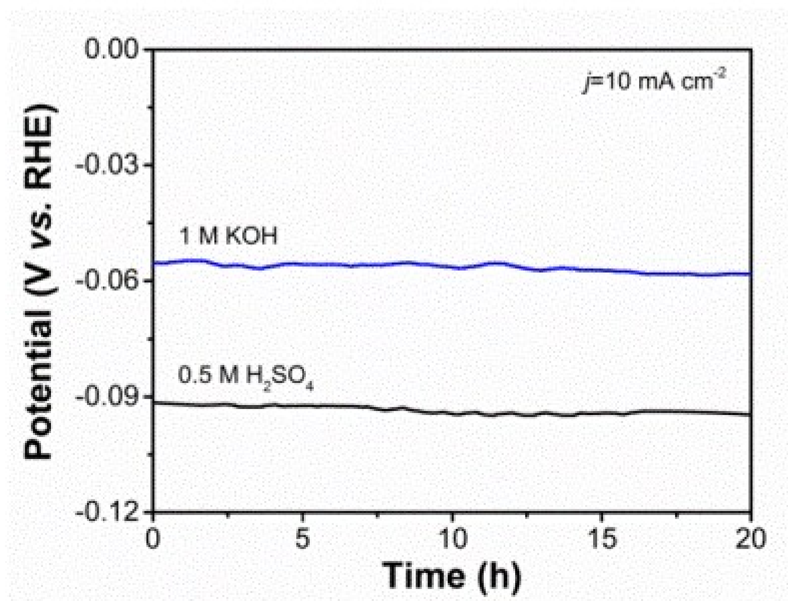

Fig. S12. Chronopotentiometry response of Ni_4Cu_2@C hollow spheres at the current density of 10 mA cm^{-2} in 1 M KOH and 0.5 M H_2SO_4.

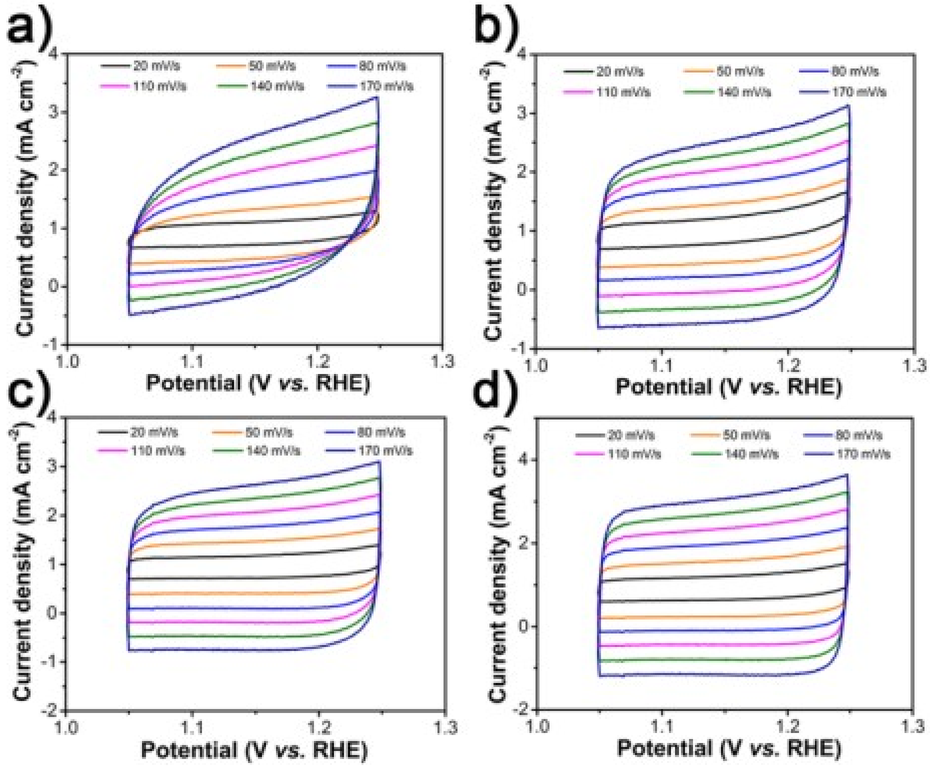

Fig. S13. Cyclic voltammograms of a) Ni@C, b) Ni_4Cu_1@C, c) Ni_4Cu_2@C and d) Ni_4Cu_3@C in 1 M KOH as OER catalysts.

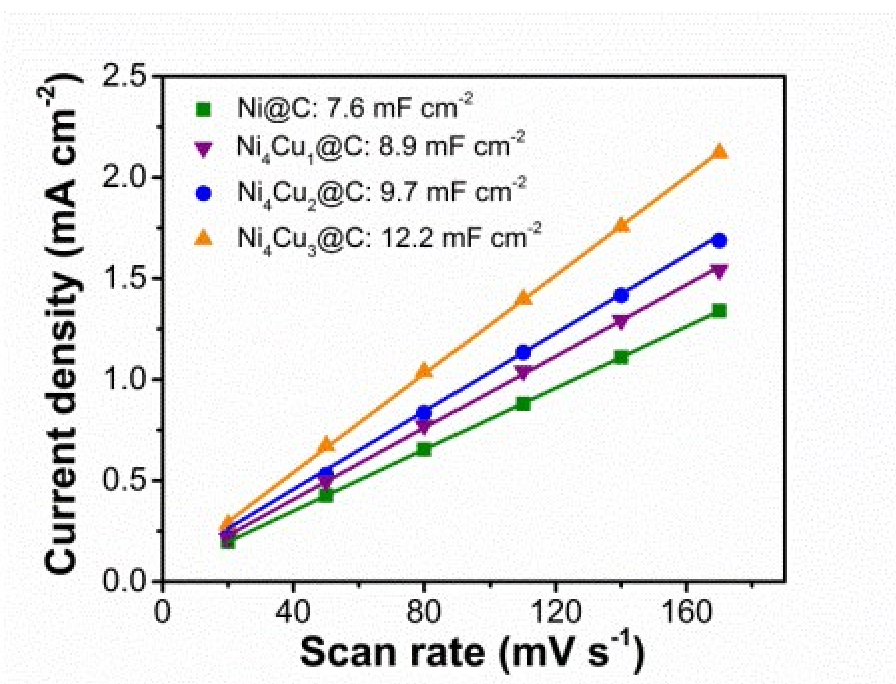

Fig. S14. Capacitive current at 1.15 V (vs RHE) as a function of scan rate obtained in 1 M KOH.

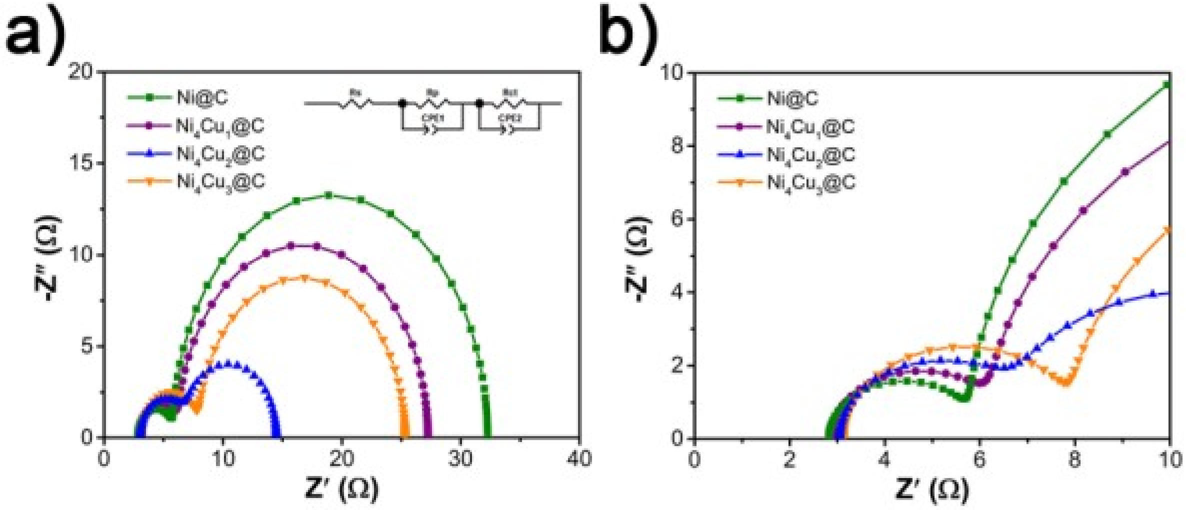

Fig. S15. a) Nyquist plots (at η=350 mV, 1.58 V *vs.* RHE) of $Ni_xCu_y@C$ as OER electrocatalysts obtained in 1 M KOH and b) the corresponding zoom-in regions. R_s, R_p, R_{ct}, CPE1, and CPE2 represent the solution resistance, electrode texture and charge transfer resistances, and constant phase elements, respectively.

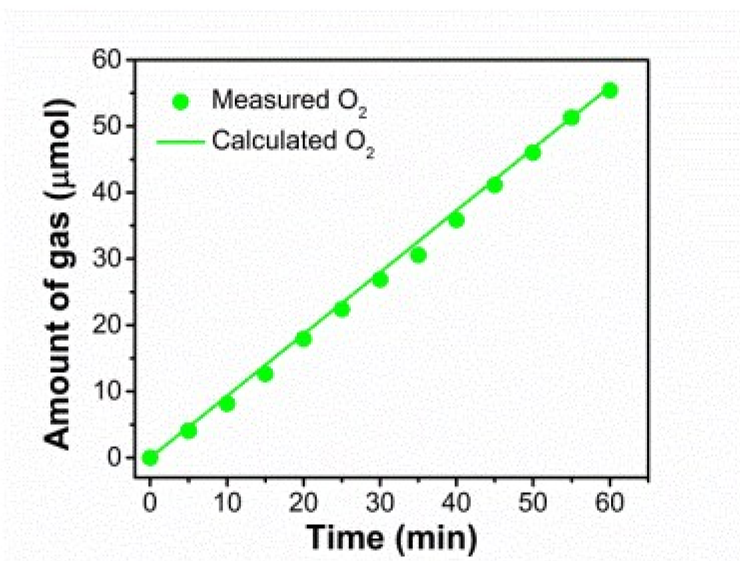

Fig.S16. The Faradaic efficiency of O_2 generation over $Ni_4Cu_2@C$ electrode at a current of 6 mA in 1 M KOH for 60 minutes.

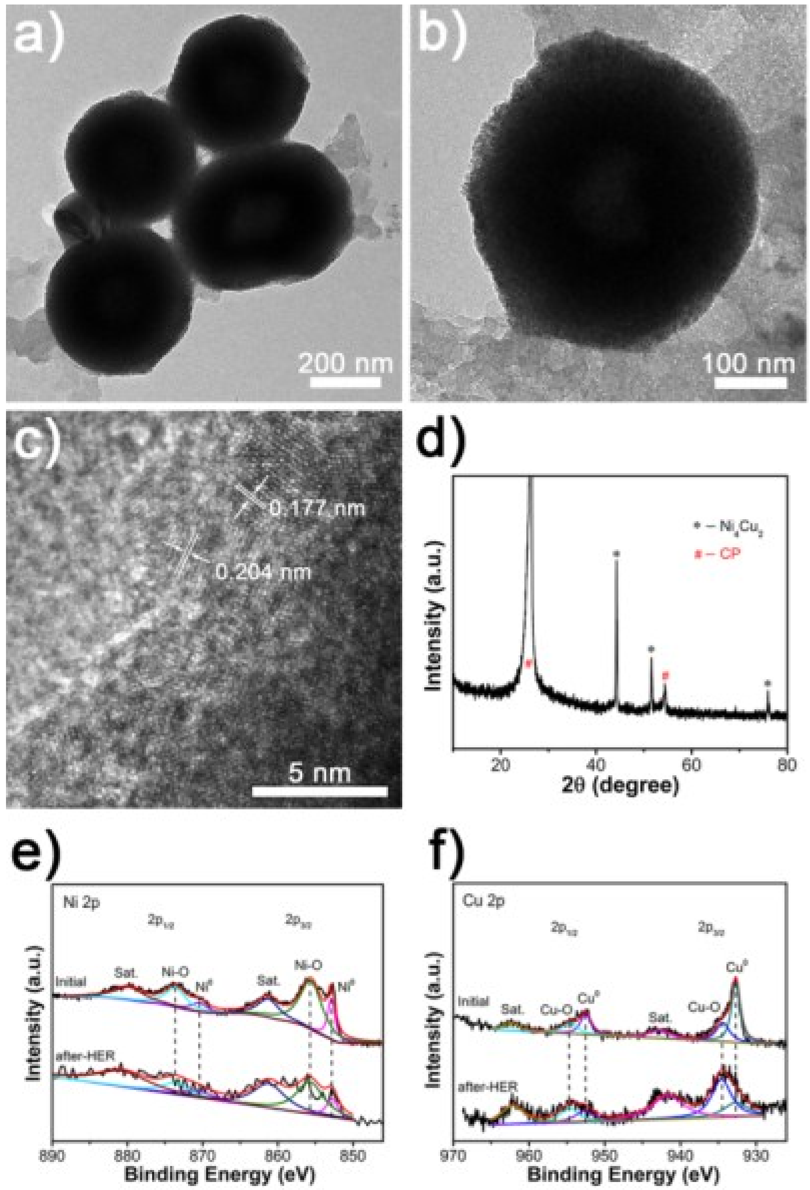

Fig. S17. a, b) TEM images, c) high-resolution TEM image, d) XRD pattern, XPS spectra of e) Ni 2p and f) Cu 2p of Ni_4Cu_2@C hollow spheres after long term overall water splitting on the cathode.

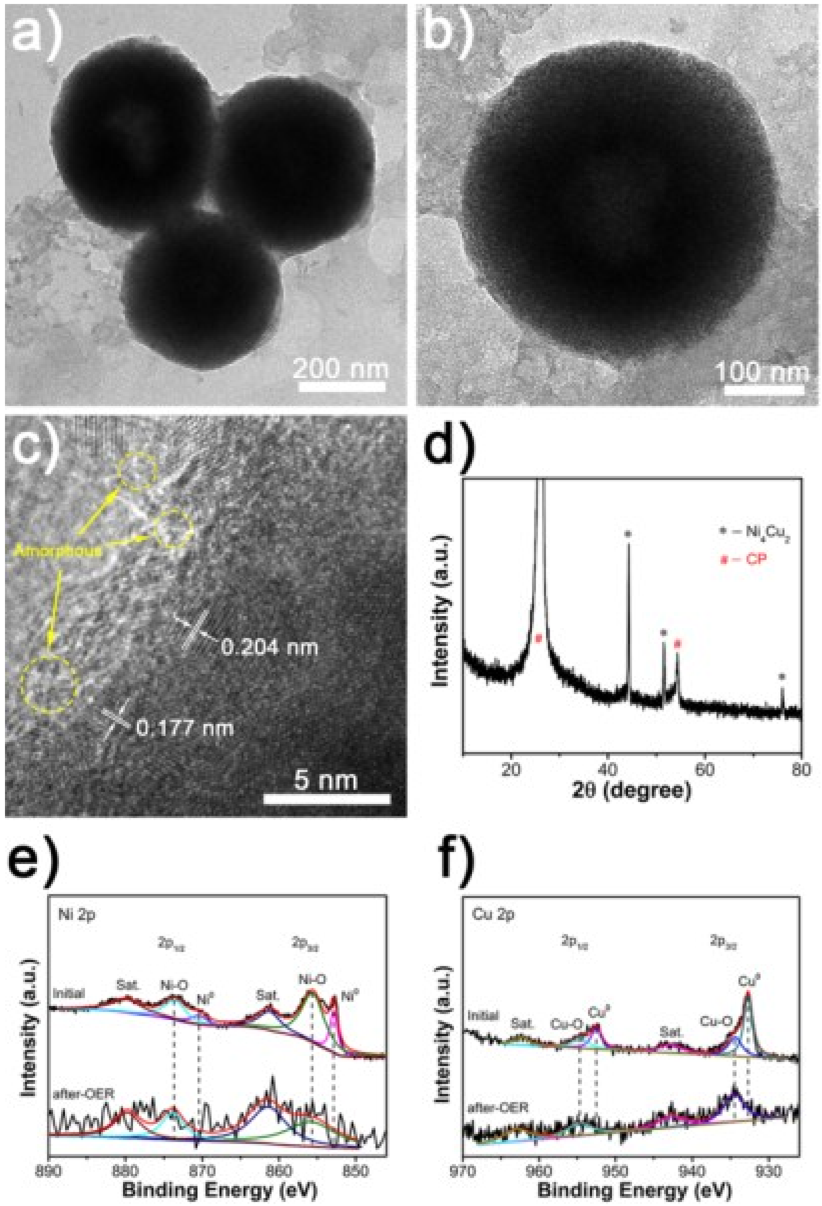

Fig. S18. a, b) TEM images, c) high-resolution TEM image, d) XRD pattern, XPS spectra of e) Ni 2p and f) Cu 2p of Ni_4Cu_2@C hollow spheres after long term overall water splitting on the anode.

Table S1. Summary of the actual molar ratios of the $Ni_xCu_y@C$ products analyzed by ICP-OES.

Sample	Ni (%)	Cu (%)	C (%)
Ni@C	11.2	0	88.8
$Ni_4Cu_1@C$	8.1	1.6	90.3
$Ni_4Cu_2@C$	7.6	3.0	89.4
$Ni_4Cu_3@C$	7.9	3.9	88.2

Table S2. HER performances of $Ni_4Cu_2@C$ hollow spheres and the reported typical electrocatalysts in alkanine medium.

Catalyst	η_{10} (mV)	Medium	Loading (mg cm^{-2})	Substrate	References
$Ni_4Cu_2@C$	**55**	**1 M KOH**	**0.2**	**GCE**	**This work**
Ni_3N-VN/NF	64	1 M KOH	-	Ni foam	*Adv. Mater.* **2019**, 31, 1901174.
$NiFeO_x@NiCu$	66	1 M KOH	0.4	GCE	*Adv. Mater.* **2019**, 31, 1806769.
$Ni_{1.8}Cu_{0.2}$-P	78	1 M KOH	-	Ni foam	*Appl. Catal. B-Environ.* **2019**, 243, 537.
Ni_2P-Ni_3S_2 HNAs/NF	80	1 M KOH	-	Ni foam	*Nano Energy* **2018**, 51, 26.
$NiPS_3/Ni_2P$	85	1 M KOH	0.56	GCE	*ACS Nano* **2019**, 13, 7, 7975
$Ni(OH)_2@CuS$	95	1 M KOH	0.286	GCE	*Nano Energy* **2018**, 44, 7.
NiCoN/C	103	1 M KOH	~0.2	GCE	*Adv. Mater.* **2019**, 31, 1805541.
NG-NiFe@MoC_2	150	1 M KOH	0.2	GCE	*Nano Energy* **2018**, 50, 212.
$Ni_{0.9}Fe_{0.1}PS_3$@MXene	196	1 M KOH	0.25	GCE	*Adv. Energy Mater.* **2018**, 8, 1801127.

Table S3. The resultant EIS parameters recorded during HER in 1 M KOH.

Sample	$R_s(\Omega)$	$R_p(\Omega)$	$R_{ct}(\Omega)$
Ni@C	2.73	2.05	107.8
$Ni_4Cu_1@C$	2.90	2.47	73.97
$Ni_4Cu_2@C$	3.17	2.56	36.07
$Ni_4Cu_3@C$	2.93	3.62	45.46

Table S4. HER performances of Ni_4Cu_2@C hollow spheres and the reported typical electrocatalysts in acidic medium.

Catalyst	η_{10} (mV)	Medium	Loading (mg cm^{-2})	Substrate	References
Ni_4Cu_2@C	**91**	**0.5 M H_2SO_4**	**0.2**	**GCE**	**This work**
WS_2/Ni_5P_4-Ni_2P	94	0.5 M H_2SO_4	30.82	Ni foam	*Nano Energy* **2019**, 55, 193.
Ni_3Cu_1@NG-NC	95	0.5 M H_2SO_4	~0.05	GCE	*Small* **2019**, 1901545.
CoMoNiS-NF	103	0.5 M H_2SO_4	1.86	Ni foam	*J. Am. Chem. Soc.* **2019**, 141, 10417.
Ni_{SA}-MoS_2/CC	110	0.5 M H_2SO_4	-	Carbon Clothes	*Nano Energy* **2018**, 53, 458.
MoPS/NC	120	0.5 M H_2SO_4	0.56	GCE	*Appl. Catal. B-Environ.* **2019**, 245, 656.
CuCo@NC	145	0.5 M H_2SO_4	0.182	GCE	*Adv. Energy Mater.* **2017**, 7, 1700193.
$Fe_{4.5}Ni_{4.5}S_8$	146	0.5 M H_2SO_4	-	Bulk	*ACS Catal.* **2018**, 8, 987.
$NiMo_3S_4$/CTs	156	0.5 M H_2SO_4	2.3	Carbon Textiles	*Nano Energy* **2018**, 49, 460.
c-NiP_2	267	0.5 M H_2SO_4	0.3	GDEs	*Chem. Mater.* **2019**, 31, 3407.

Table S5. The resultant EIS parameters recorded during HER in 0.5 M H_2SO_4.

Sample	$R_s(\Omega)$	$R_p(\Omega)$	$R_{ct}(\Omega)$
Ni@C	6.74	1.35	195
Ni_4Cu_1@C	6.72	1.56	105.1
Ni_4Cu_2@C	6.75	1.00	28.64
Ni_4Cu_3@C	6.74	1.64	55.22

Table S6. HER performances of Ni_4Cu_2@C hollow spheres and the reported typical electrocatalysts in alkanine and acidic media.

Catalyst	Alkanine η_{10} (mV)	Acidic η_{10} (mV)	Loading (mg cm^{-2})	Substrate	References
Ni_4Cu_2@C	**55**	**91**	**0.2**	**GCE**	**This work**
Co_2P@CP	70	120	3.2	Carbon paper	*ACS Energy Lett.* **2018**, 3, 1360.
MoP/CNT	86	83	0.5	Carbon paper	*Adv. Funct. Mater.* **2018**, 28, 1706523.
Co-Fe-P	86	66	0.285	GCE	*Nano Energy* **2019**, 56, 225.
Ni-doped FeP/C	95	72	0.4	Carbon paper	*Sci. Adv.* **2019**, 5: eaav6009.
Ni_{SA}-MoS_2	98	110	-	Carbon clothes	*Nano Energy* **2018**, 53, 458.
$(Fe_xNi_{1-x})_2P$	103	81	1	Ni foam	*Nano Energy* **2019**, 56, 813.
Co@N-CNTs@rGO	108	87	0.5	GCE	*Adv. Mater.* **2018**, 30, 1802011.
CoMoNiS-NF	113	103	1.86	Ni foam	*J. Am. Chem. Soc.* **2019**, 141, 10417.
$FePSe_3$/NC	118.5	70	0.212	GCE	*Nano Energy* **2019**, 57, 222.
Ni_3Cu_1@NG-NC	122	95	~0.05	GCE	*Small* **2019**, 1901545.

Table S7. OER performances of Ni_4Cu_2@C hollow spheres and the reported typical electrocatalysts in alkanine medium.

Catalyst	η_{10} (mV)	Medium	Loading (mg cm^{-2})	Substrate	References
Ni_4Cu_2@C	**283**	**1 M KOH**	**0.2**	**GCE**	**This work**
$NiPS_3$-G	294	0.1 M KOH	0.2	GCE	*ACS Nano* **2018**, 12, 5297.
NiCoP@Cu_3P	309	1 M KOH	-	Cu foam	*J. Mater. Chem. A* **2018**, 6, 2100.
PA-NiO	310	1 M KOH	-	Ni foam	*ACS Energy Lett.* **2018**, 3, 892.
Co-Cu-W oxide	313	0.1 M KOH	1.25	Cu foam	*Angew. Chem. Int. Ed.* **2019**, 58, 4644.
$Ni_{14}Cu_{55}P_1$	319	1 M KOH	-	Cu foil	*Appl. Catal. B-Environ.* **2018**, 237, 409.
NG-NiFe@MoC_2	320	1 M KOH	0.2	GCE	*Nano Energy* **2018**, 50, 212.
Co_3O_4-N-C	324	0.1 M KOH	0.4	GCE	*Nano Energy* **2018**, 48, 600.
$Co(OH)_2$-Au-$Ni(OH)_2$	340	1 M NaOH	-	GCE	*Adv. Funct. Mater.* **2018**, 28, 1804361.
MoS_2-NiS_2/NGF	370	1 M KOH	-	Graphene foam	*Appl. Catal. B-Environ.* **2019**, 254, 15.

Table S8. The resultant EIS parameters recorded during OER in 1 M KOH.

Sample	$R_s(\Omega)$	$R_p(\Omega)$	$R_{ct}(\Omega)$
Ni@C	2.87	3.32	21.04
Ni_4Cu_1@C	2.82	2.95	26.49
Ni_4Cu_2@C	3.01	3.67	7.78
Ni_4Cu_3@C	3.14	4.78	17.41

Table S9. HER and OER performances of Ni_4Cu_2@C hollow spheres and the reported typical bifunctional electrocatalysts in alkanine medium.

Catalyst	HER η_{10} (mV)	OER η_{10} (mV)	Loading (mg cm^{-2})	Substrate	References
Ni_4Cu_2@C	**55**	**283**	**0.2**	**GCE**	**This work**
NiS/G	70	300	2.4	Carbon cloth	*Appl. Catal. B-Environ.* **2019**, 254, 471.
$Fe_{0.09}Co_{0.13}$-$NiSe_2$	92	251	-	Carbon cloth	*Adv. Mater.* **2018**, 30, 1802121.
NC–NiCu–NiCuN	93	232	-	Ni foam	*Adv. Funct. Mater.* **2018**, 28, 1803278.
Co-NC@Mo_2C	99	347	0.83	GCE	*Nano Energy* **2019**, 57, 746.
Cu_3N/NF	118	286	3	Ni foam	*ACS Energy Lett.* **2019**, 4, 747.
Ni/Mo_2C-NCNFs	143	288	1.4	GCE	*Adv. Energy Mater.* **2019**, 9, 1803185
NiCoP/SCW	178	220	4.01	Cu mesh	*Adv. Energy Mater.* **2018**, 8, 1802615
Cr-doped FeNi–P/NCN	190	240	0.48	GCE	*Adv. Mater.* **2019**, 31, 1900178.
$Ni_{0.9}Fe_{0.1}PS_3$@MXene	196	282	0.25	GCE	*Adv. Energy Mater.* **2018**, 8, 1801127.
Fe-Ni@NC-CNT	202	274	0.5	GCE	*Angew. Chem. Int. Ed.* **2018**, 57, 8921

Table S10. Overall water splitting performances of $Ni_4Cu_2@C$ hollow spheres and the reported typical electrocatalysts.

Catalyst	Cell Voltage (V)	*j* (mA cm^{-2})	Loading (mg cm^{-2})	Substrate	Stability	References
$Ni_4Cu_2@C$	**1.49**	**15**	**1.5**	**Carbon paper**	**50 h @ 40 mA cm^{-2}**	**This work**
Ni_3N-VN/NF	1.51	10	-	Ni foam	100 h @ 1.51 V	*Adv. Mater.* **2019**, 31, 1901174.
NC–NiCu–NiCuN	1.56	10	-	Ni foam	50 h @ 1.56 V	*Adv. Funct. Mater.* **2018**, 28, 1803278.
$Co_3S_4@MoS_2$	1.58	10	0.6	Carbon paper	10 h @ 10 mA cm^{-2}	*Nano Energy*, **2018**, 47, 494.
$NiCo_2$S4	1.58	10	-	Ni foam	72 h @ 1.64 V	*Adv. Funct. Mater.* **2019**, 29, 1807031.
NiCoP/SCW	1.59	10	4.01	Cu mesh	24 h @ 1.59 V	*Adv. Energy Mater.* **2018**, 8, 1802615.
Cu_3N/NF	1.60	10	3	Ni foam	10 d @ 10 mA cm^{-2}	*ACS Energy Lett.* **2019**, 4, 747.
NCO/G NSs	1.61	10	0.31	Ti mesh	10 h @ 1.61 V	*Nano Energy* **2018**, 48, 284.
Ni/Mo_2C-NCNFs	1.64	10	2	Ni foam	100 h @ 10 mA cm^{-2}	*Adv. Energy Mater.* **2019**, 9, 1803185.
$Ni_{0.9}Fe_{0.1}PS_3$@MXene	1.65	10	2	Ni foam	50 h @ 1.65 V	*Adv. Energy Mater.* **2018**, 8, 1801127.
$(Co_{1-x}Ni_x)(S_{1-y}P_y)_2$/G	1.65	10	3.0	Carbon paper	50 h @ 20 mA cm^{-2}	*Adv. Energy Mater.* **2018**, 8, 1802319.
Co-NC@ Mo_2C	1.685	10	0.83	GCE	20 h @ 1.69 V	*Nano Energy* **2019**, 57, 746.
PO-Ni/Ni-N-CNFs	1.69	10	8	Ni foam	40 h @ 10 mA cm^{-2}	*Nano Energy* **2018**, 51, 286.