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Supporting Information

3D Ordered Macroporous Copper Nitride-Titanium Oxynitrides as Highly Efficient Electrocatalysts for Universal-pH Hydrogen Evolution Reaction

Yuchen Wu[12], Fanghua Ning[3], Zhiwei Wang[12], Ali Saad[2], Xiuting Li[*1] and Dingguo Xia[*3]

[1] *Institute for Advanced Study, Shenzhen University, Shenzhen 518060, China.*

[2] *Key Laboratory of Optoelectronic Devices and Systems, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.*

[3] *Beijing Key Laboratory of Theory and Technology for Advanced Batteries Materials, School of Materials Science and Engineering, Peking University, Beijing 100871, P. R. China.*

*Correspondence and requests for materials should be addressed to X.L. (email: xiuting.li@szu.edu.cn) or to D.X. (email: dgxia@pku.edu.cn).

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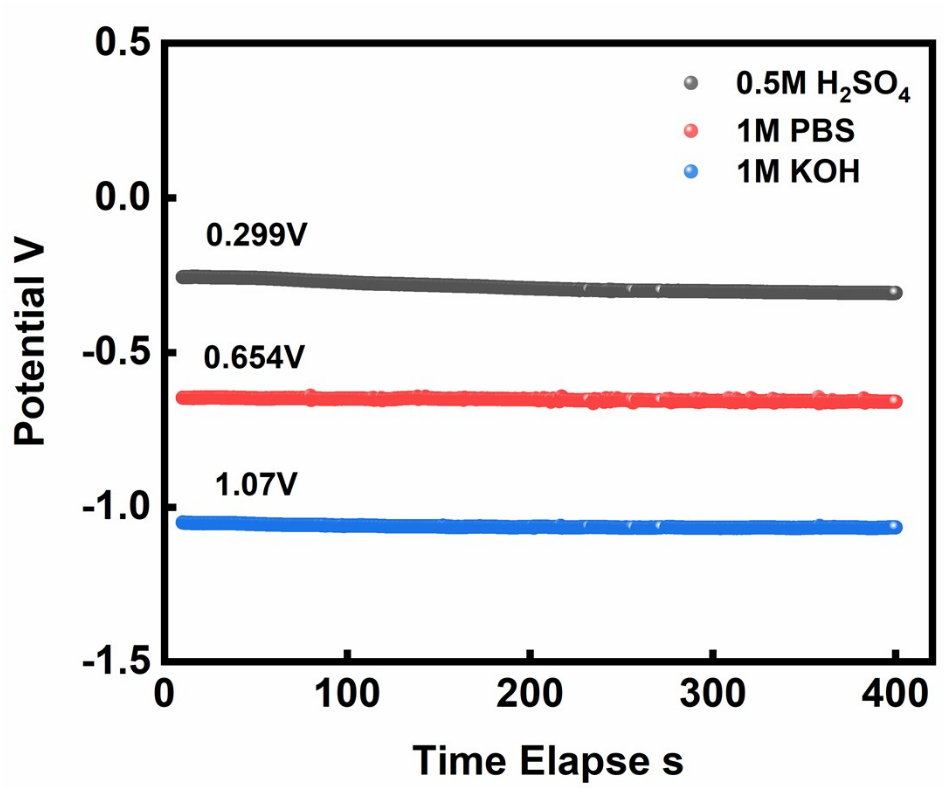

Fig. S1 Calibration curve of SCE vs RHE in 0.5M H_2SO_4, 1M PBS and 1M KOH electrolyte solution.

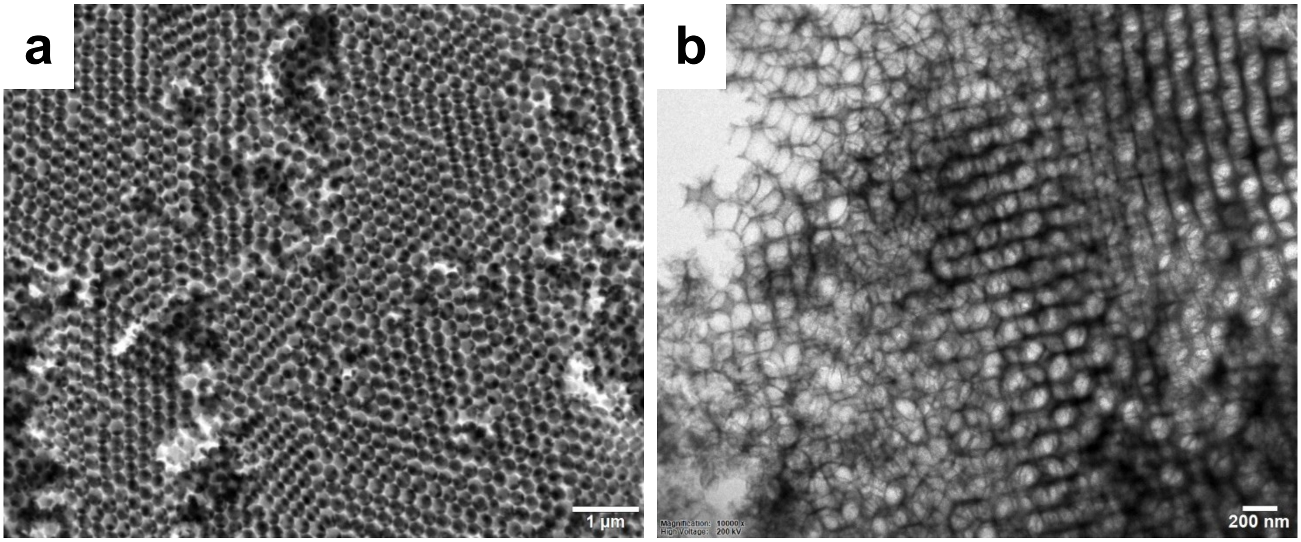

Fig. S2 (a)SEM, (b) TEM of Cu_3N(20)@3DOM-TiO_xN_y at low magnitude.

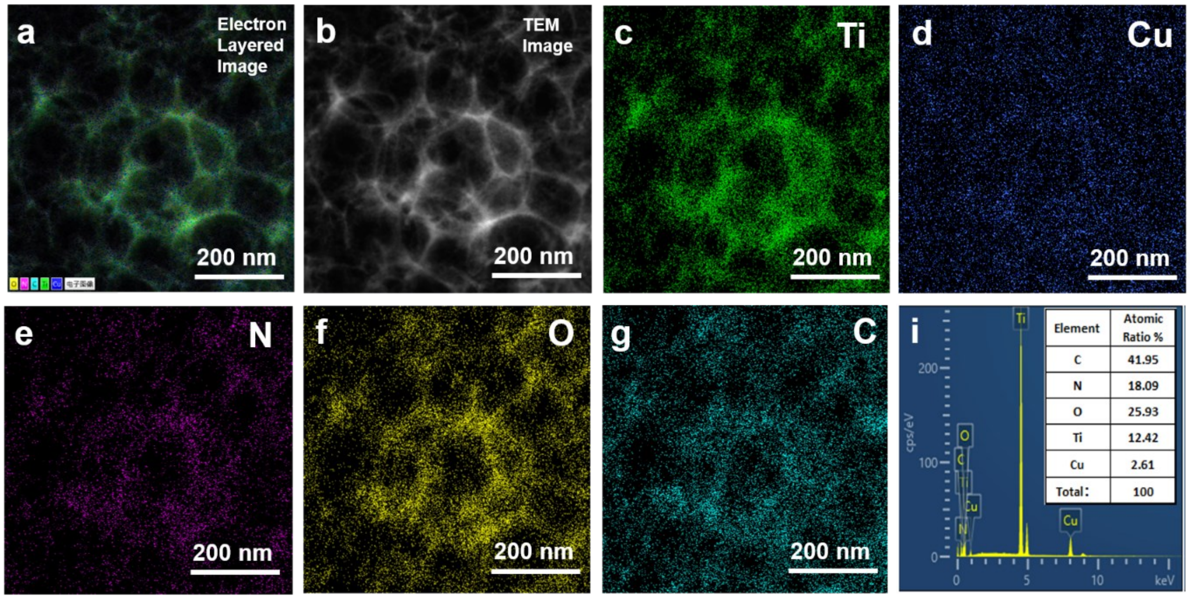

Fig. S3 TEM scanning of Cu_3N(20)@3DOM-TiO_xN_y, a) Electron layered image, b) TEM image, EDS mapping of c) Ti, d) Cu, e) N, f) O, g) C, and i) atomic ratio.

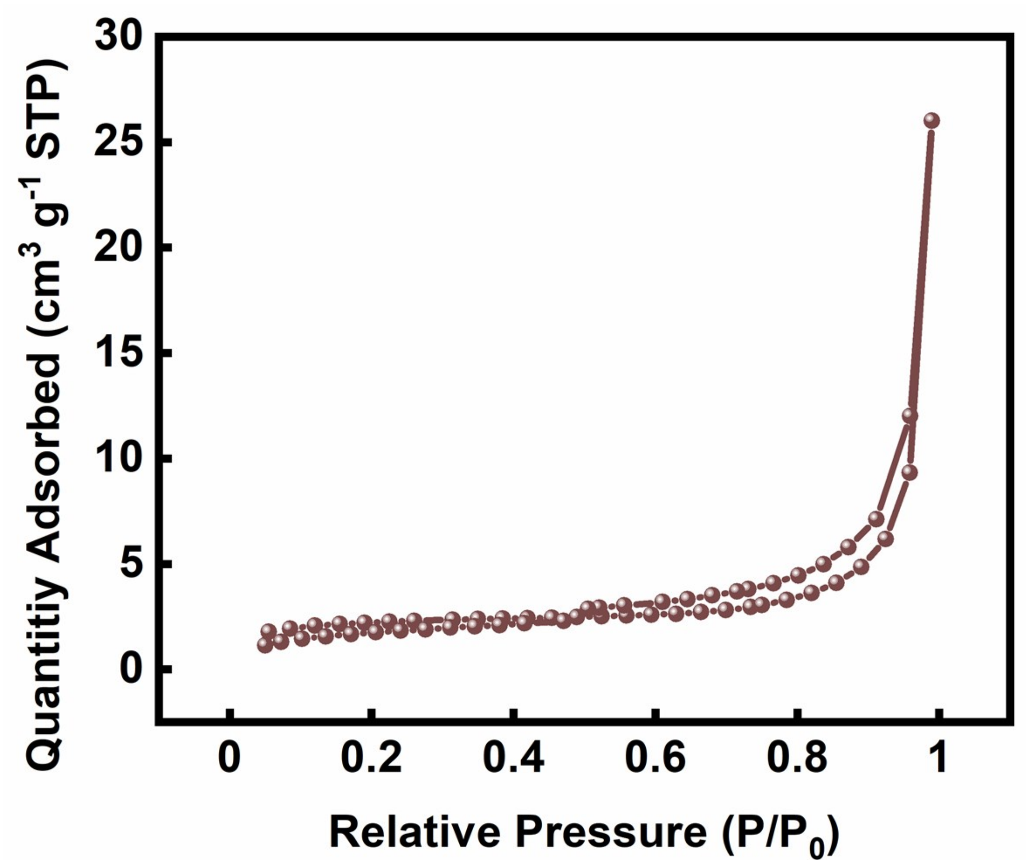

Fig. S4 N_2 ad/desorption isotherm of bulk-Cu_3N(20)@TiO_xN_y.

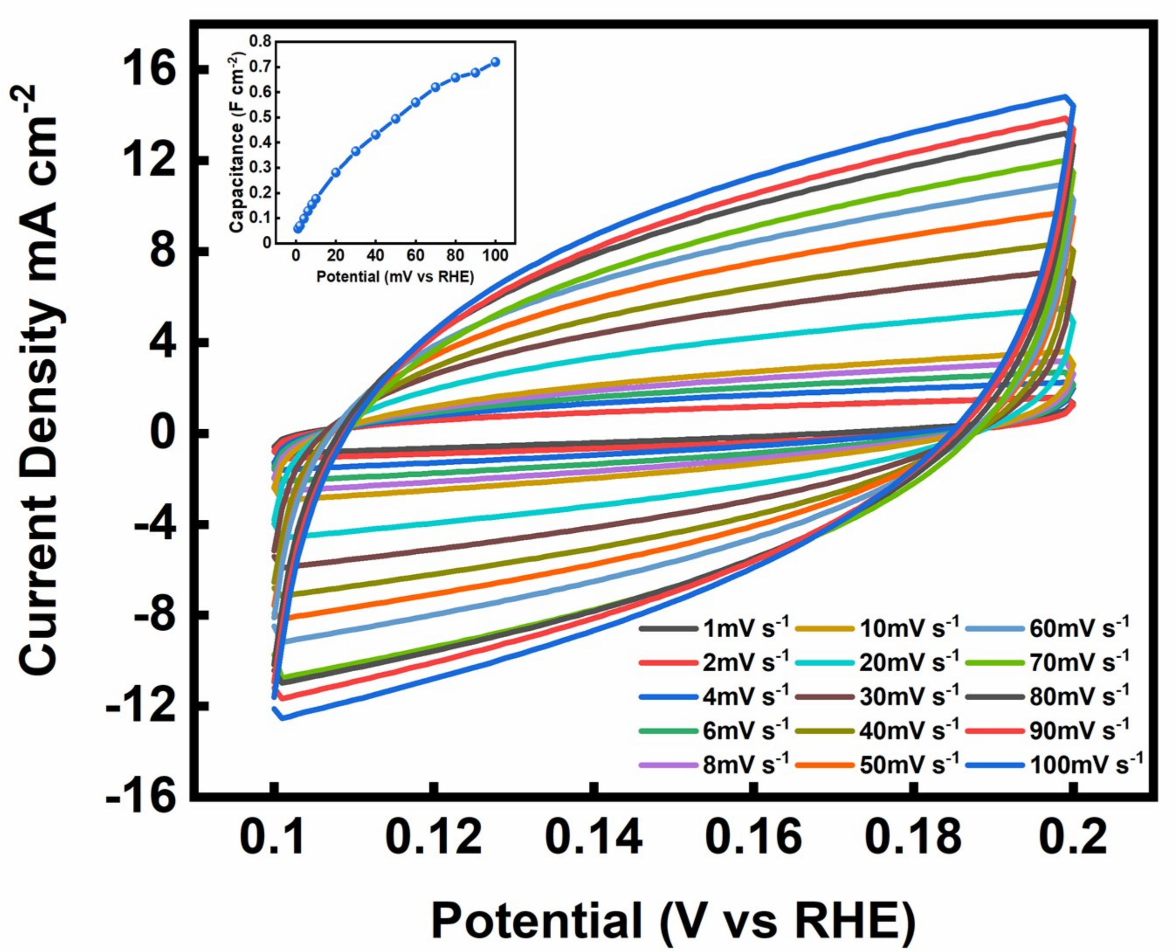

Fig. S5 CV and specific capacitance curve of Cu_3N(20)@3DOM-TiO_xN_y under scan rates from 1 mV s^{-1} to 100 mV s^{-1}.

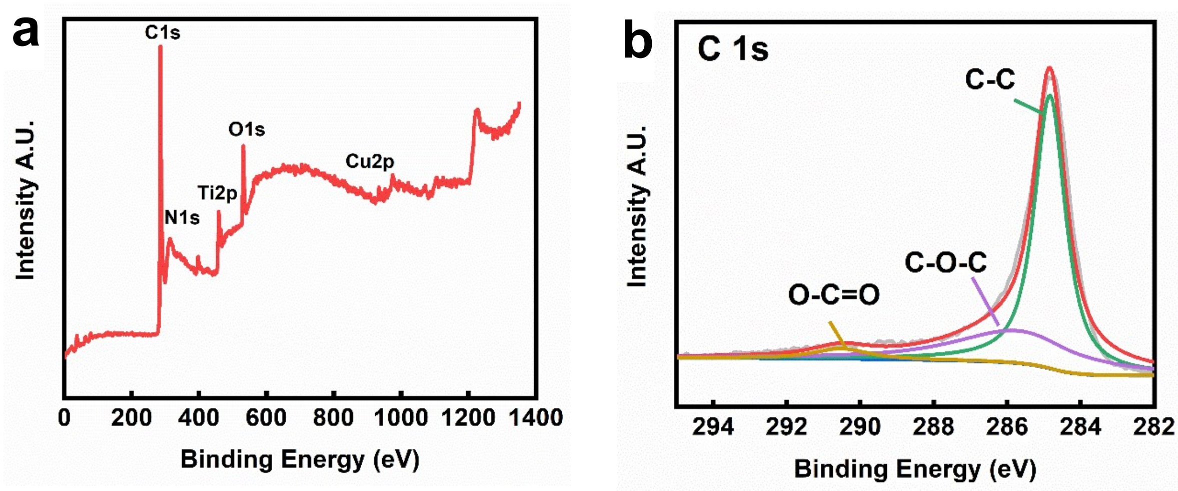

Fig. S6 (a) XPS survey, and (b) C1s scan of Cu_3N(20)@3DOM-TiO_xN_y.

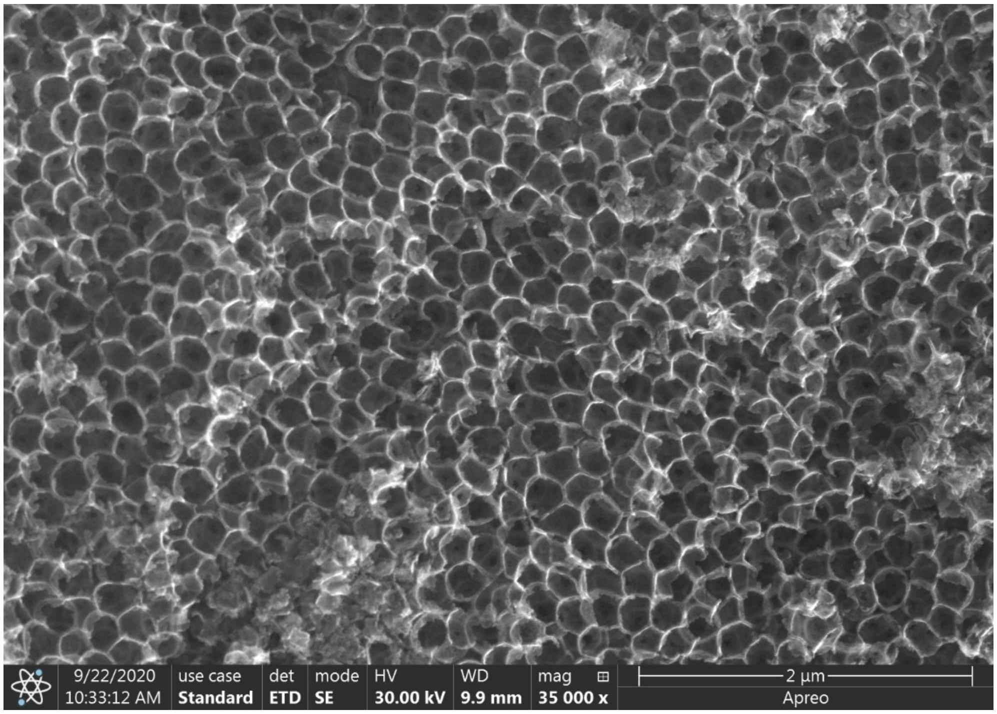

Fig. S7 Broken 3DOM porous structure of $Cu_3N(40)@3DOM\text{-}TiO_xN_y$.

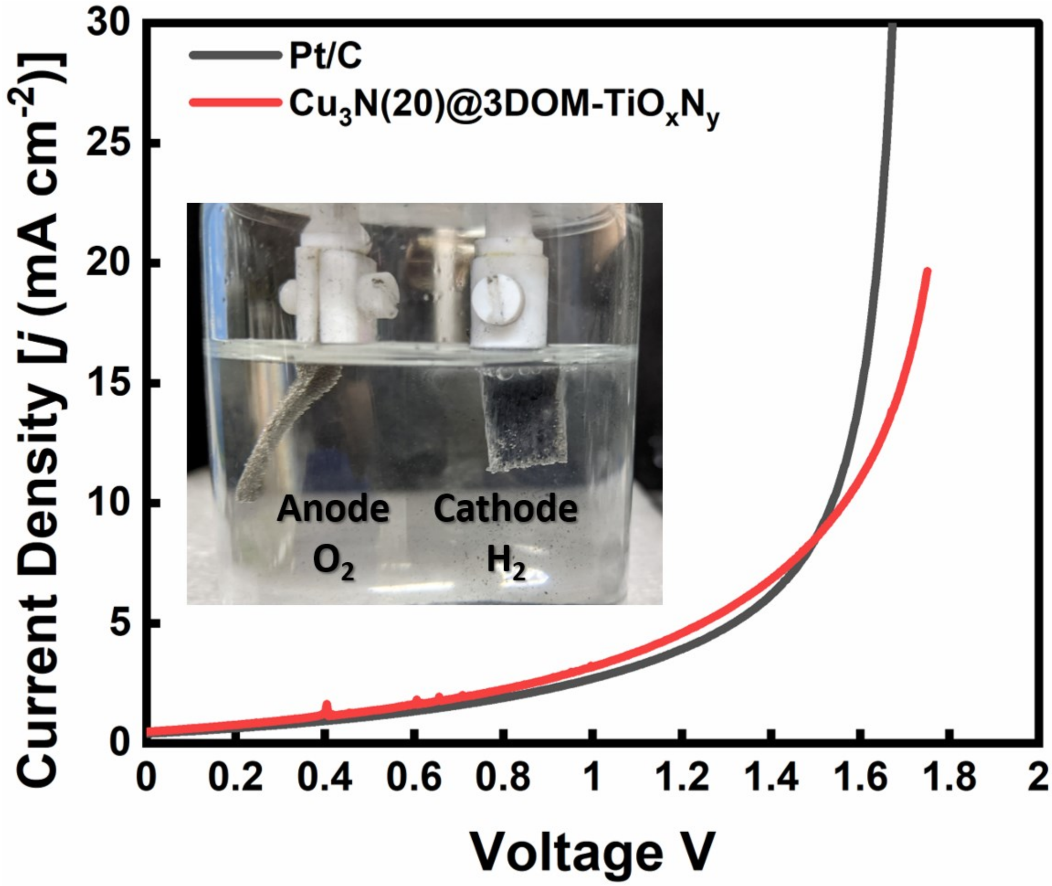

Fig. S8 Water splitting electrolyzer using $Cu_3N(20)@3DOM\text{-}TiO_xN_y$ electrocatalyst cathode.

The $Cu_3N(20)@3DOM\text{-}TiO_xN_y$ on nickel foam acted as the cathode and displayed a high performance with a cell voltage of 1.57 V, which is close to the 1.51 V of Pt/C to afford 10 mA cm^{-2} water splitting current in 1.0 M PBS with continuous gas evolution on both electrodes in a two-electrode water electrolyzer.

Additionally, a video showing the same two-electrodes electrolyzer driven by a 2V solar-panel generating H_2 bubbles can be found in the supporting material.

Table S1 Ti and Cu ratio obtained from ICP-OES test.

Element	Mass ratio wt (%)	Atomic Percentage (%)
Cu	13.74	20.8%
Ti	39.40	79.2%

Table S2 Surface area, pore distribution and pore volume comparison of $Cu_3N(20)@3DOM\text{-}TiO_xN_y$ and bulk-$Cu_3N(20)@TiO_xN_y$.

	$Cu_3N(20)@3DOM\text{-}TiO_xN_y$	Bulk-$Cu_3N(20)@TiO_xN_y$
Surface Area m_2 g^{-1}	163.7521	7.3568
Pore Volume cm^3 g^{-1}	0.260232	0.039090
Pore size nm	6.3567	21.25396

Table S3 Surface elemental weight ratio and atomic ratio of the C, N, O, Ti, Cu and Cl.

Element	Mass ratio wt/%
Cu	11.85
Ti	5.45
N	5.63
O	32.64
C	8.27
Cl	<0.1
Total	100.00

Table S4 HER performance comparison of several up to date related electrocatalysts.

Electrocatalyst	Electrolyte	Overpotential mV (@10mA cm^{-2})	Tafel Slope mV dec^{-1}	References
Pt/C	Universal pH	50~55	42~47	This work
Cu_3N@3DOM-TiO_xN_y	Universal pH	71.1~79.3	55~63	This work
Cu_2O-Cu_2Se nanoflake arrays	Universal pH	52.9~77.8	78.7~173.5	1
Cu-doped CoP arrays	Universal pH	81~137	102~144	2
Cu(0)-based catalyst	Neutral	70	127	3
MOF-derived copper nitride/phosphide	Neutral	109	69.0~138.3	4
Cu-Ti	Alkaline	108	~120	5
Mesoporous Cu-Ni	Alkaline	140	79	6
Holey Ni-Cu sheets	Alkaline	100	~70	7
NiMo-NiCu	Alkaline	154	42	8
Co_3O_4-CuO	Alkaline	288	65	9
Hierarchical nanoporous Ni(Cu)@NiFeP	Alkaline	128	121.8	10
Cu@Cu_2O@C	Alkaline	97	274~307	11
Cu-Mo-O nanosheets	Alkaline	112	136	12
Cu-MOF	Alkaline	89.3	33.4	13
Cu_2O layer/TiO_2 nanodots	Alkaline	96	160	14
Cu-Co_2P/NCNTs	Acidic	140	112	15
Hollow Cu/Cu_2O/Cu_2S	Acidic	86	107	16
Cu_3P-CoP nanowire	Acidic	59	96	17
Cu-MoS_2/rGO	Acidic	126	90	18
Hemi-core@frame AuCu@IrNi	Acidic	355	58	19
Cu@graphdiyne core–shell nanowires array	Acidic	79	89	20
$NiMo_6O_{24}$@Cu/TNA	Acidic	130	89.2	21

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