

**Metal-Organic Framework Derived Carbon-Encapsulated Hollow  
CuO/Cu<sub>2</sub>O heterostructure heterohedron as an Efficient  
Electrocatalyst for Hydrogen Evolution Reaction**

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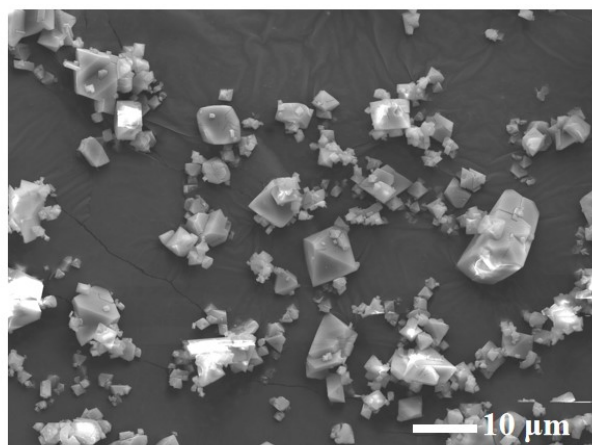
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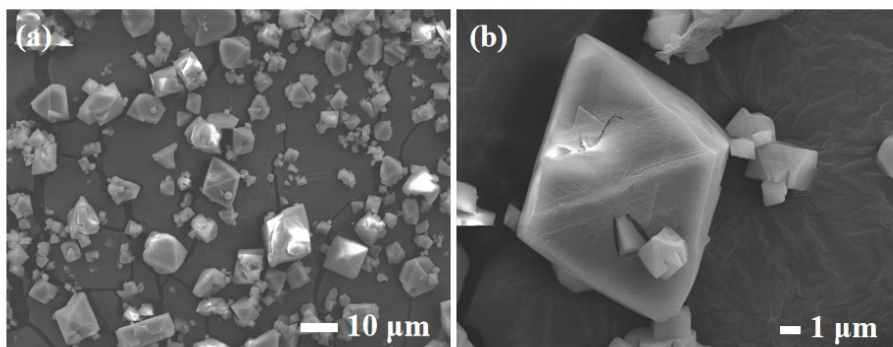
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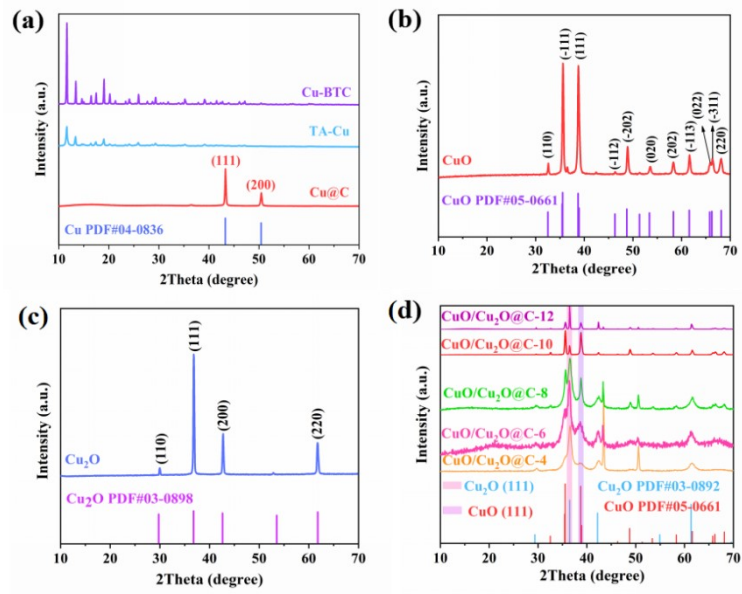
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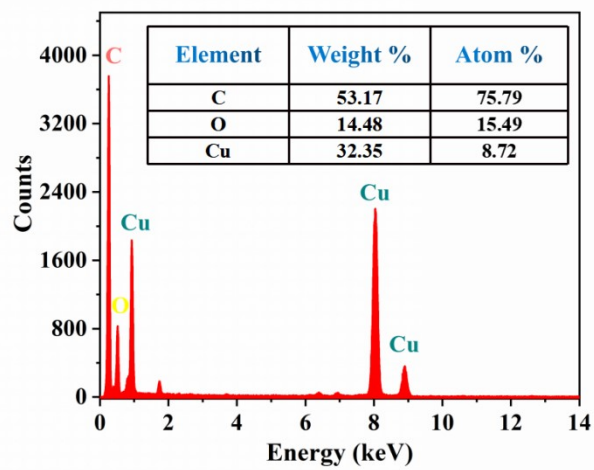
**Fig. S1.** SEM image of Cu-BTC.



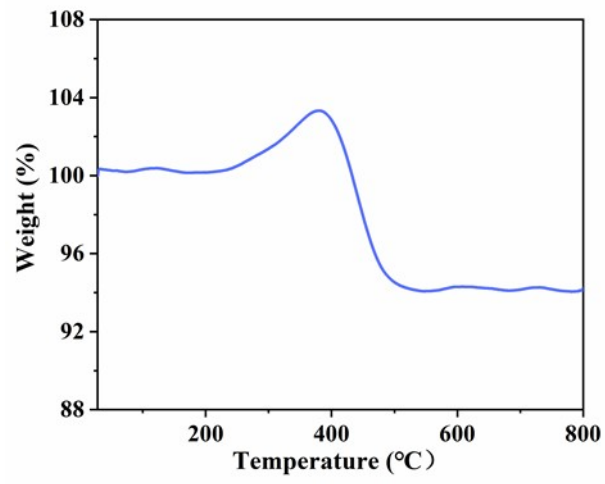
**Fig. S2.** SEM images of TA-Cu.



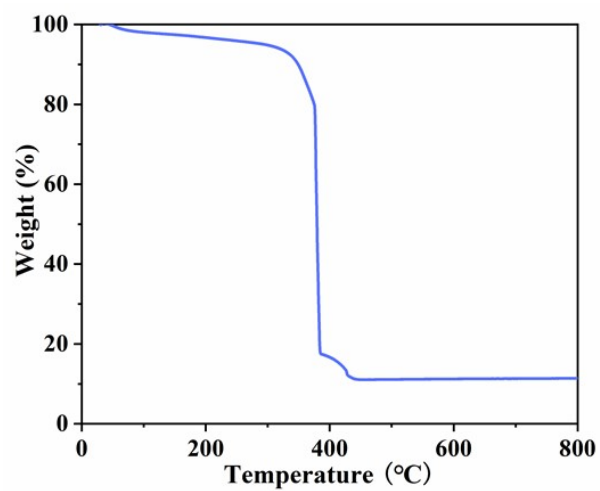
**Fig. S3.** XRD patterns of (a) Cu-BTC, TA-Cu, Cu@C, (b) pure CuO, (c) pure Cu<sub>2</sub>O, (d) CuO/Cu<sub>2</sub>O@C materials with different oxidation time.



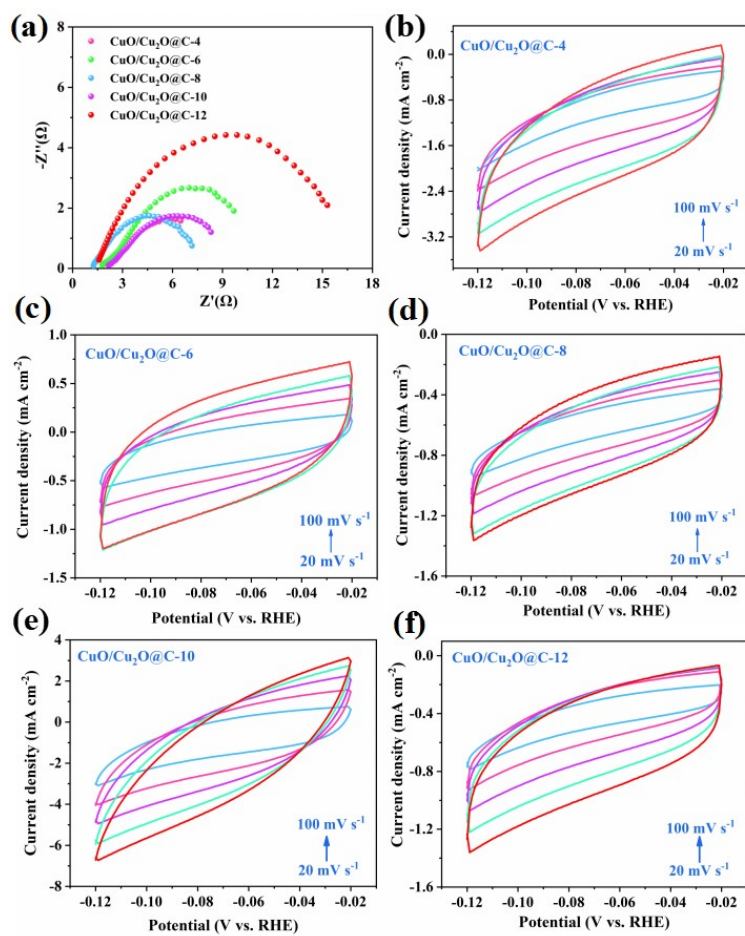
**Fig. S4.** EDS of C, O, Cu elements in the composites, and the insets are the weight and atom ratio.



**Fig. S5.** TG curve of CuO/Cu<sub>2</sub>O@C-10 material.

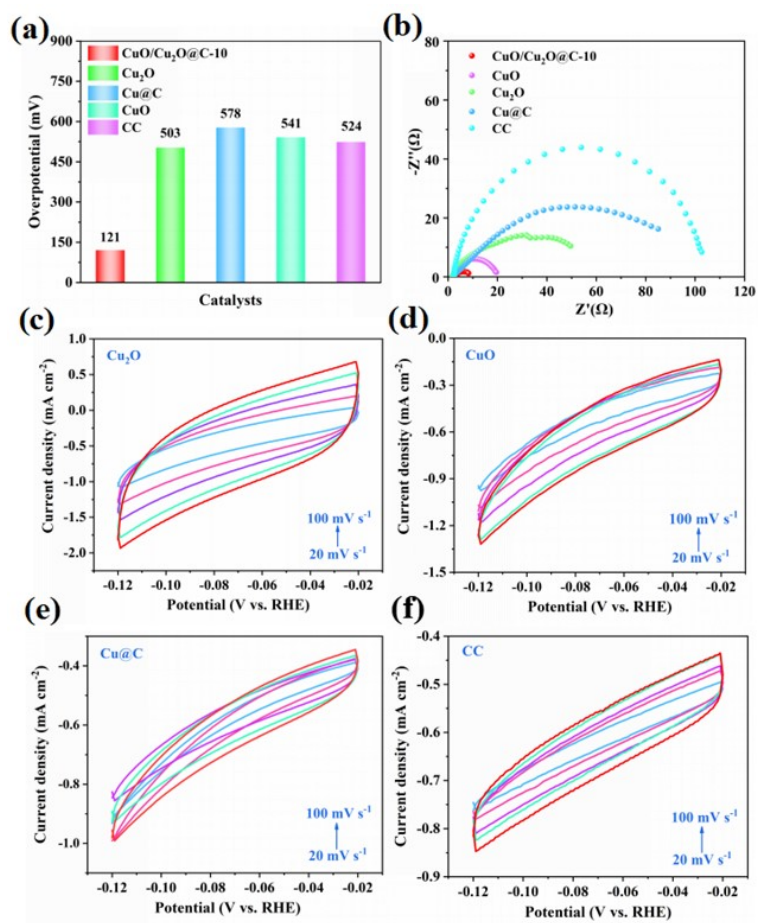


**Fig. S6.** TG curve of cure C.

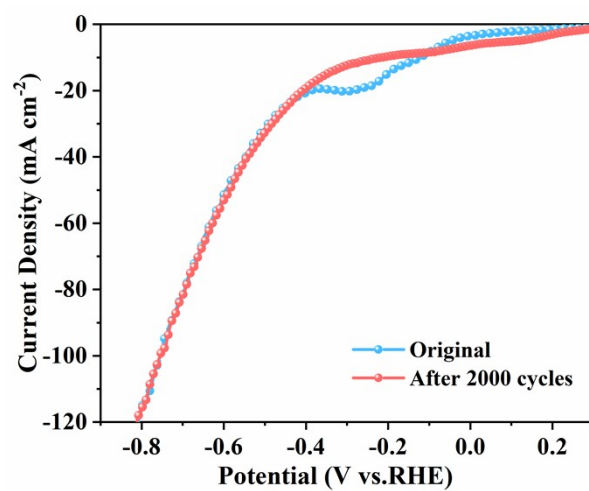


**Fig. S7.** (a) Nyquist plots of CuO/Cu<sub>2</sub>O@C with different oxidation time. (b-f) CV curves of CuO/Cu<sub>2</sub>O@C-4, CuO/Cu<sub>2</sub>O@C-6, CuO/Cu<sub>2</sub>O@C-8, CuO/Cu<sub>2</sub>O@C-10, CuO/Cu<sub>2</sub>O@C-12, respectively.

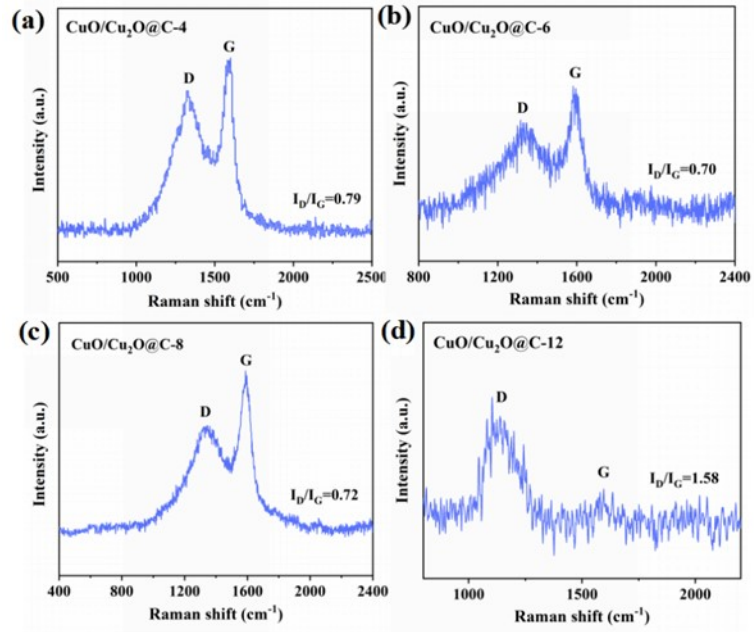




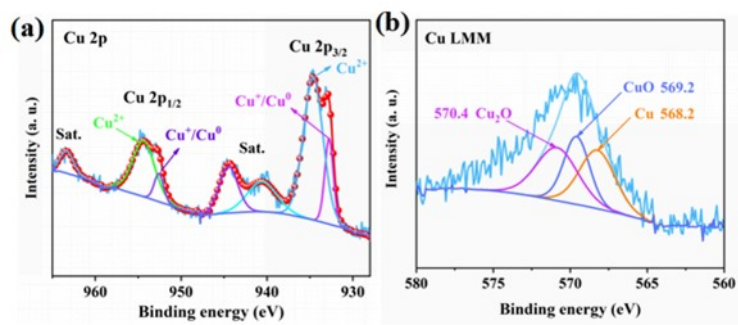
**Fig. S8.** (a) Overpotential column graphs of the different materials, (b) Nyquist plots, (c-f) CV curves of Cu<sub>2</sub>O, CuO, Cu@C, CC respectively.



**Fig. S9.** The polarization curves of CuO/Cu<sub>2</sub>O@C-10 before and after 2000 CV scan cycles.



**Fig. S10.** Raman spectroscopy of CuO/Cu<sub>2</sub>O@C with different oxidation time (4, 6, 8, 12 h).



**Fig. S11.** XPS of CuO/Cu<sub>2</sub>O@C-10 after HER test. (a) Cu 2p, (b) Cu LMM.

**Table. S1.** Comparison of HER performance with reported Copper-based electrocatalysts in alkaline media

Catalysts	J (mA cm <sup>-2</sup> )	$\eta$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Stability test	Ref.
CuO/Cu <sub>2</sub> O@C	10	121	81.58	20 h	This work
Cu <sub>2</sub> O@TiO <sub>2</sub>	10	114	67	24 h	[19]
CuO@Cu <sub>2</sub> O	10	135	135	20 h	[20]
Cu <sub>2</sub> O/g-C <sub>3</sub> N <sub>4</sub>	12.8	148.7	55	None	[22]
CuO/NH <sub>2</sub> -UiO-66	10	166	86	continuous 1000 LSV sweeps	[23]
Ag@Cu <sub>2</sub> O/CF	10	108	58	20 h	[49]
Cu NDs/Ni <sub>3</sub> S <sub>2</sub> /NTs-carbon fibers	10	128	76.2	30 h	[50]
Cu <sub>2</sub> O	10	145	229	None	[51]
Cu <sub>2</sub> O-200	10	184	106	20 h	[52]
Cu <sub>2</sub> O@Fe <sub>2</sub> O <sub>3</sub> @CC-500	10	188	55	20 h	[53]
Cu <sub>2</sub> O/NF	10	197	138.65	24 h	[54]
CuO@UiO-66/NF	10	220	164	600 sec	[55]
Cu/Cu-MOF/GO	10	250	201	15 h	[56]
Cu <sub>2</sub> O/C	10	284	225	10 h	[57]