

## Supporting Information

Synergistic copper nanoparticles and adjacent single atoms on biomass-derived N-doped carbon toward overall water splitting

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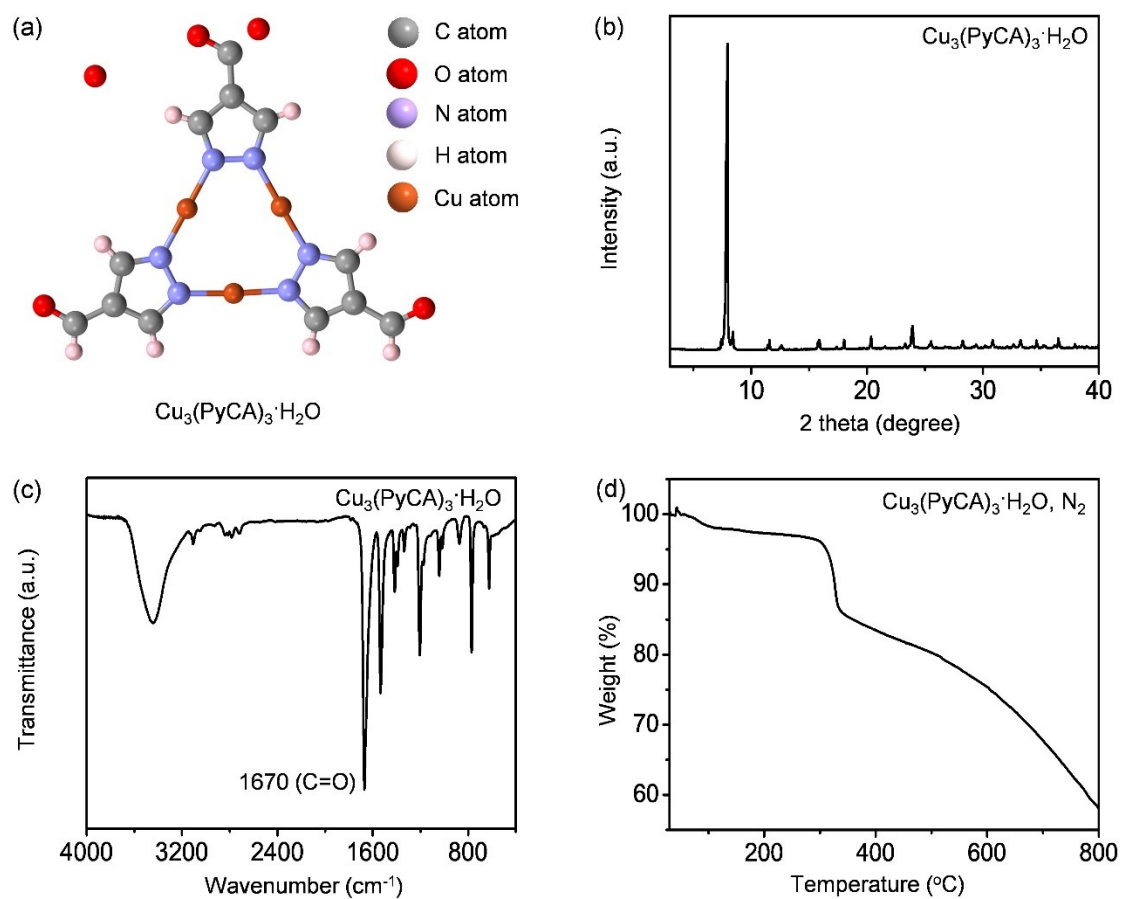
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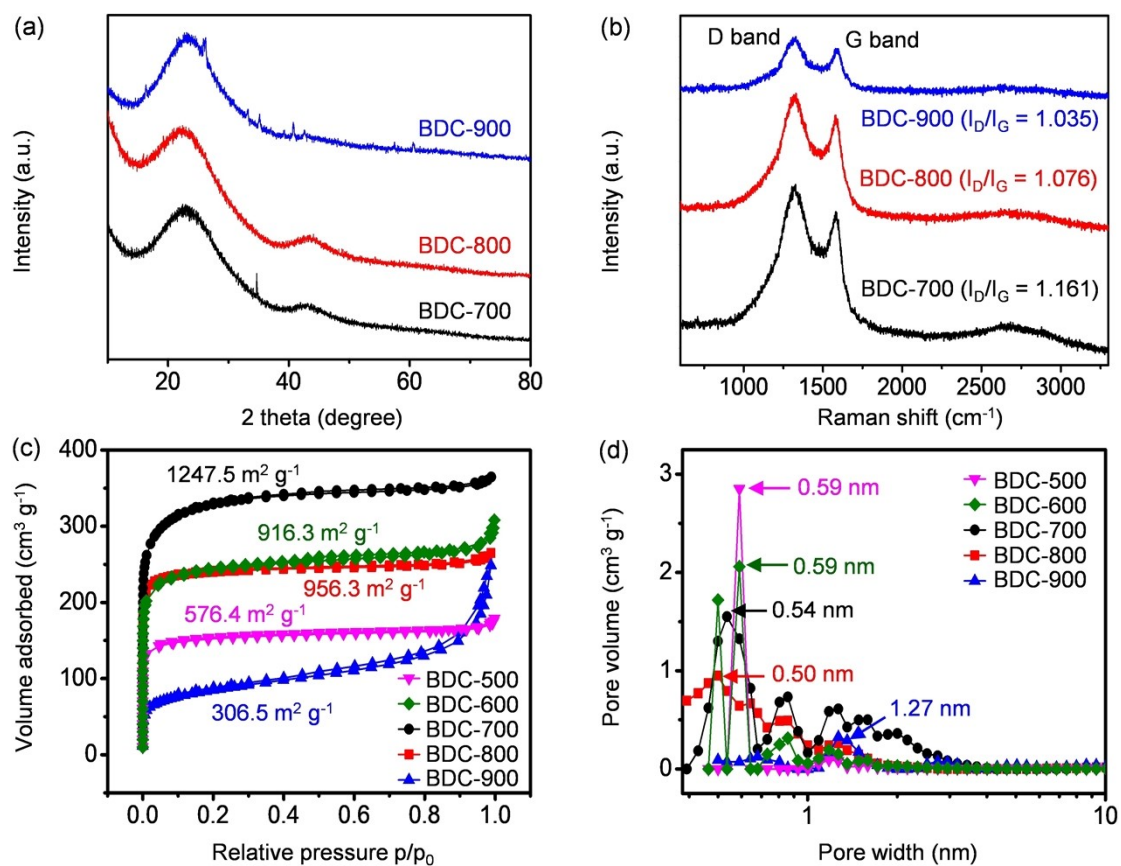
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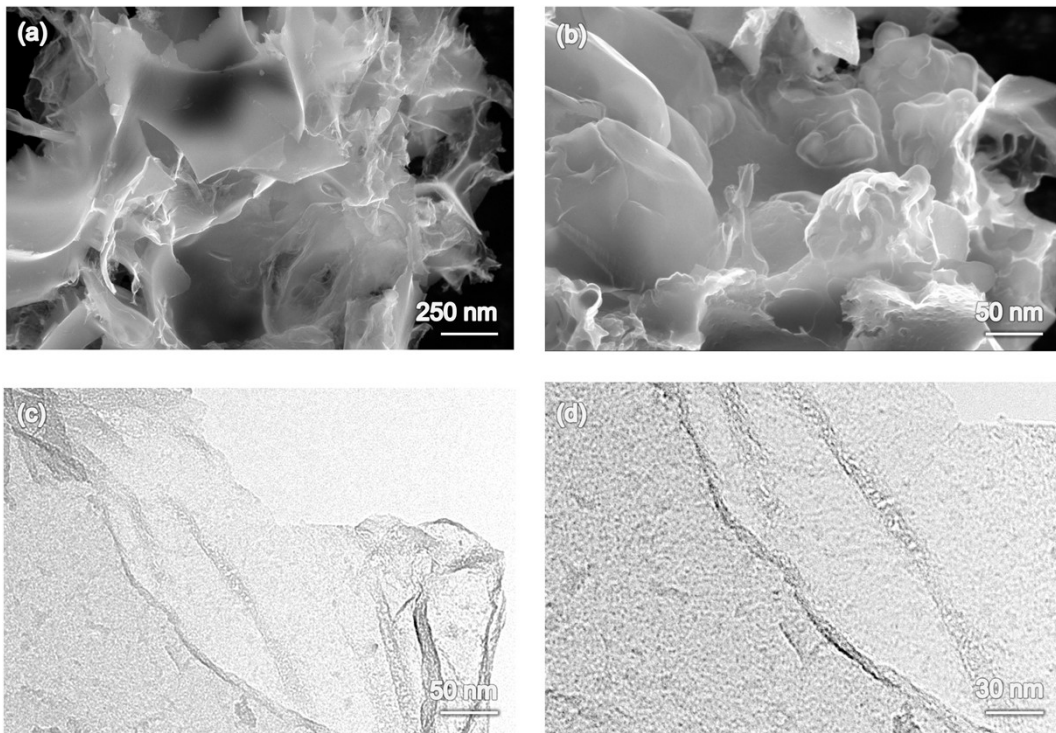
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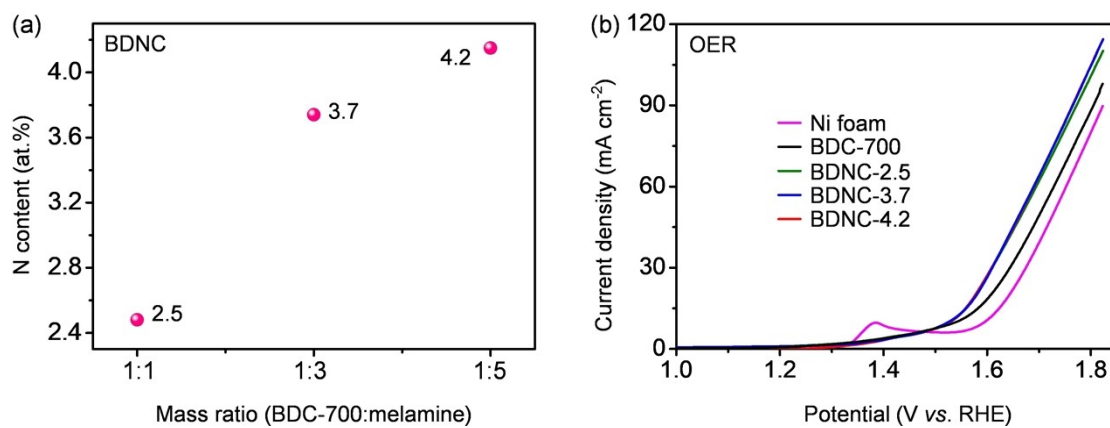
**Fig. S1.** (a) Ball and stick illustration of  $\text{Cu}_3(\text{PyCA})_3 \cdot \text{H}_2\text{O}$  complex in single crystal form. (b) PXRD pattern and (c) FT-IR spectrum of  $\text{Cu}_3(\text{PyCA})_3 \cdot \text{H}_2\text{O}$ . (d) TG curve of  $\text{Cu}_3(\text{PyCA})_3 \cdot \text{H}_2\text{O}$  measured in  $\text{N}_2$  atmosphere.



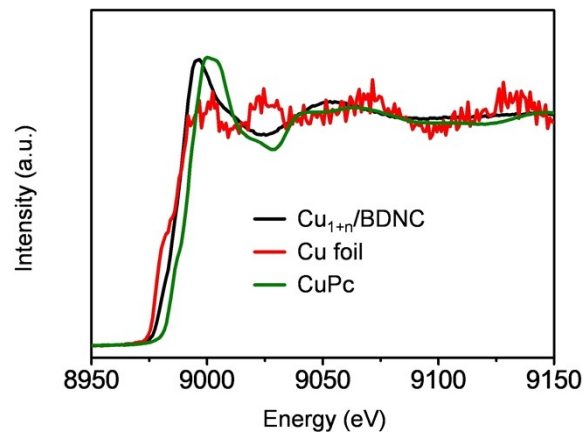
**Fig. S2.** (a) XRD patterns, (b) Raman spectra, (c) N<sub>2</sub> adsorption/desorption isotherms, and (d) the corresponding pore-size distribution curves of BDC-x prepared at five different temperatures (*i.e.*, 500, 600, 700, 800, and 900 °C).



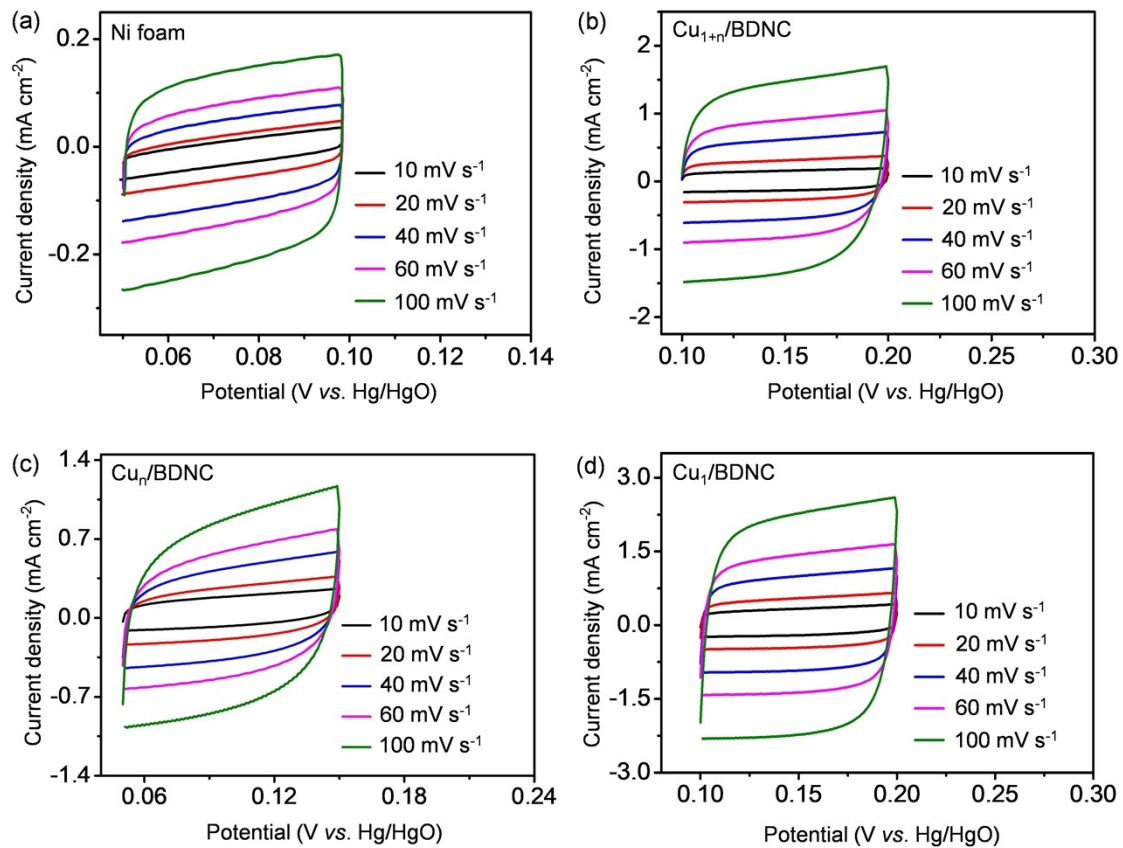
**Fig. S3.** (a,b) SEM, and (c,d) TEM images of BDC-700.



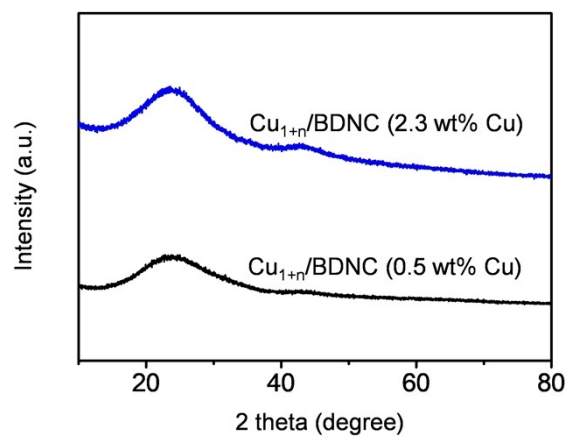
**Fig. S4.** (a) The dependency of the N contents doped in BDNCs on the mass ratio between BDC-700 and melamine. (b) OER polarization curves of Ni foam, BDC-700, and BDNC with different N contents supported on Ni foams.



**Fig. S5.** Cu K-edge XANES spectra of  $\text{Cu}_{1+n}/\text{BDNC}$ , Cu foil, and CuPc samples.

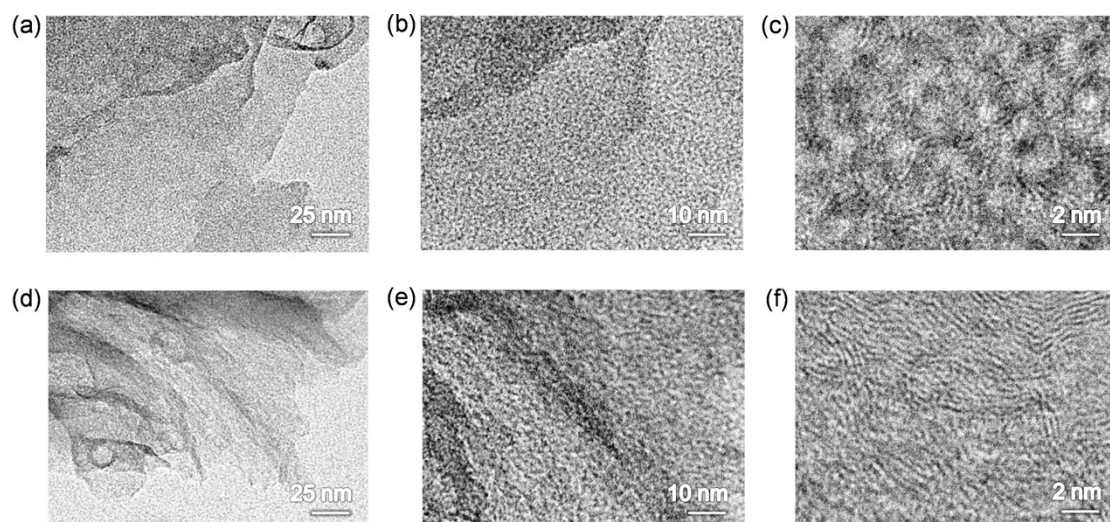


**Fig. S6.** CV curves of (a) Ni foam, (b)  $\text{Cu}_{1+n}/\text{BDNC}$ , (c)  $\text{Cu}_n/\text{BDNC}$ , and (d)  $\text{Cu}_1/\text{BDNC}$  at different scanning rates.

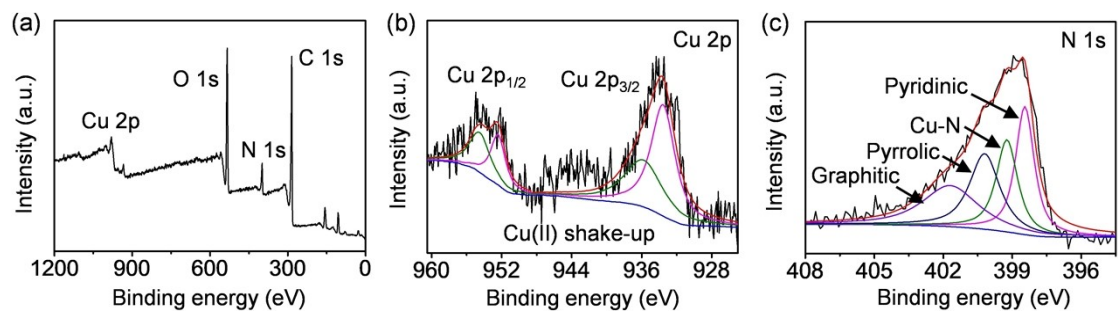


**Fig. S7.** PXRD patterns of Cu<sub>1+n</sub>/BDNC with Cu contents of 0.5 and 2.3 wt.%.

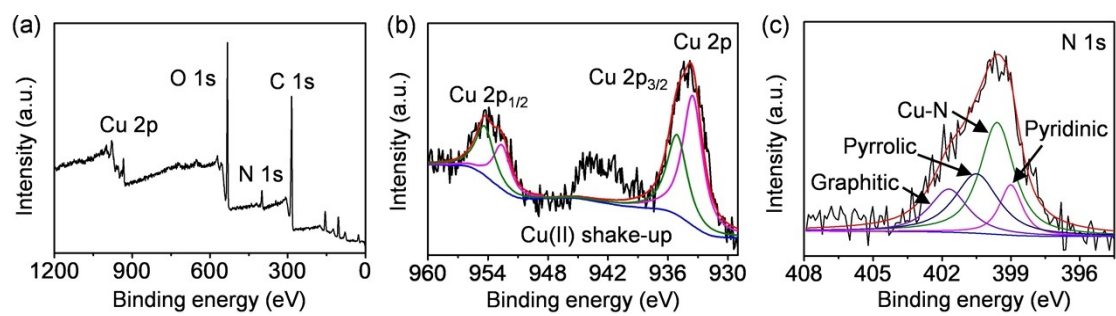




**Fig. S8.** (HR)TEM images of (a-c)  $\text{Cu}_{1+n}/\text{BDNC}$  (0.5 wt.% Cu) and (d-f)  $\text{Cu}_{1+n}/\text{BDNC}$  (2.3 wt.% Cu).



**Fig. S9.** (a) XPS survey, (b) Cu 2p, and (c) N 1s spectra of Cu<sub>1+n</sub>/BDNC (0.5 wt.% Cu).



**Fig. S10.** (a) XPS survey, (b) Cu 2p, and (c) N 1s spectra of  $\text{Cu}_{1+n}/\text{BDNC}$  (2.3 wt.% Cu).

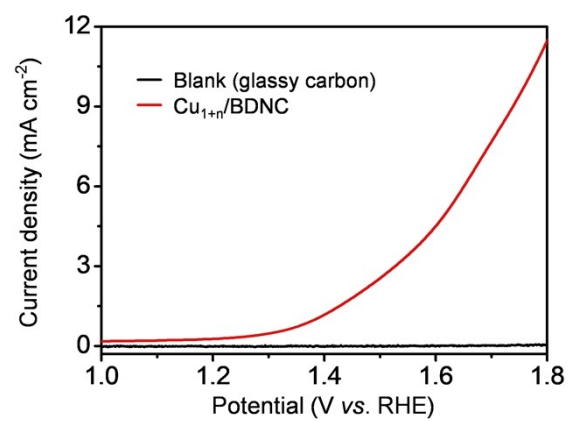
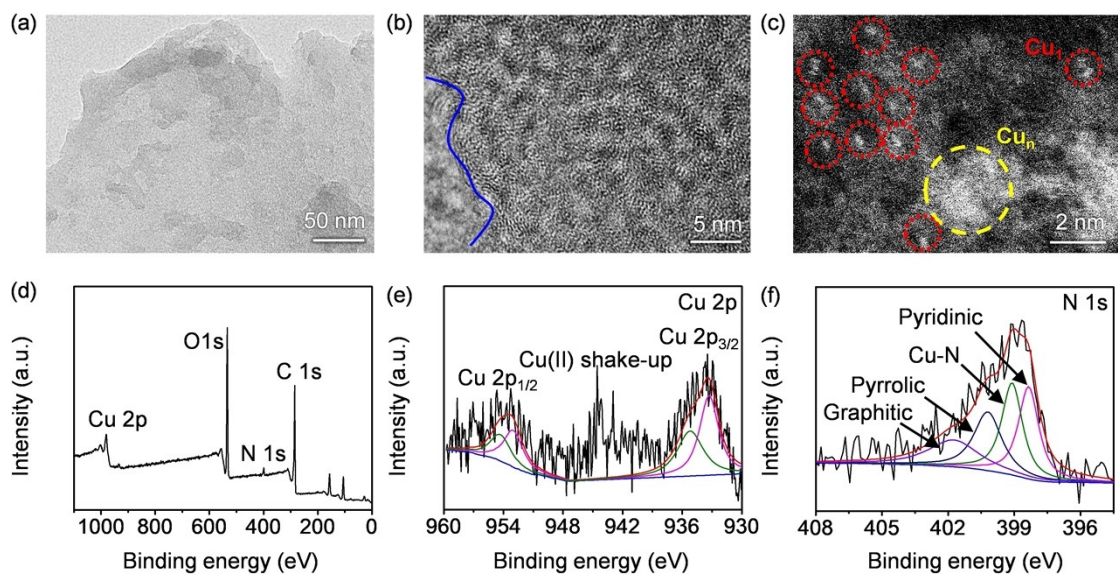


Fig. S11. LSV curves of Cu<sub>1+n</sub>/BDNC on GCE for electrochemical OER testing.



**Fig. S12.** (a) TEM, (b) HRTEM, and (c) HAADF-STEM images, (d) XPS survey, (e) Cu 2p, and (f) N 1s spectra of the used  $\text{Cu}_{1+n}/\text{BDNC}$  after 10 h OER test.