Electronic Supplementary Material (ESI)

Highly Dispersed Copper Phosphide Nanoparticles Accelerate Electrolytic Water Oxidation Process

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Experiment

Electrochemical measurement

The evaluation of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) performance within the typical three-electrode system in the 1M KOH solution (the actual pH tested was 13.8), and all measurements were carried out on the CHI 920C workstation. The prepared material was used as work electrode (1.5 cm * 0.5cm), the counter electrode was graphite plate (1cm * 3cm * 3mm) and Hg/HgO was used as reference electrode, respectively. Cyclic voltammetry (CV) curves were obtained at scan rate of 20 mV s^{-1} until the end of two completely overlapping CV curves from -0.22 ~ 0.52V vs. Hg/HgO, Linear sweep voltammetry (LSV) carried out with iR compensation (90%) at a sweep rate of 2 mV s^{-1} and the potential versus reversible hydrogen electrode (RHE) was calculated by Nernst equation, as follow,

$E_{vs.RHE} = E_{vs.Hg/HgO} + 0.0592*pH + 0.098V$

Electrochemical impedance measurements were executed in FRA impedance potentiostatic mode from 0.1 HZ to 100K HZ. Besides, double-layer capacitance (C_{dl}) measurements were tested with the scan rate from 10 to 80 mV s^{-1}, where the potential range for HER from -0.65V to -0.75V and OER from 0.15V to 0.25V refer to the Hg/HgO electrode, respectively.

Supplementary Experimental Figures

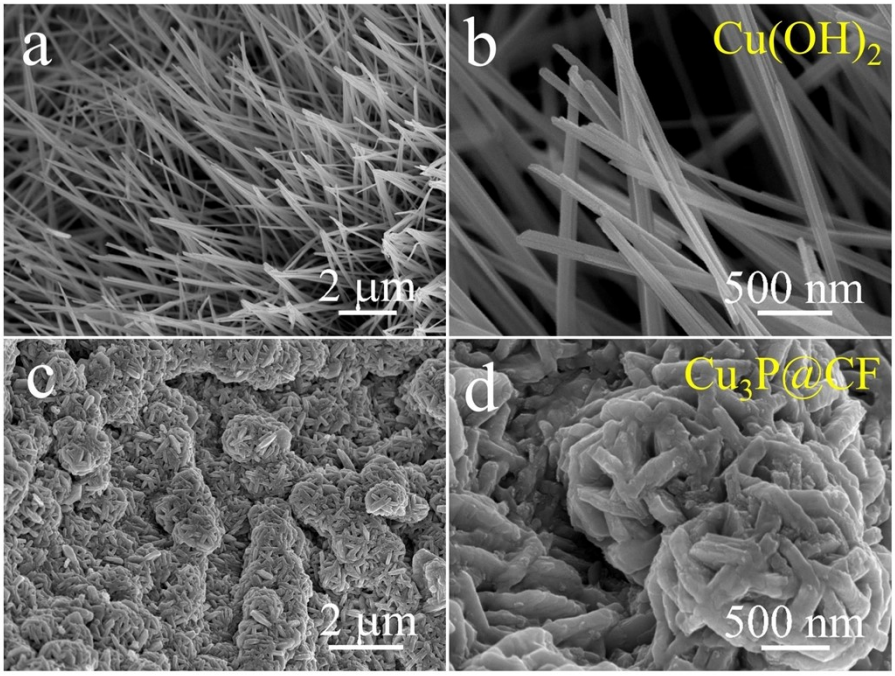

Figure S1. SEM images of $Cu(OH)_2$ NRs (a, b) on the CF and Cu_3P@CF (c, d).

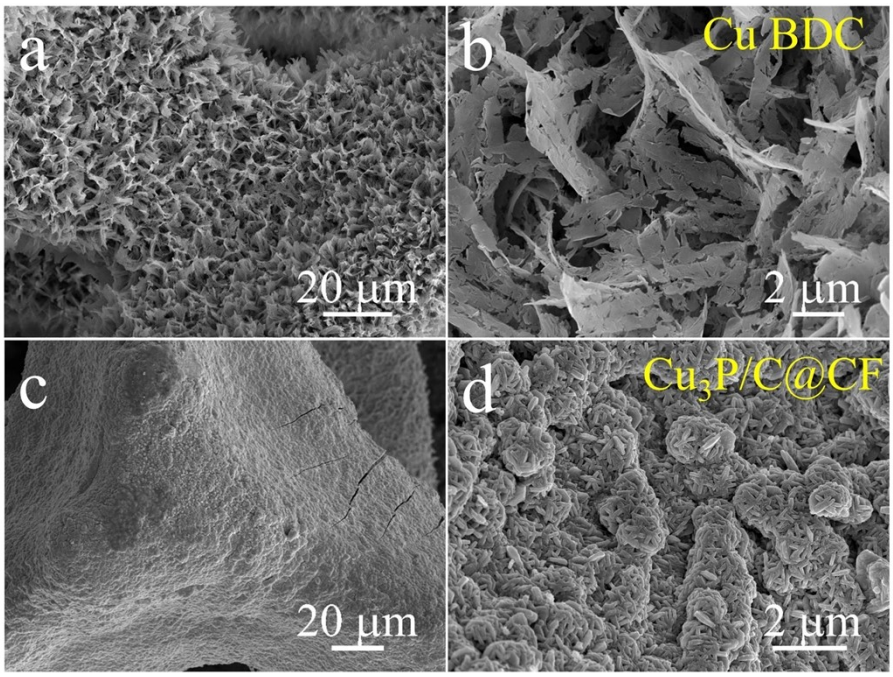

Figure S2. SEM images of Cu MOF nanosheets (a, b) on the CF and (c, d) Cu_3P/C@CF.

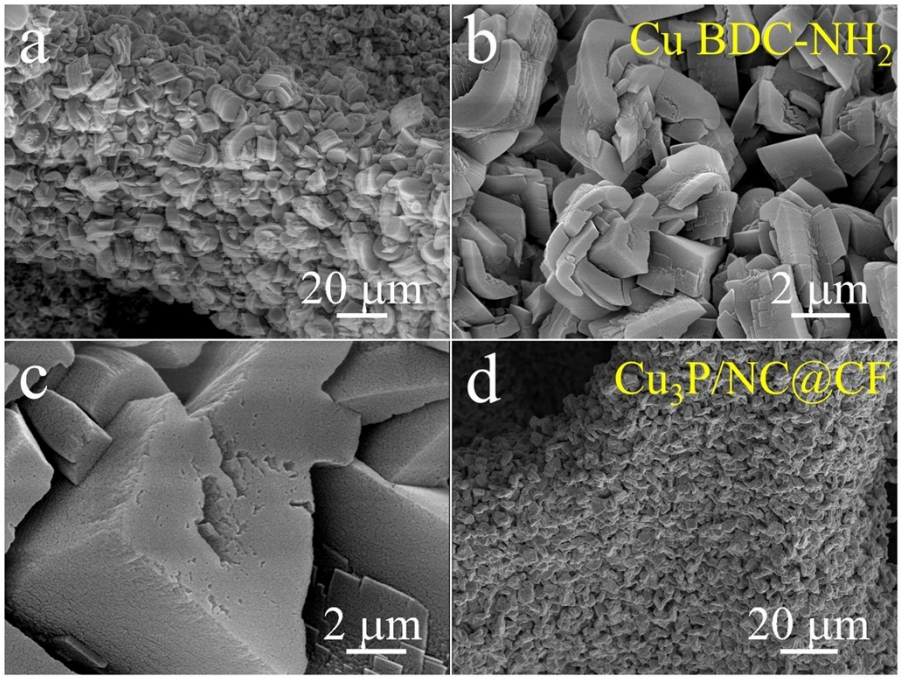

Figure S3. SEM images of Cu MOF-NH_2 (a-c) nanocubes on the CF and Cu_3P/NC@CF (d).

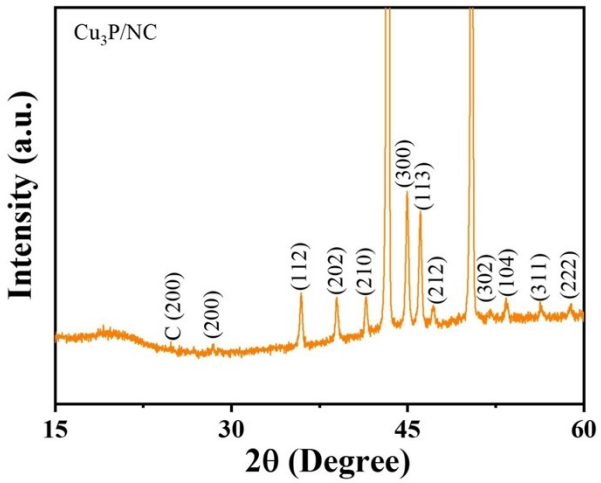

Figure S4. The XRD pattern of Cu_3P/NC@CF corresponding to the crystal plane.

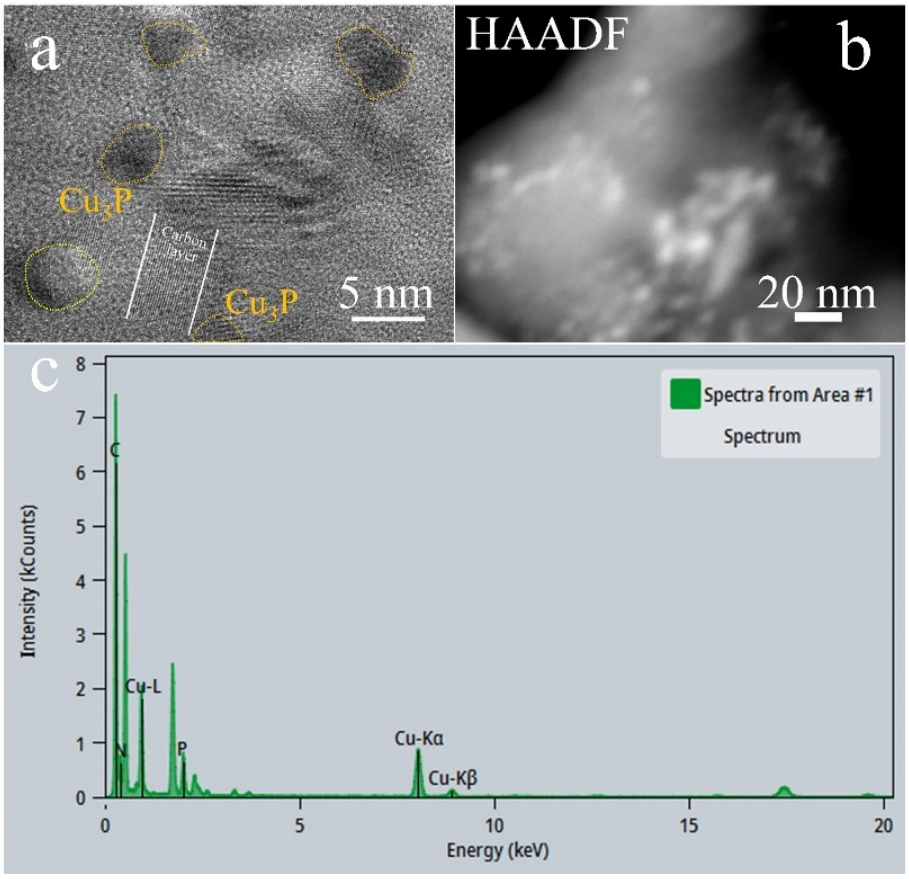

Figure S5 Cu_3P/NC@CF (a) TEM image (The yellow circle contains the isolated Cu_3P NPs and the Cu_3P is surrounding by Carbon matrix), (b) HAADF-TEM image (c) and corresponding with EDX element mapping.

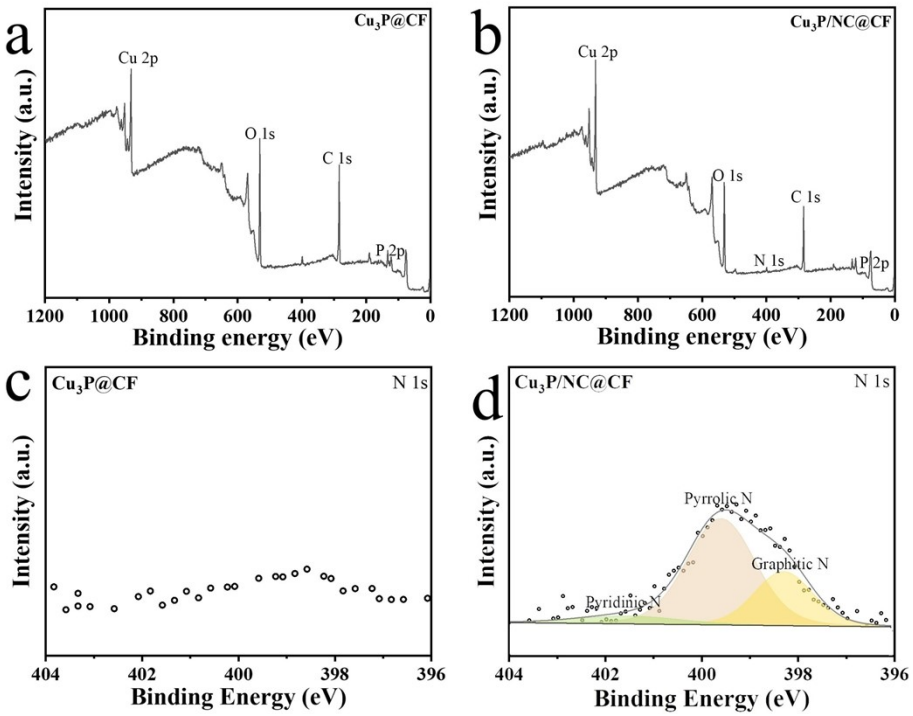

Figure S6. (a) and (b) The XPS full spectra of Cu_3P@CF and Cu_3P/NC@CF, (c) and (d) the N1s fine resolution of Cu_3P@CF and Cu_3P/NC@CF, respectively.

Generally, the HER process is a two-electron process in alkaline solution in individual Volmer-Heyrovsky or Volmer-Tafel mechanism, details of the above-discussed mechanism and the rate-determining step (RDS, Tafel slope value) are equated as below,

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

（1） $H_2O + e^- \rightarrow H^* + OH^-$ (Volmer step) Eq. S1

$$b = \frac{2.303RT}{\alpha F} \approx 120mV / \text{dec}$$

（2） $H_2O + e^- + H^* \rightarrow H_2\uparrow + OH^-$ (Heyrovsky step) Eq. S2

$$b = \frac{2.303RT}{(1+\alpha)F} \approx 40mV / \text{dec}$$

（3） $H^* + H^* \rightarrow H_2\uparrow$ (Tafel step) Eq. S3

$$b = \frac{2.303RT}{2F} \approx 30mV / dec$$

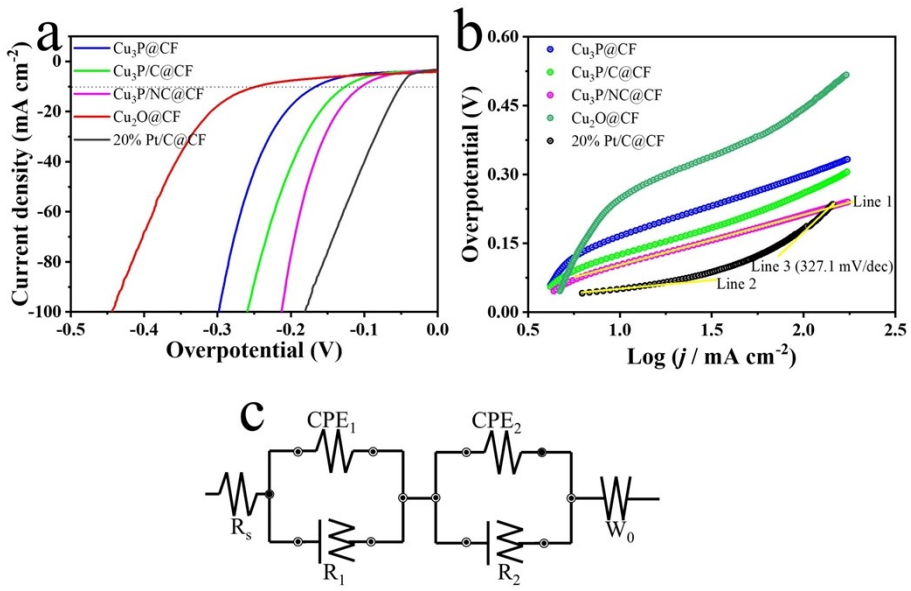

Figure S7. (a - b) LSV curves and Tafel slopes of Cu_3P@CF, Cu_3P/C@CF, Cu_2O@CF and 20% Pt/C@CF, (c) Equivalent circuit model that contains the electrolyte resistance (R_s), constant phase element ($CPE_{1, 2}$) and charge transfer resistance ($R_{1, 2}$).

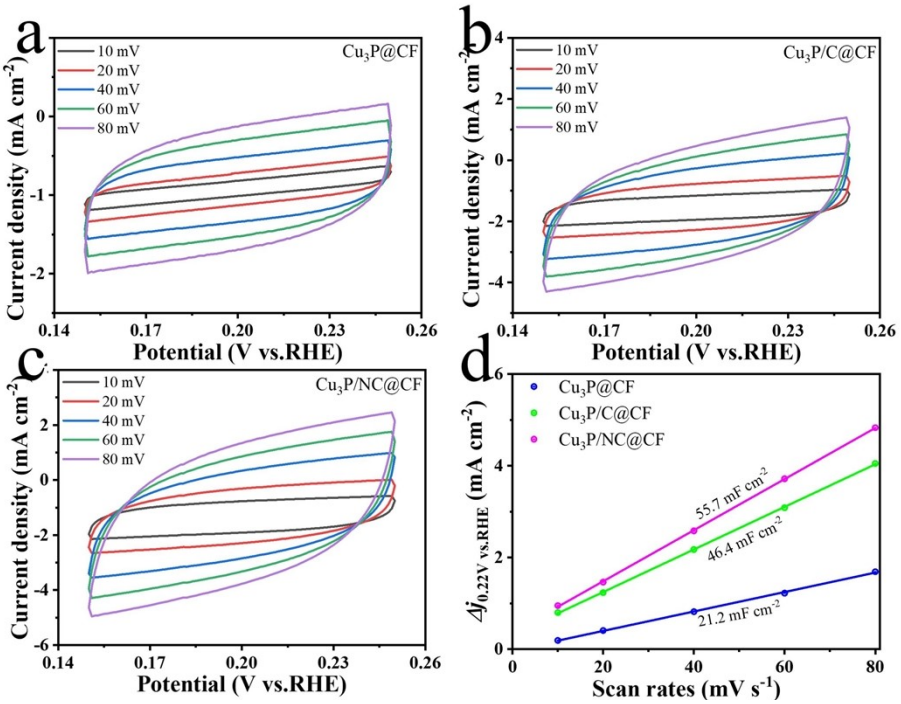

Figure S8. (a - c) CV curves of Cu_3P@CF, Cu_3P/C@CFF and Cu_3P/NC@CF at the scan rates from 10 to 80 mV s^{-1}, (d) and the corresponding capacitive currents at 0.22V vs.RHE as a linear fitting function.

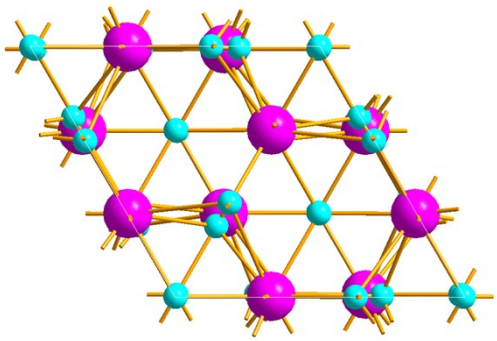

Figure S9. The crystal structure of Cu_3P (Atoms: Turquiose Cu and Pink P. The Volume=299.6Å^3).

As for accurate active sites it is difficult to determine, in Fig. S9, the Monoclinic crystal cell of copper phosphide contains 4 Cu-P constituted. So, the definition of active sites that obtained a close value relevant with real number of atoms per real surface area. We get some experience from previous works[S1].

Number of active sites per square specific surface area:

$$N_{active\ sites} = \left(\frac{4\ (atoms\ active\ center)\ unit\ cell^{-1}}{299.6\text{Å}^3\ unit\ cell^{-1}}\right)^{\frac{2}{3}} = 5.68 \times 10^{14}\ atoms$$ Eq. S4

#active sites per real surface area:

$$A_{ECSA}^{Cu_3P} = \frac{21.2\ mF\ cm^{-2}}{40\ \mu F\ cm^{-2}\ percm^2} = 503\ cm^2$$ Eq. S5

$$A_{ECSA}^{Cu_3P/C} = \frac{46.4\ mF\ cm^{-2}}{40\ \mu F\ cm^{-2}\ percm^2} = 1160\ cm^2$$ Eq. S6

$$A_{ECSA}^{Cu_3P/NC} = \frac{55.7\ mF\ cm^{-2}}{40\ \mu F\ cm^{-2}\ percm^2} = 1392\ cm^2$$ Eq. S7

Convert the total hydrogen calculated from the current density, as follows,

$$H_2(per\ mA/cm^{-2}) = \left(j\frac{mA}{cm^2}\right)\left(\frac{1C\ s^{-1}}{1000\ mA}\right)\left(\frac{1mol\ e^{-1}}{96485.3C}\right)\left(\frac{1mol\ H_2}{2\ mol\ e^{-1}}\right)\left(\frac{6.022 \times 10^{23} H_2\ mol}{1\ mol\ H_2}\right)$$

$$= 7.8 \times 10^{14} H_2\ s^{-1}\ cm^{-2}\ per\ (mA\ cm^{-2})$$ Eq. S8

Turnover frequency caculation of catalysts as follows[S2],

$$TOF\ per\ sites = \frac{total\ oxygen\ turnovers\ cm^{-2}\ \times\ geometric\ area}{active\ sites\ cm^{-2}\ \times\ geometric\ area}$$ Eq. S9

Converted to a new TOF calculation formula according to the definition formula Eqs.9

$$TOF = \frac{5.68 \times 10^{14} H_2\ s^{-1} cm^{-2}\ per\ (mA\ cm^{-2})\ \times |j|}{7.8 \times 10^{14}\ atoms\ \times A_{ECSA}}$$ Eq. S10

At the overpotential of -200 mV, the TOF value of the pristine Cu_3P@CF is 0.0258 H_2 s^{-1}, but the Cu_3P/C@CF and Cu_3P/NC@CF get a better value is 0.0259 H_2 s^{-1} and 0.0406 H_2 s^{-1}.

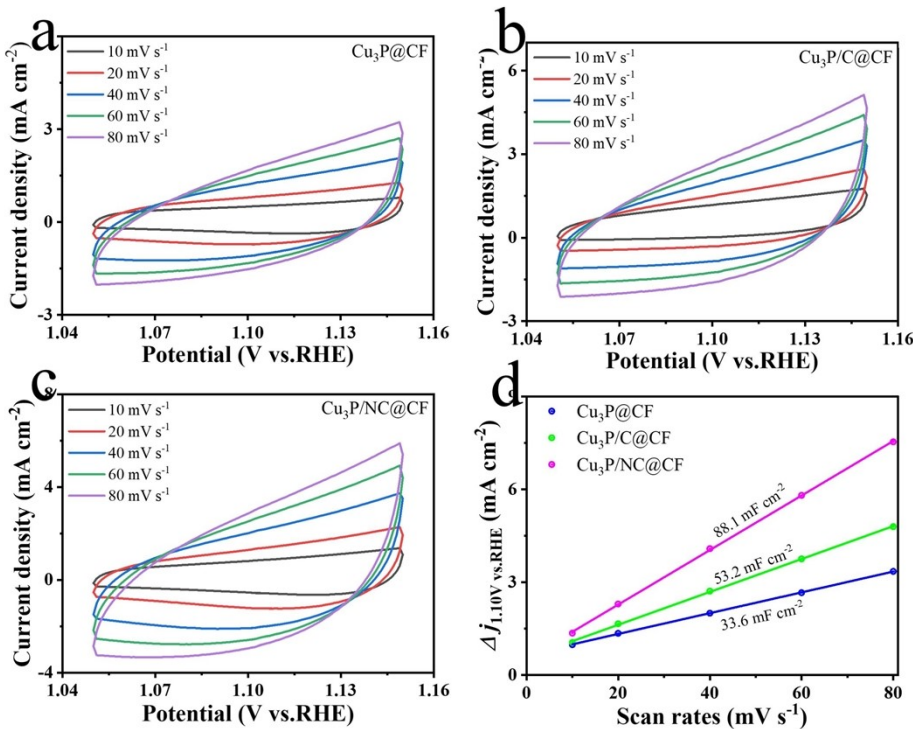

Figure S10. CV curves of Cu_3P@CF, Cu_3P/C@CF and Cu_3P/NC@CF at the scan rates from 10 to 80 mV s^{-1}.

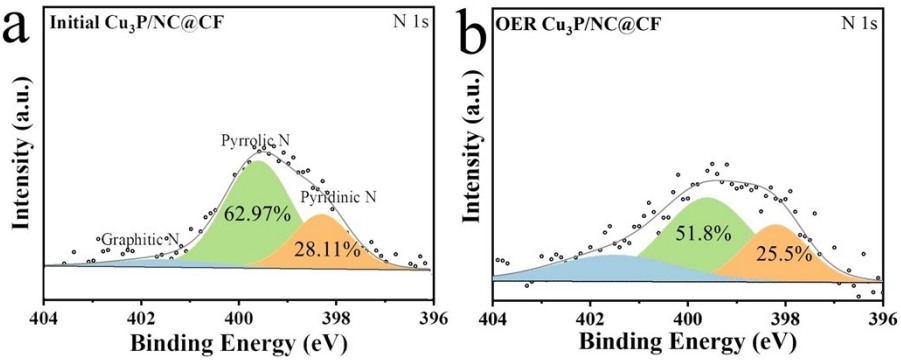

Figure S11. The N 1s XPS spectra resolution of Cu_3P/NC@CF before and after OER tested for 36 hours.

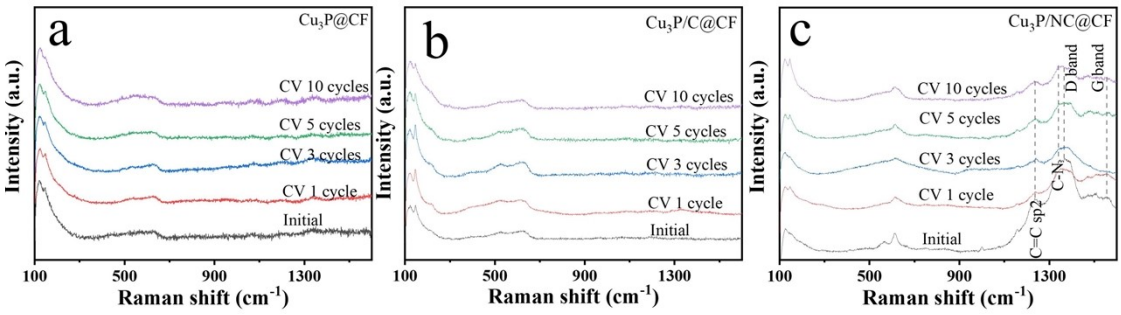

Figure S12. Raman spectra of Cu_3P@CF, Cu_3P/C@CF and Cu_3P/NC@CF.

Table S1. The Raman shift is 607 cm^{-1} of Cu_3P@CF, Cu_3P/C@CF and Cu_3P/NC@CF with CV cycles

Intensity (a.u.)	Cu_3P@CF	Cu_3P/C@CF	Cu_3P/NC@CF
0	1092.11	13837.68	26614.57
CV 1 cycle	1936.39	10627.45	9029.63
CV 3 cycles	2383.06	7699.98	13951.90
CV 5 cycles	1530.71	6484.57	22241.68
CV 10 cycles	1537.81	5197.00	25389.14

Table S2. The Raman shift is 274 cm^{-1} of Cu_3P@CF, Cu_3P/C@CF and Cu_3P/NC@CF CV cycles

Intensity (a.u.)	Cu_3P@CF	Cu_3P/C@CF	Cu_3P/NC@CF
0	1905.77	15028.70	10697.88
CV 1 cycle	1753.47	12830.83	10495.28
CV 3 cycles	1757.28	9743.06	18266.33
CV 5 cycles	2056.08	8282.70	25675.30
CV 10 cycles	2146.09	6102.84	28597.23

The Oxygen evolution reaction mechanism alkaline solution, as follows[S3]:

i) $M + OH^- \rightarrow M\text{-}OH + e^-$ Eq. S11

ii) $M\text{-}OH + OH^- \rightarrow M\text{-}O + e^- + H_2O$ Eq. S12

iii) $M\text{-}O + OH^- \rightarrow M\text{-}OOH + e^- + H_2O$ Eq. S13

iv) $M\text{-}OOH + OH^- \rightarrow M\text{-}OO + e^- + H_2O$ Eq. S14

v) $M\text{-}OO + OH^- \rightarrow M + O_2$ Eq. S15

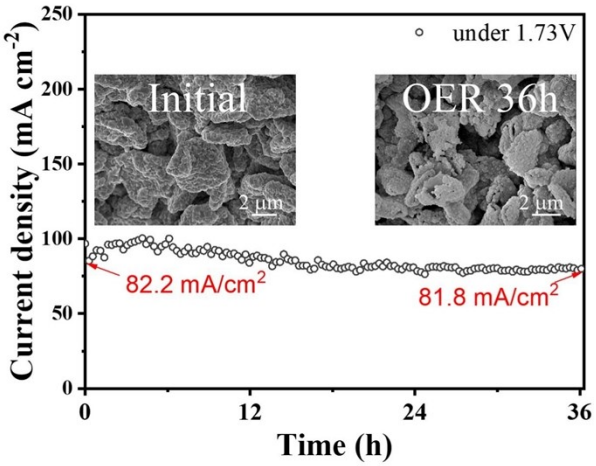

Figure S13. Chronopotentiometric measurement of Cu_3P/NC @CF and the insert diagrams are the SEM images before and after water splitting for 36 hours in 1M KOH solution.

Supplementary References

[S1] E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, J. Am. Chem. Soc., 2013, 135, 9267–9270.

[S2] T. Tian, H. Gao, X. Zhou, L. Zheng, J. Wu, K. Li and Y. Ding, ACS Energy Lett., 2018, 3, 2150–2158.

[S3] H. Sun, Z. Yan, F. Liu, W. Xu, F. Cheng and J. Chen, Adv. Mater., 2020, 32, 1–18.