Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Electrochemical active surface area (ECSA)

The electrochemically active surface area (ECSA) of each catalyst was inferred from their electrochemical capacitances, determinable through the cyclic voltammetry technique. The potential was varied from 0.15 to 0.25 V versus RHE at five distinct scan rates, which are 10, 20, 30, 40, and 50 mV /s^{-1}, respectively. By correlating the scan rate with the current density differential (ΔJ) at a constant potential from the anodic to cathodic sweeps, a consistent linear correlation emerges. This slope correlates directly with the ECSA. Such capacitance values (C_{dl}) facilitate the evaluation of the relative surface activities of diverse electrodes, particularly when utilized within identical electrolyte environments[1].

The turnover frequency (TOF)

The per-site TOF was calculate by the following formula:

$$\mathrm{TOF} = \frac{0.064 \times 6.02 \times 10^{23}}{64.4\% \times \frac{12g}{mol} + 27.8\% \times \frac{16g}{mol} + 3.2\% \times \frac{14g}{mol} + 1.8\% \times 31g/mol}$$

The hydrogen turnovers was calculate by the this formula:

$$\# H_2 = (j\frac{mA}{cm^2})(\frac{1Cs^{-1}}{1000mA})(\frac{1molH_2}{2mole^{-1}})(\frac{6.022\times10^{23}H_2molecules}{1molH^2})$$

$$=3.12\times10^{15}\ \frac{H_2/\mathrm{s}}{cm^2}\ per\frac{mA}{cm^2}$$

From the results from XPS and DFT calculation, For N and P co-doped catalyst, we suppose that graphitic nitrogen and C_3PO have co-catalytic activity, and the neighboring and interstitial carbons of them (12 carbon atoms) are catalytically active. For N doped catalyst, we identified that graphitic nitrogen have catalytic activity, and the neighboring and interstitial carbons of them (6 carbon atoms) are catalytically active. For P doped catalyst, we suppose that C_3PO have co-catalytic activity, and the neighboring and interstitial carbons of them (6 carbon atoms) are catalytically active. The number of electrochemically operative surface sites on the catalyst was calculated as:

Mass of an electrode:

(1) Total number of atoms of an electrode for N, P-G:

$$Mass = \frac{2mg\times 8\ \mu L}{250\mu L}=0.064\mathrm{mg}$$

$$\frac{Mass\ of\ electrode * N_A}{\sum(atomic\% * M_{atom})}$$

$$= 2.92 \times 10^{18}$$

Active sites of N, P-G:

the total number of atoms of an electrode × ($atomic$ graphitic N × 6 + $atomic$

$= 3.5 \times 10^{17}$

$C_3PO \times 6)$

$= 2.92 \times 10^{18} \times (3.2\% \times 43.5\% \times 6 + 1.8\% \times 34\% \times 6)$

$$= \frac{0.064 \times 6.02 \times 10^{23}}{65.4\% \times \frac{12g}{mol} + 27.5\% \times \frac{16g}{mol} + 7.1\% \times \frac{14g}{mol}}$$

$= 2.9 \times 10^{18}$

(2) Total number of atoms of an electrode for N-G:

Active sites of P-G:

the total number of atoms of an electrode $\times$ $atomic$ GN $\times$ 6)

$= 2.9 \times 10^{18} \times (7.1\% \times 53.4\% \times 6)$

(3) Total number of atoms of an electrode for P-G:

$$= \frac{0.064 \times 6.02 \times 10^{23}}{69.3\% \times \frac{12g}{mol} + 24.9\% \times \frac{16g}{mol} + 5.8\% \times \frac{31g}{mol}}$$

Active sites of P-G:

$= 2.7 \times 10^{18}$

$= 2.7 \times 10^{18} \times (5.8\% \times 61.4\% \times 6)$

$= 5.77 \times 10^{17}$

the total number of atoms of an electrode $\times$ $atomic$ $C_3PO \times 6)$

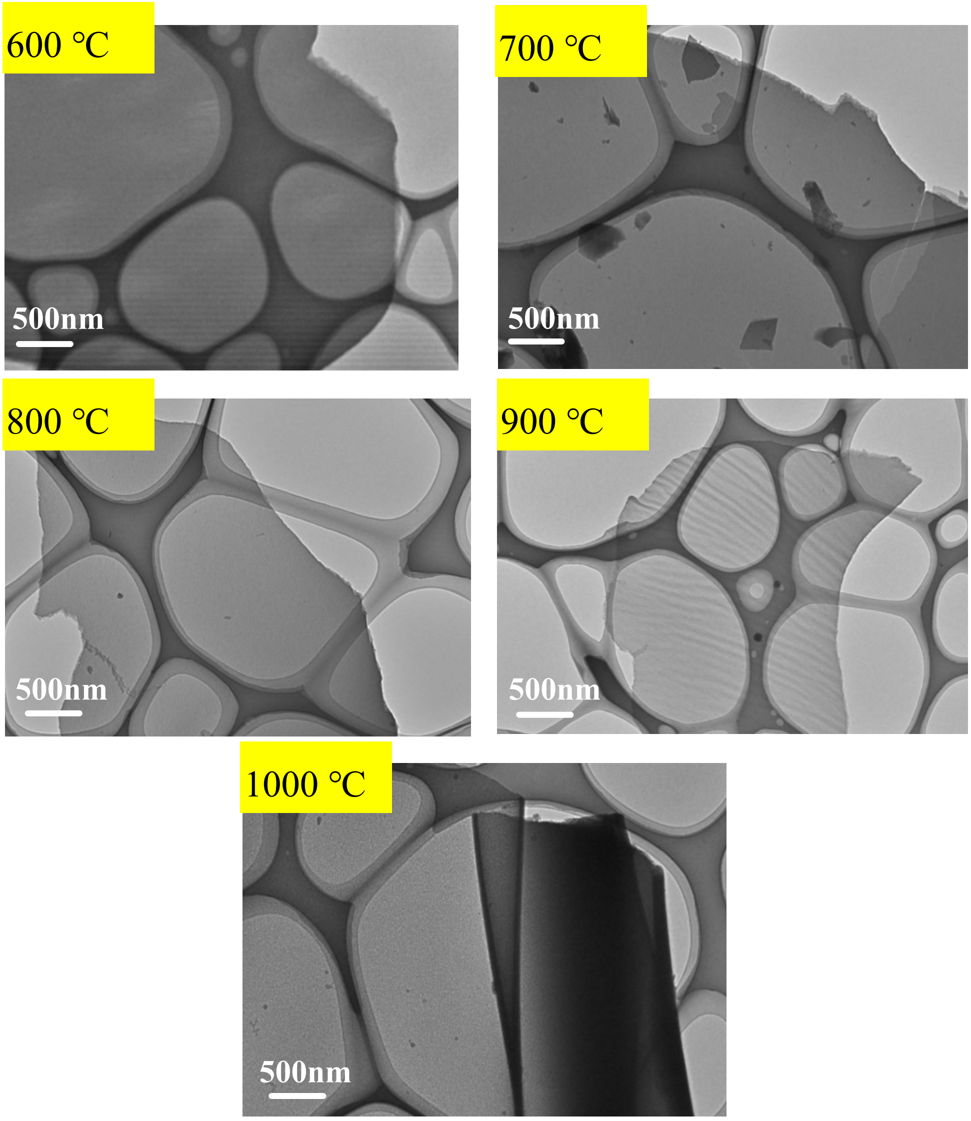


Fig. S1 TEM images of various samples.

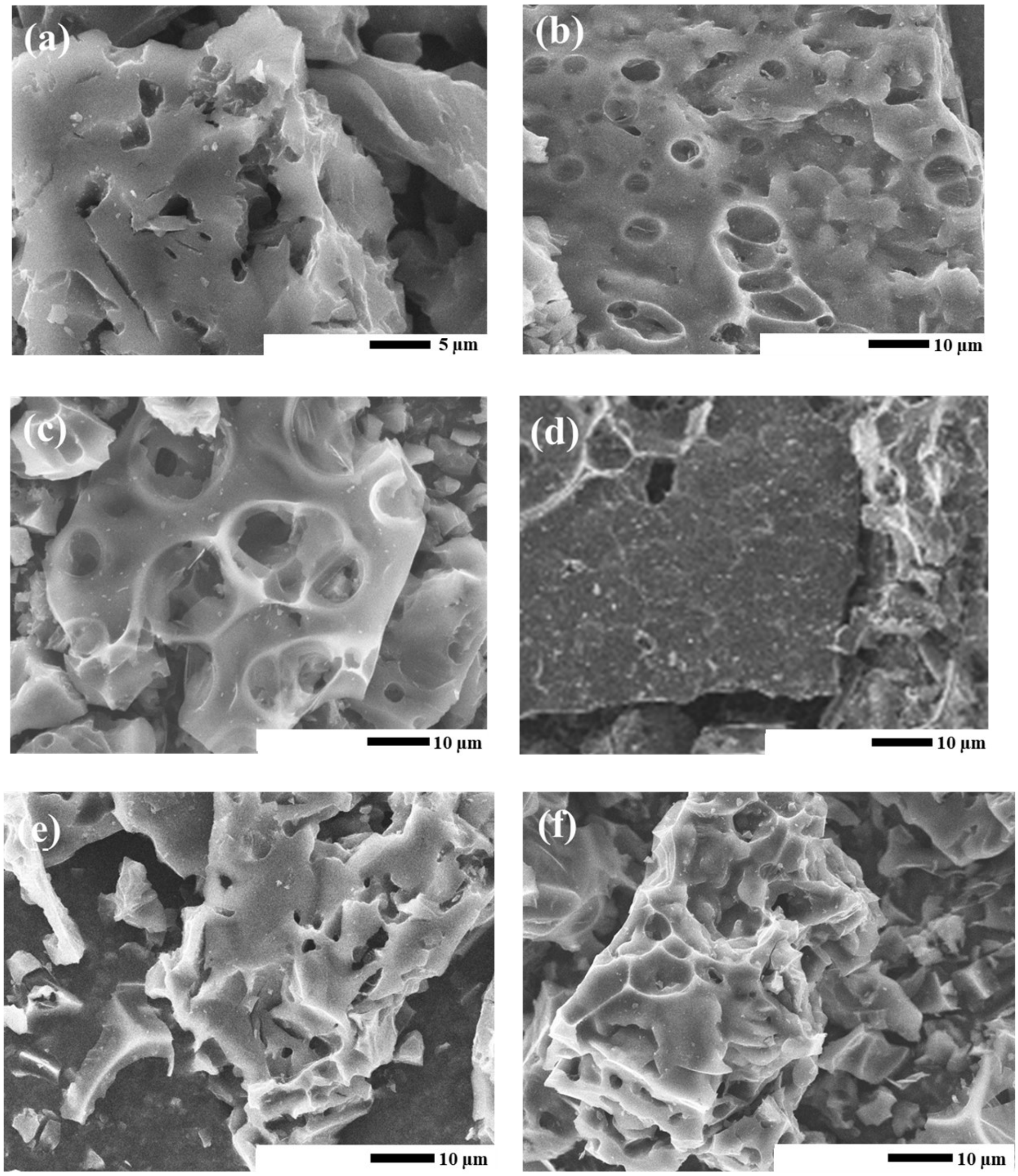


Fig. S2 SEM images of (a) CNP0.2, (b) CNP0.6 (c) CNP0.8, (d) T=700 °C, (e) T=800 °C and (f) T=1000 °C.

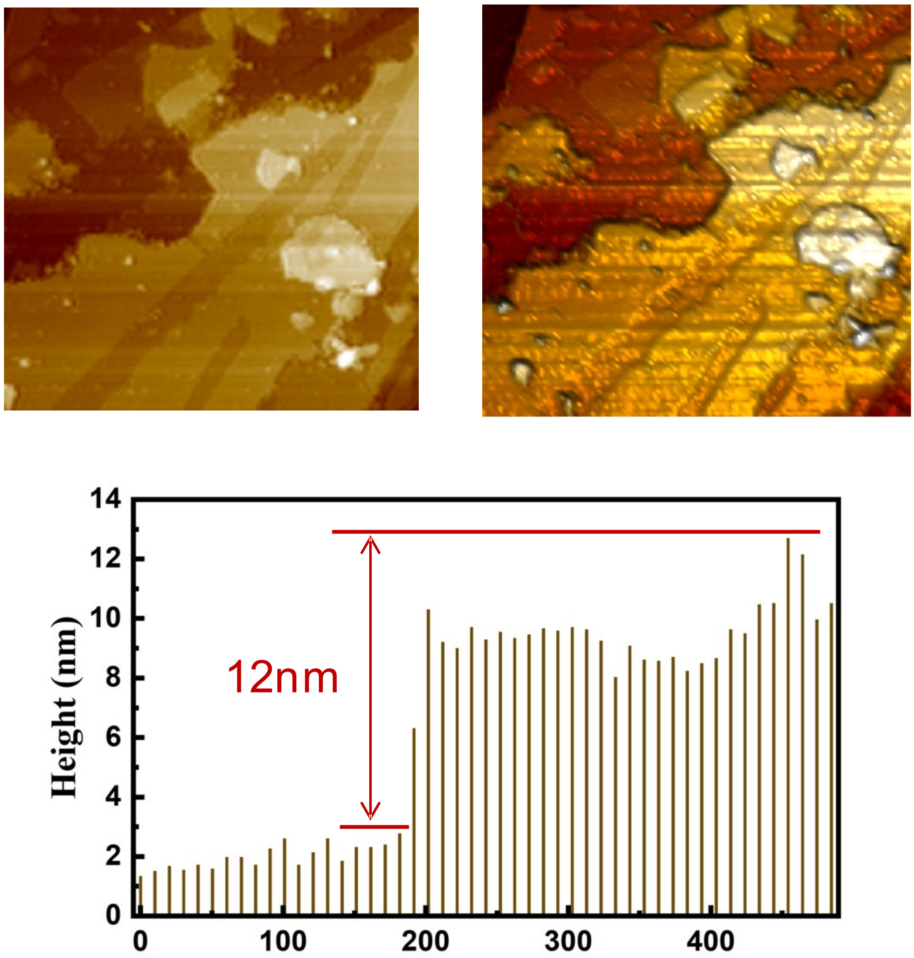


Fig. S3 AFM images and height distributions of CNP0.4 at the scale of micron meter.

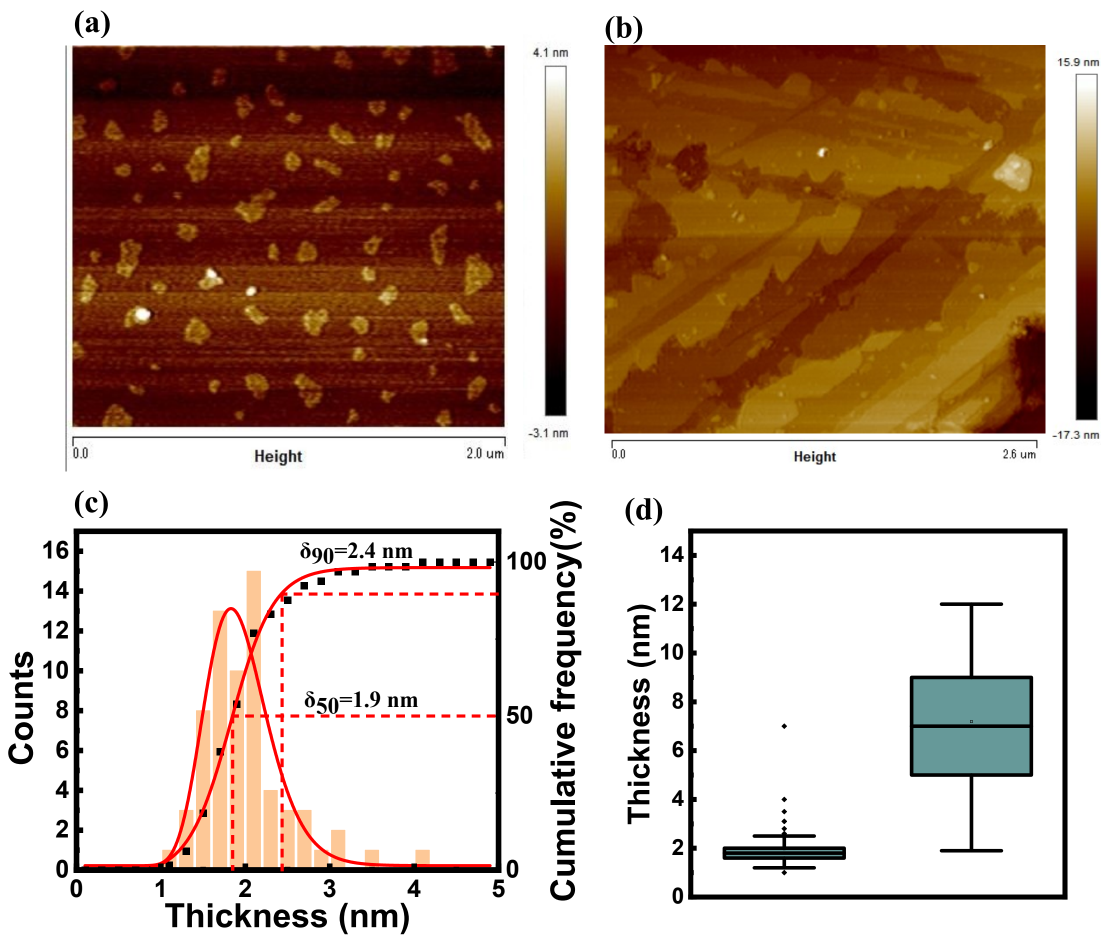


Fig. S4 (a) AFM images of CNP0.4 at the scale less than 800nm. (b) AFM images of CNP0.4 at the scale of 0.8-2 micro meter. (c) Cumulative frequency of thickness for the samples in CNP0.4 at the scale less than 800nm. (d) Thickness distribution box diagram or the samples in CNP0.4 at the scale less than 800nm (left) and the scale of 0.8-2 micro meter (right).

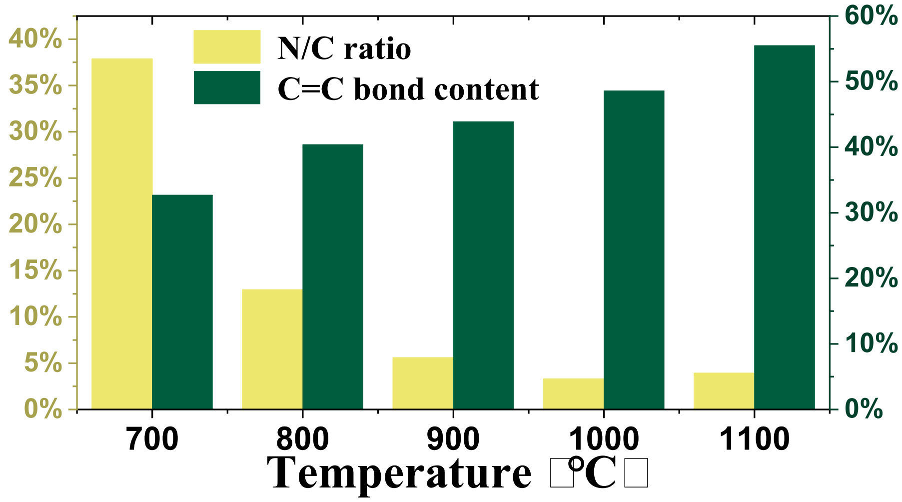


Fig. S5 The changing trend of C=C bonds and N/C ratio of the sample under different heating temperatures.

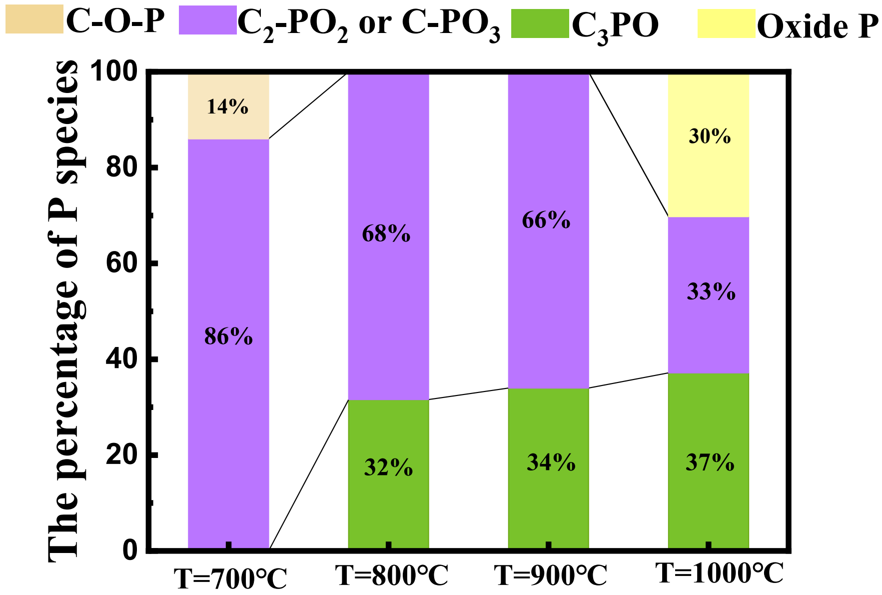


Fig. S6 The P species percentage of T=700 °C, T=800°C, T=900 °C and T=1000 °C.

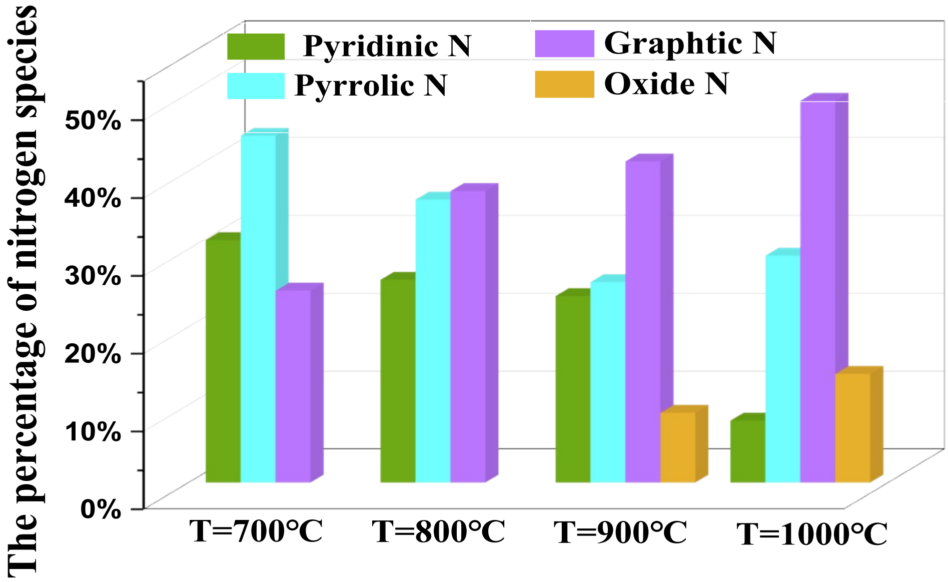


Fig. S7 The N species percentage of T=700 °C, T=800°C, T=900 °C and T=1000 °C.

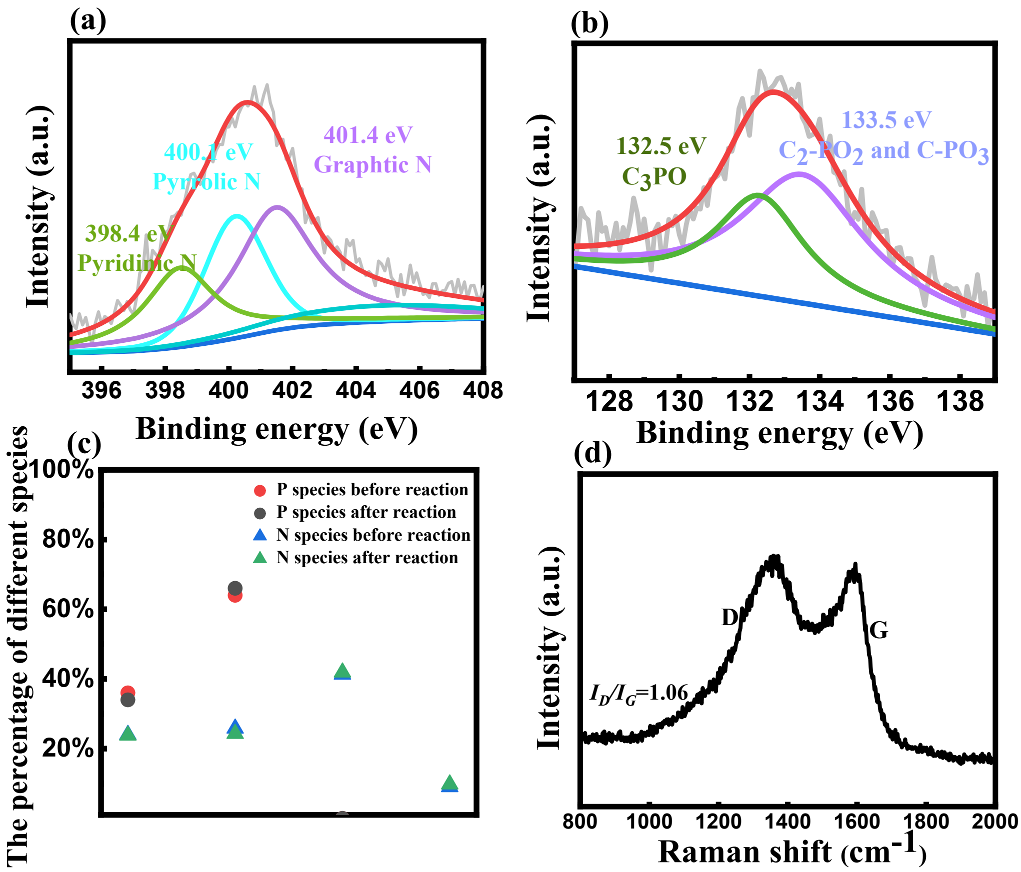


Fig. S8 (a) The N 1s spectrum of CNP0.4 after 100 LSV cycles for HER. (b) The P 2p spectrum of CNP0.4 after 100 LSV cycles for HER. (c) The percentage of different N and P species of CNP0.4 before and after 100 LSV cycles for HER. (d) The Raman spectra of CNP0.4 after 100 LSV cycles for HER.

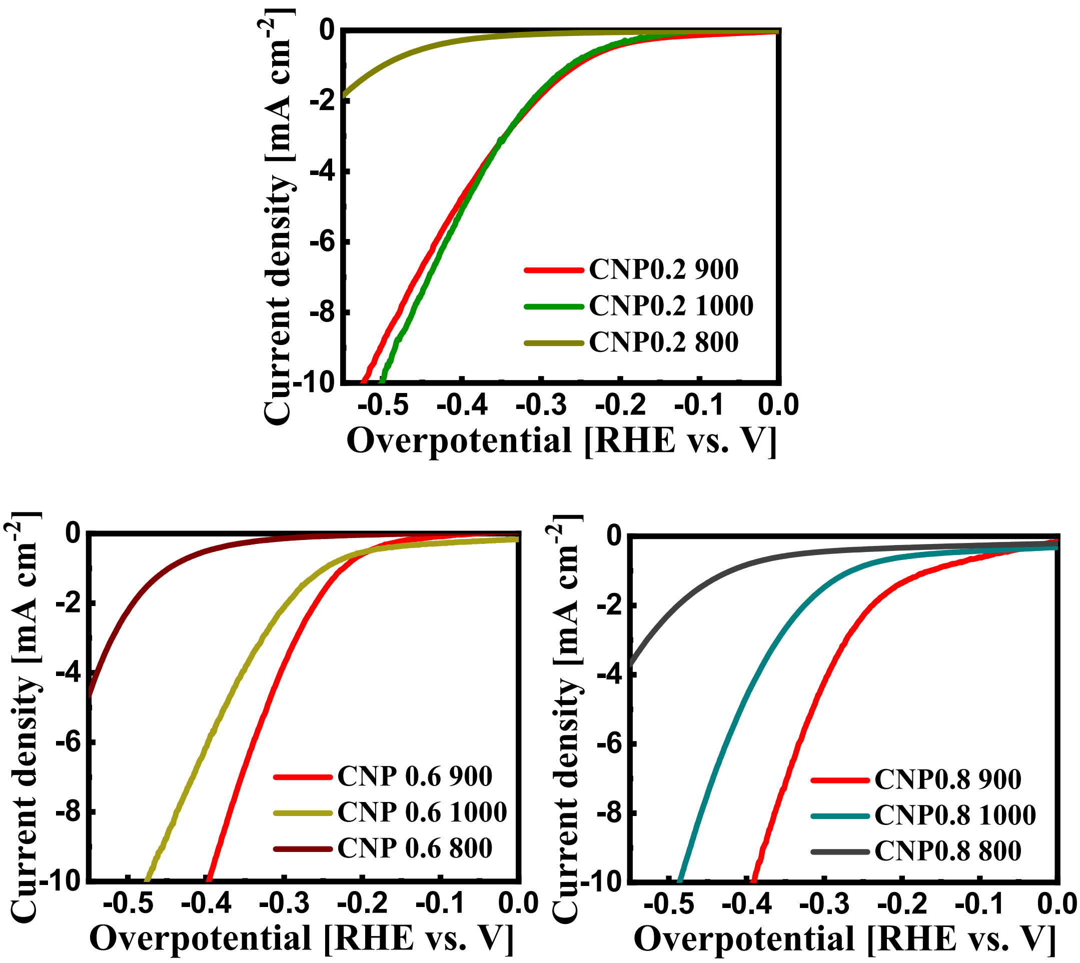


Fig. S9 The as-prepared catalysts using glycine/50% phytic acid =0.2, 0.6 and 0.8 ratio at different carbonization temperatures (800 °C, 900 °C and 1000 °C).

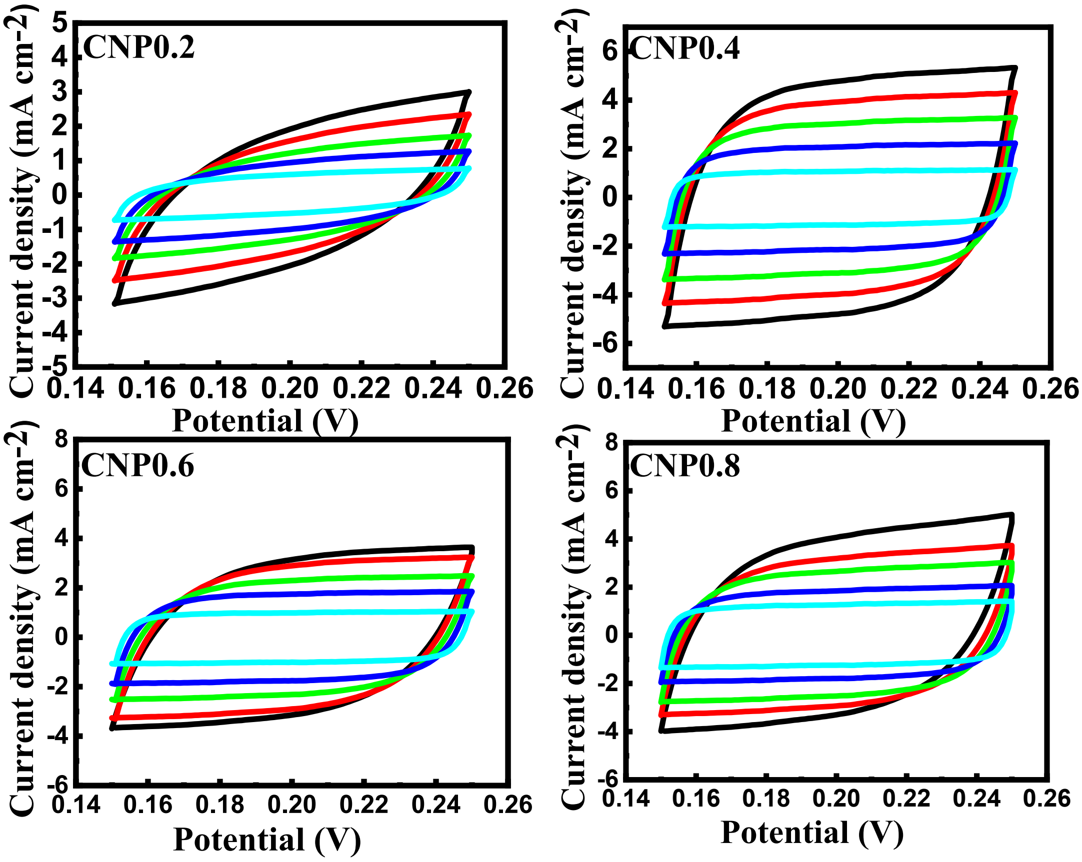


Fig. S10 CV curves of various samples with a sweep speed range from 10 mV s^{-1} to 50 mV s^{-1}.

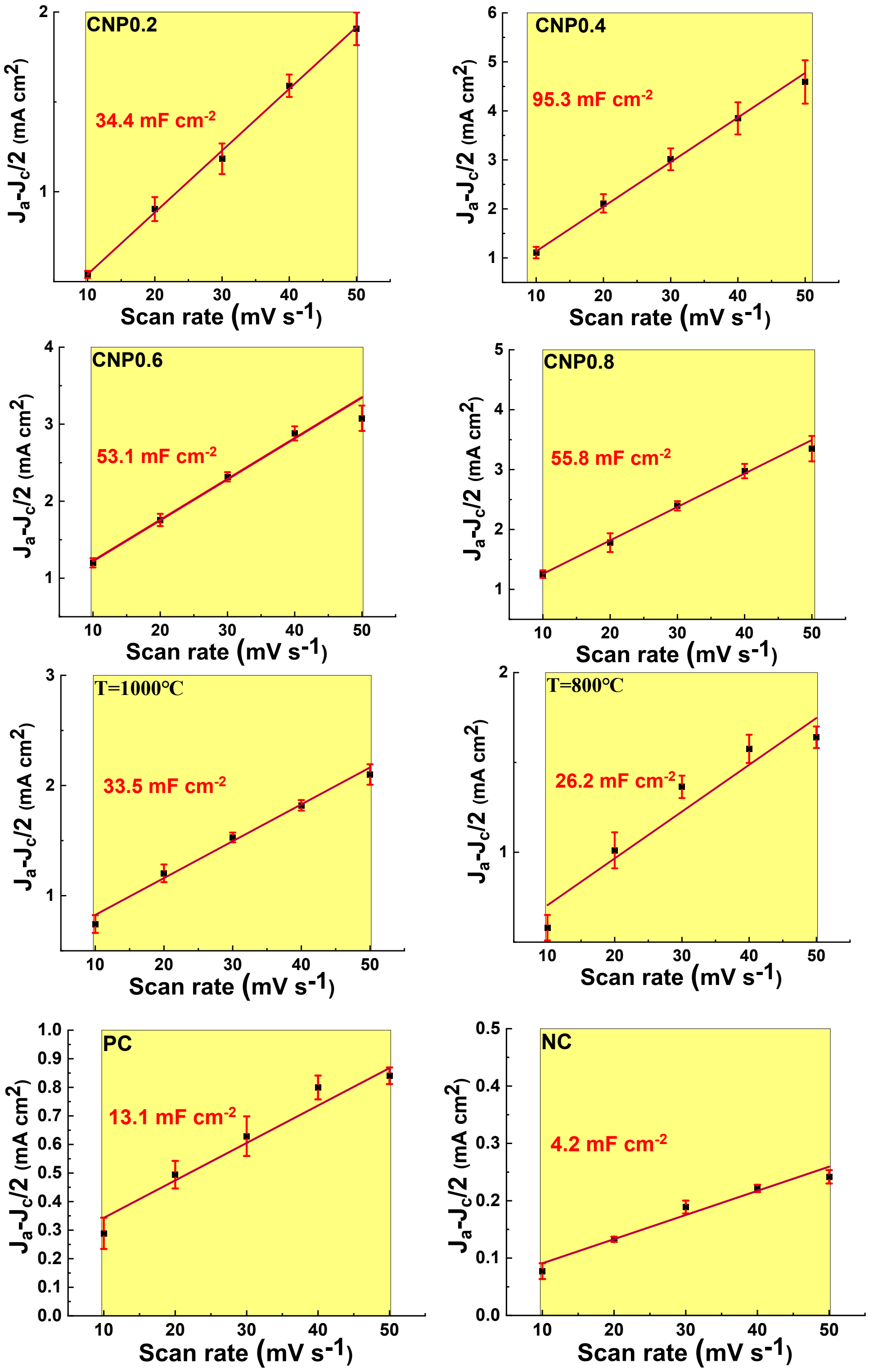


Fig. S11 Error bars of the ESCA of three independent samples.

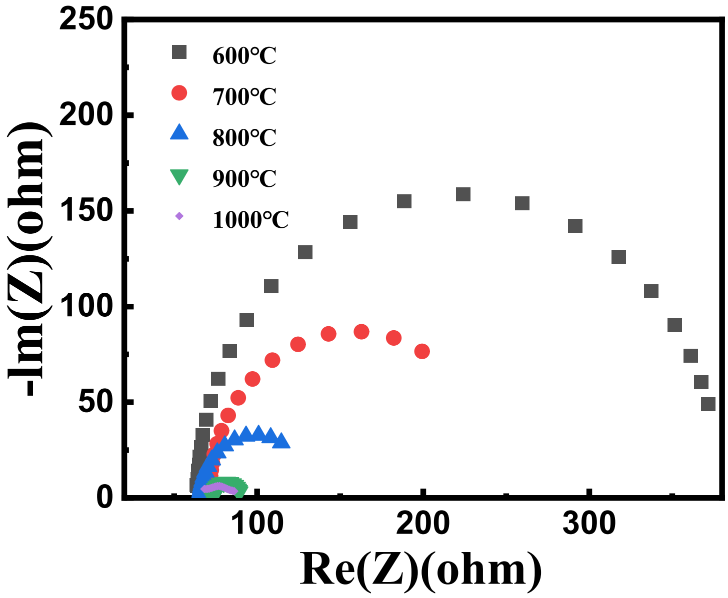


Fig. S12 EIS Nyquist plots for the samples with different heating temperatures.

Fig. S13 TOF per active sites of sample CNP0.4, PC and NC.

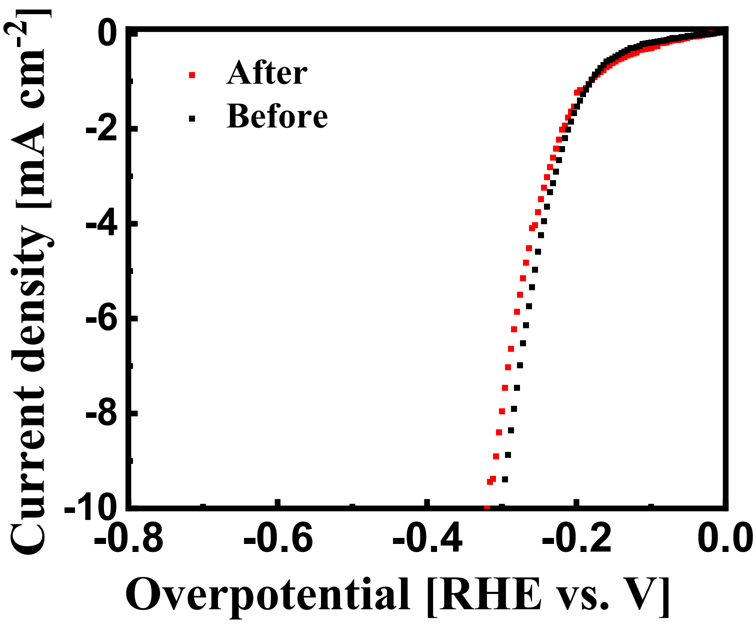


Fig. S14 LSV curves of CNP0.4 before and after 2000 CV cycles.

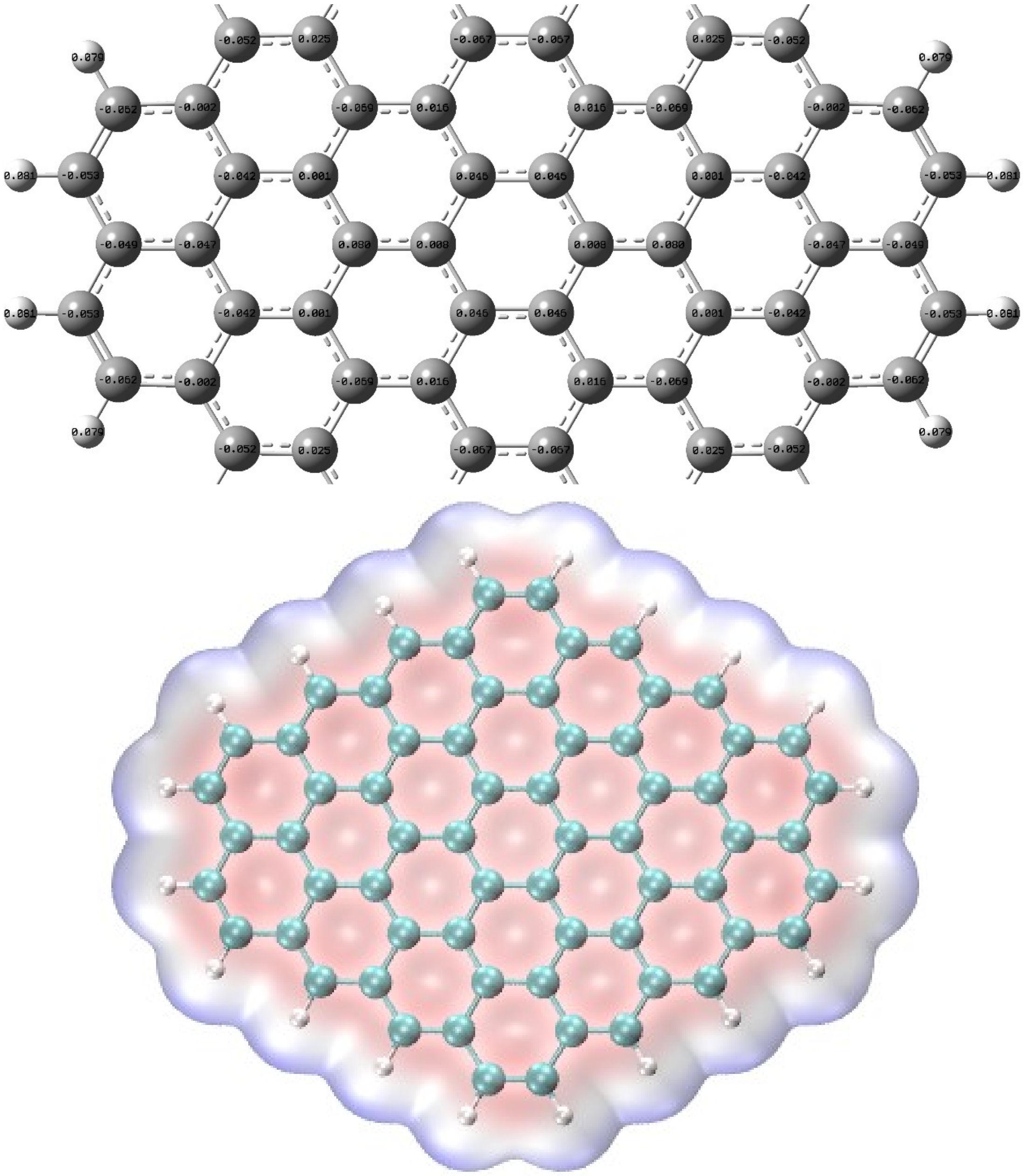


Fig. S15 Mulliken charges and ESP of pure graphene.

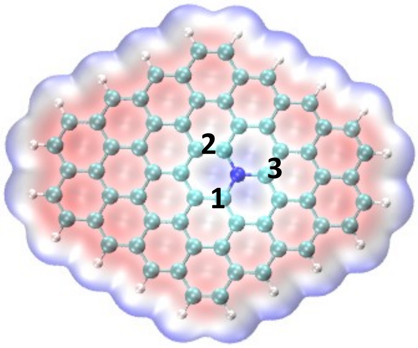
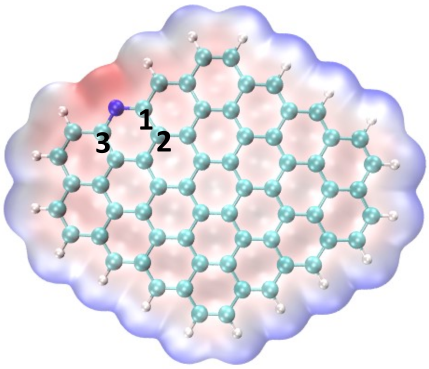
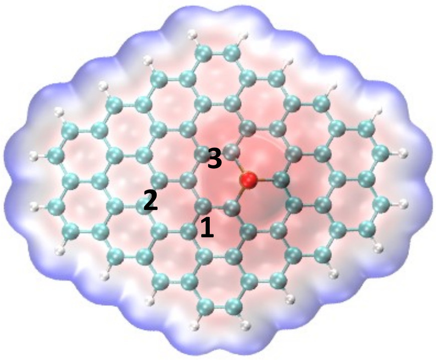
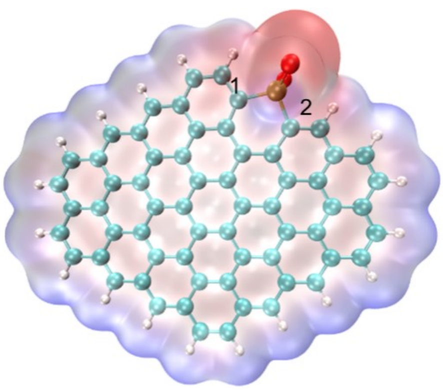
	ESP	Cluster	Mulliken charges
NG		C1	0.362
		C2	0.367
		C3	0.392
		N	-0.8
PN		C1	0.129
		C2	-0.142
		C3	0.109
		N	-0.382
C_3PO-G		C1	-0.45
		C2	-0.391
		C3	-0.45
		P	1.183
		O	-0.535
C_2PO_2-G		C1	-0.485
		C2	-0.494
		P	1.262
		O(H)	-0.528
		O(P)	-0.55

Fig. S16 Mulliken charges and ESP of pure graphene.

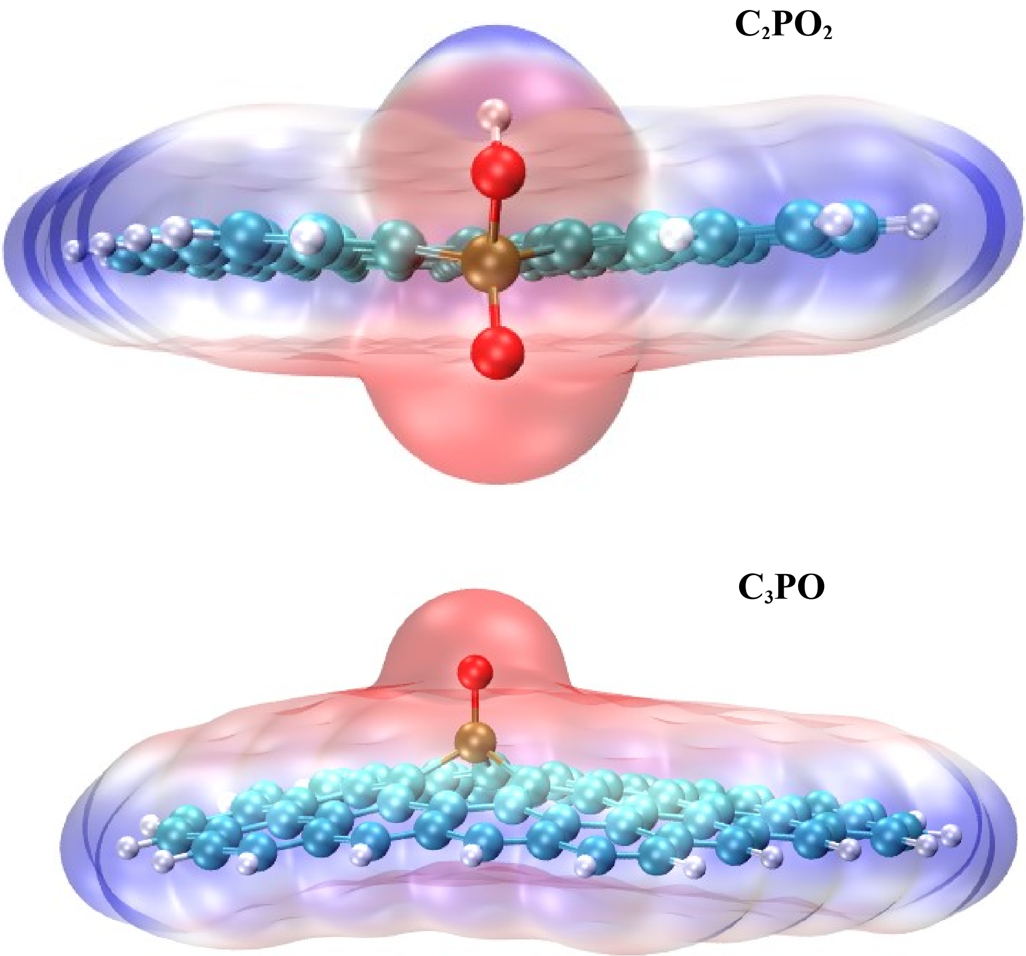


Fig. S17 Side ESP of C_2PO_2 and C_3PO Mulliken charges and ESP of pure graphene.

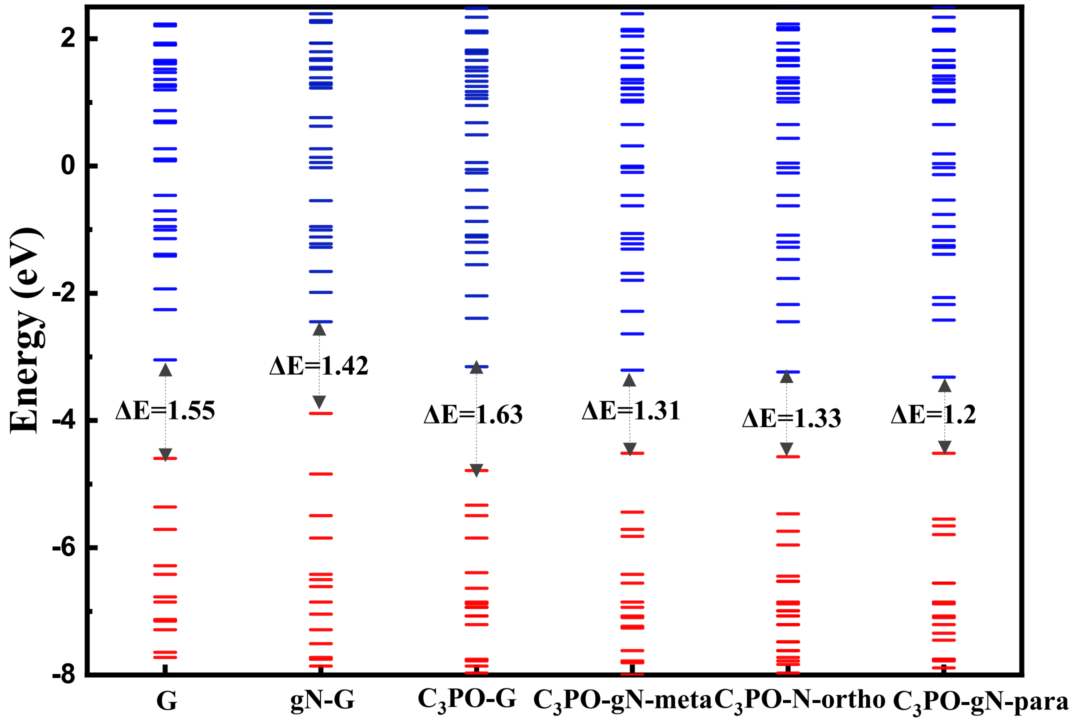


Fig. S18 E(HOMO)-E(LIMO) of the various samples.

Table S1 Mass ratio of starting materials and carbonized temperature.

Sample name	Mass ratio [-]		Carbonized temperature [°C]
	Glycine	50% Phytic acid	
CNP0.2	0.2	0.12	900
CNP0.4	0.2	0.16	900
CNP0.6	0.2	0.24	900
CNP0.8	0.2	0.32	900
NC	0.2	/	900
PC	/	0.16	900
T=600°C	0.2	0.16	600
T=700°C	0.2	0.16	700
T=800°C	0.2	0.16	800
T=900°C	0.2	0.16	900
T=1000°C	0.2	0.16	1000

Table S2 The lattice constant (physics) of various samples.

Catalyst	FWHM	2θ	d_{002} [nm]	R^2
T=600℃	10.89	22.63	0.4	0.975
T=700℃	10.72	22.7	0.399	0.983
T=800℃	10.5	23.9	0.380	0.973
T=900℃	9.7	24.34	0.373	0.966
T=1000℃	9.7	24.2	0.376	0.967

The half-peak widths (FWHM) and 2θ were obtained by fitting the characteristic peaks of (002) crystal plane. The d spacing of (002) was calculate by Bragg equation.

The R^2 denotes the coefficient of determination.

Table S3 The atomic content of C and P in samples.

Ratio	C [%]	P[%]	P/C[%]
CNP0.2	88.78	2.37	2.7
CNP0.4	86.17	2.57	2.98
CNP0.6	92.03	2.43	2.6
CNP0.8	86.07	2.61	3

Table S4 Height distributions of CNP0.4 at the scale of micron meter.

Area	Average height (nm)	Maximum height (nm)	Surface area (nm^2)
Polygon 1	8.7	12	693000
Polygon 2	5.3	6.7	127500

Table S5 The Overpotentials and Tafel slopes of the samples.

Sample	Overpotential (mV vs. RHE)	Tafel slop (mV dec)
Pt	67	43
CNP0.2	524	193
CNP0.4	306	104
CNP0.6	396	152
CNP0.8	401	186
NC	>600	/
PC	>600	/
T=600℃	>600	/
T=700℃	>600	/
T=800℃	>600	228
T=900℃	306	104
T=1000℃	361	131

Table S6 Comparisons of HER activity with CNP samples in the literature.

Sample	Overpotential (mV vs. RHE)	Tafel slop (mV dec)	Reference
CNP0.4	**306**	**121**	**This work.**
N,P-CN[2]	550	118	ACS Nano 2017, 11, 7293−7300
N, P-codoped carbon nanotube[2]	550	139	ACS Nano 2017,11(7), 7293-7300
N,P-graphene[3]	420	145	ACS Nano 2014, 8, 5, 5290–5296
N,P–C[4]	293	130.89	Journal of Solid State Chemistry 284 (2020) 121182
PNG-4-1000[5]	338	88	International journal of hydr ogen energy 46 (2021) 2192 4 e21938
N, P, F-tri-doped graphene	520	/	Chem. Int.Ed. 2016,55(42), 13296-13300

Table S7 Comparisons of Cdl with other carbon material with special morphology in the literature.

Catalyst	ESCA(mF cm^{-2})	Morphology	Reference
This work.	93.5	Nanosheet	/
N,P-CN	4.5	Nanosheet	ACS Nano 2017, 11, 7293−7300
3DNG-P	22.3	Plasma-etched graphene	
N,S-CN	11.5	Nanosheet	ACS Nano 2017, 11, 7293−7300
NCNS-900	28.8	Nanosheet	Nanoscale, 2017, 9, 16342
SG-P	16.5	Plasma-etched graphene	International Journal of Hydrogen Energy, Volume 43, Issue 6, 8 February 2018, Pages 3366
NCNT	5.11	CNT	Nano Lett. 2014, 14, 3, 1228–1233

Reference

1 Jieming Huang et al., Chemical Engineering Journal, 2023, 469, 143908.
2 Konggang Qu et al., ACS Nano, 2017, 11, 7293−7300.
3 Yao Zheng et al., ACS Nano, 2014, 8, 5, 5290–5296.
4 Yu Sun et al., Journal of Solid State Chemistry, 2020, 284, 121182.
5 Balasingh T. J et al., International journal of hydrogen energy, 2021, 4,21924.