Supplementary Information

Electrocatalytic oxygen reduction to hydrogen peroxide through a biomass-derived nitrogen and oxygen self-doped porous carbon metal-free catalyst

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Test 1 The Koutecky-Levich equation

$$\frac{1}{I} = \frac{1}{nFkC_{O_2}} + \frac{1}{0.62nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2}\omega^{1/2}}$$

(1)

Where I is the density, n is the number of transferred electrons, F is the Faraday constant, k presents the constant of electron transfer rate, ν is the kinematic viscosity of the electrolyte, ω is the rotation speed, D_{O_2} and C_{O_2} are the diffusivity and solubility of O_2, respectively.

Fig. S1. The preparation procedures of the alfalfa-derived NO/PCs.

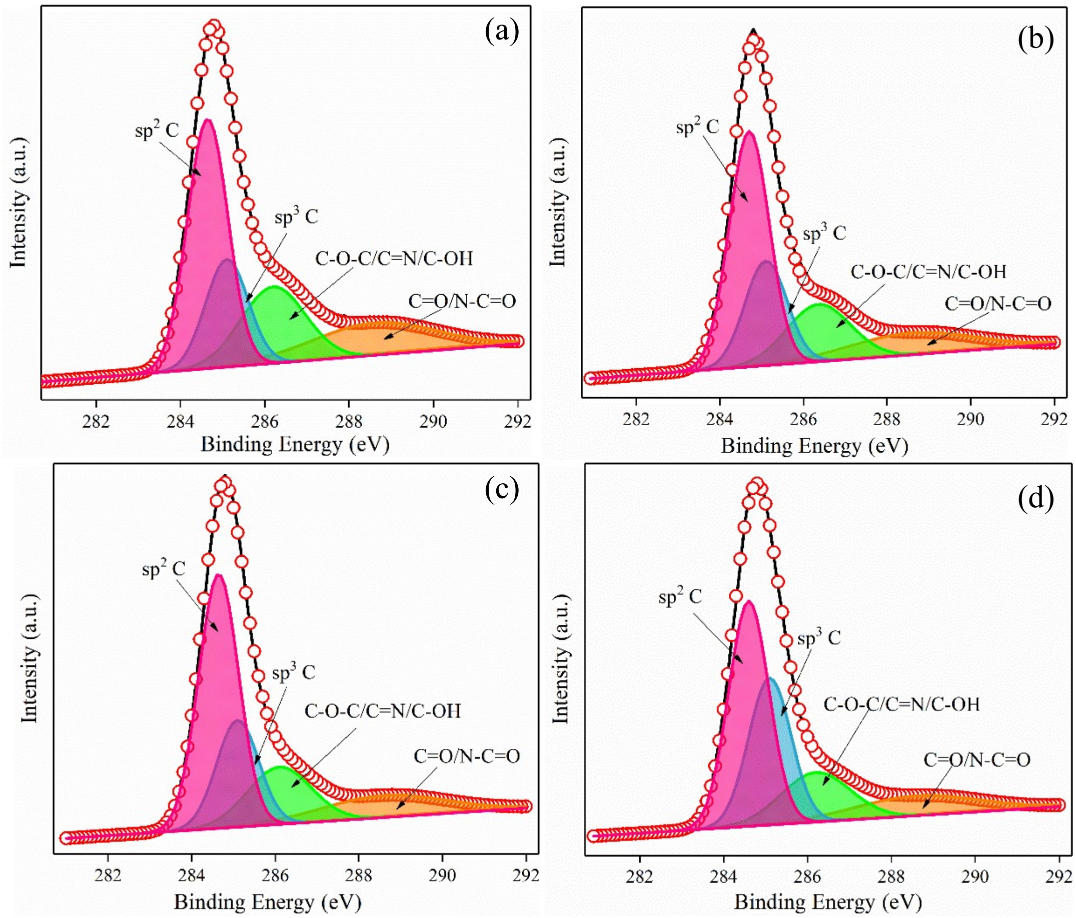

Fig. S2. The C 1s spectra of NO/PC-450 (a), NO/PC-500 (b), NO/PC-600 (c) and NO/PC-700 (d) recorded by high resolution XPS characterization.

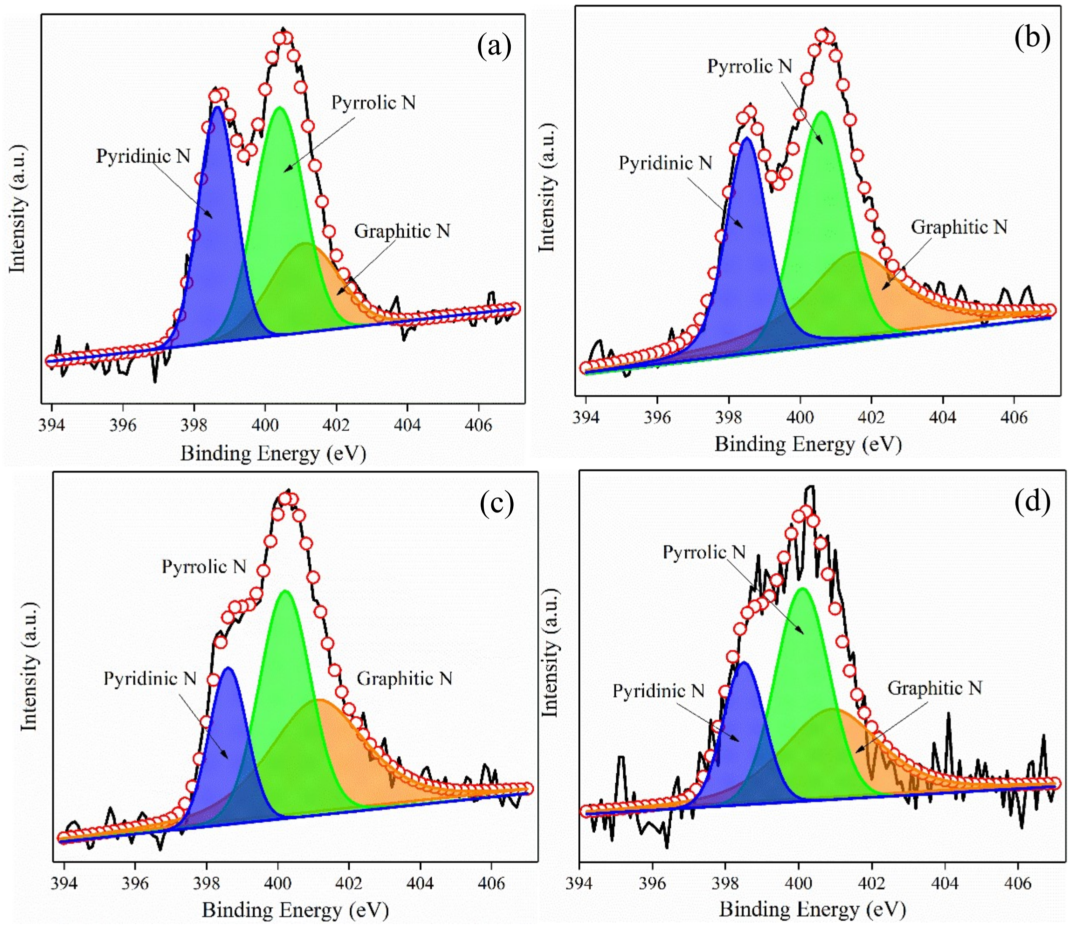

Fig. S3. The N 1s spectra of NO/PC-450 (a), NO/PC-500 (b), NO/PC-600 (c) and NO/PC-700 (d) recorded by high resolution XPS characterization.

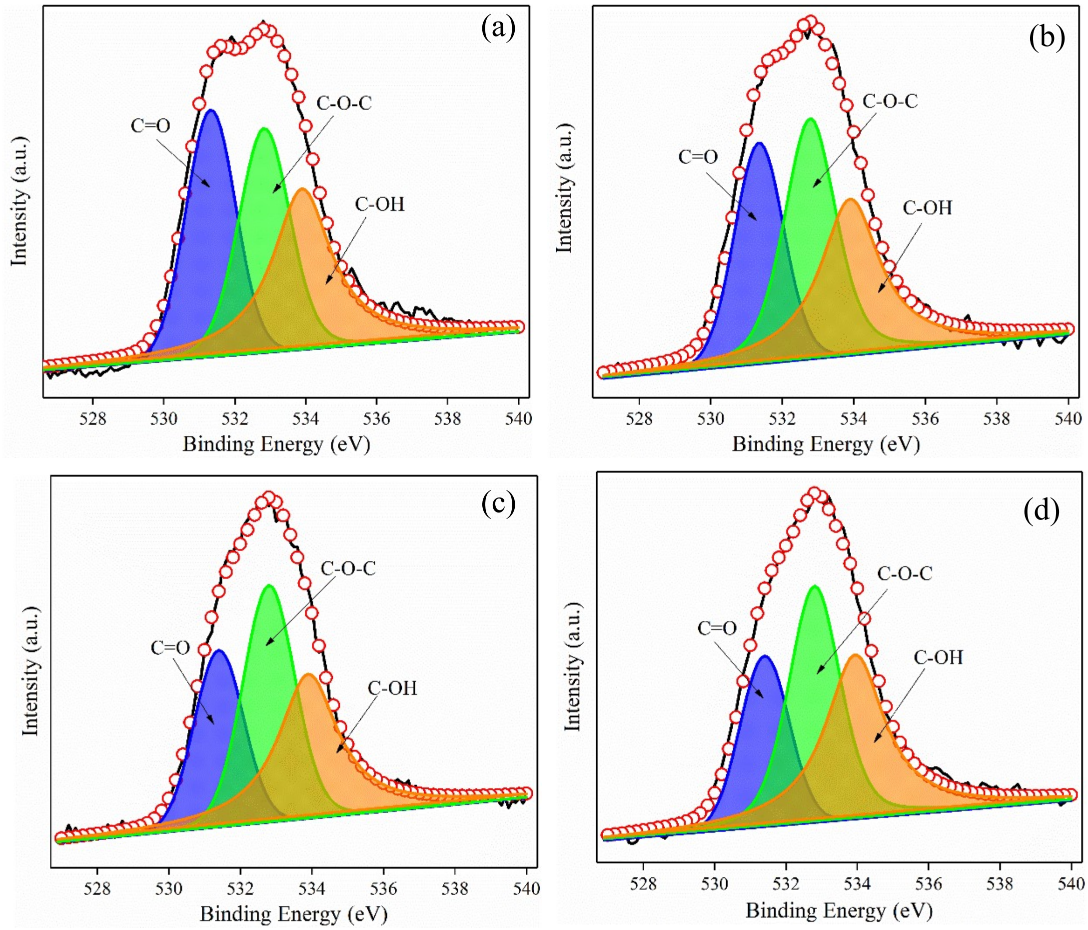

Fig. S4. The O 1s spectra of NO/PC-450 (a), NO/PC-500 (b), NO/PC-600 (c) and NO/PC-700 (d) recorded by high resolution XPS characterization.

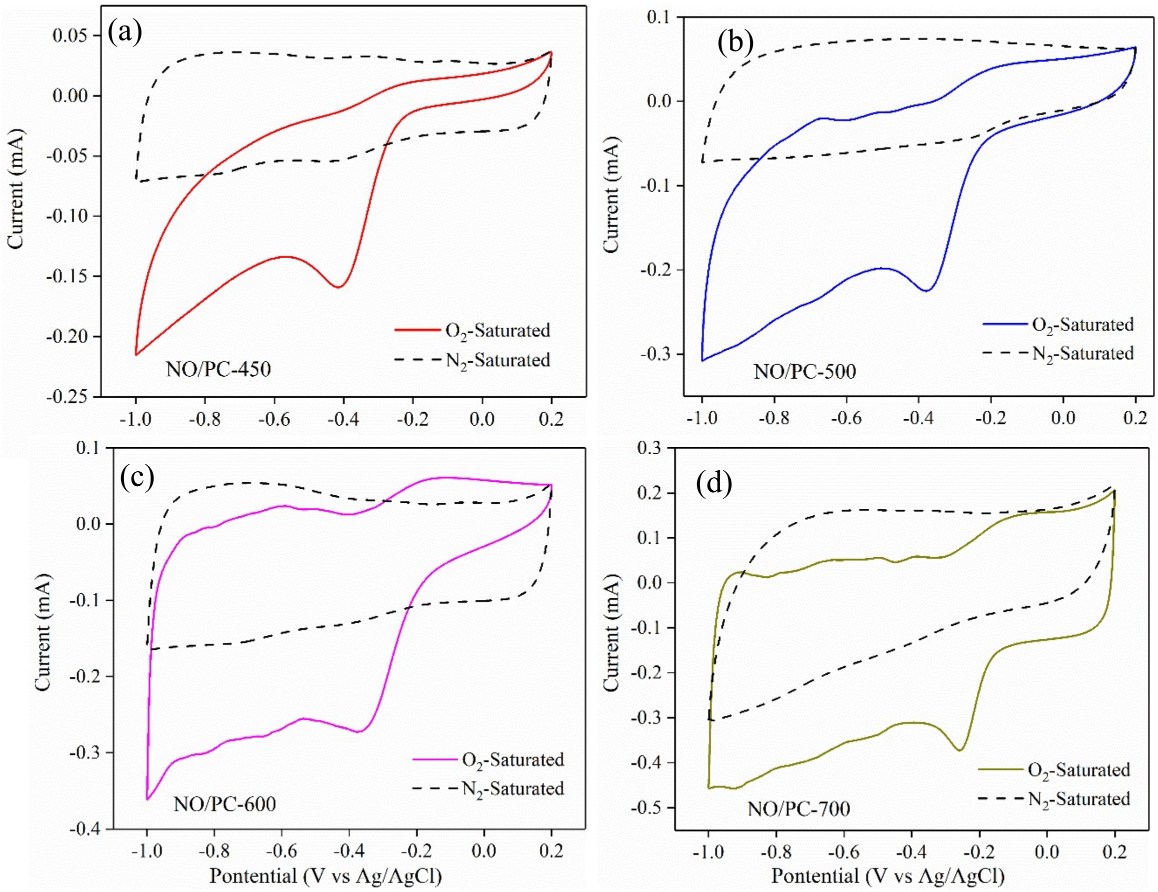

Fig. S5. The CV curves with scan rates of 50 mV s^{-1} of various NO/PCs in O_2-saturated and N_2-saturated solution.

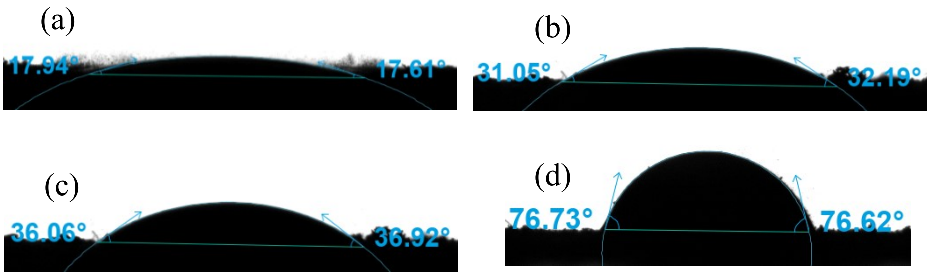

Fig. S6. The contact angle of NO/PC-450 (a), NO/PC-500 (b), NO/PC-600 (c) and NO/PC-700 (d) with water.

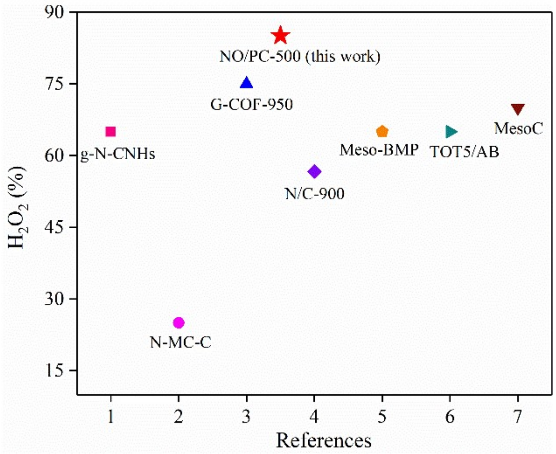

Fig. S7. Comparison of the two-electron ORR selectivity for H_2O_2 generation of NO/PC-500 with other metal-free carbon materials.

References

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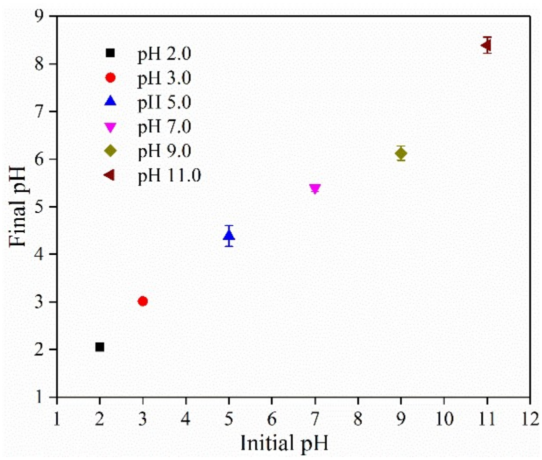


Fig. S8. The final solution pH in various initial pH after 240 min electrolysis.

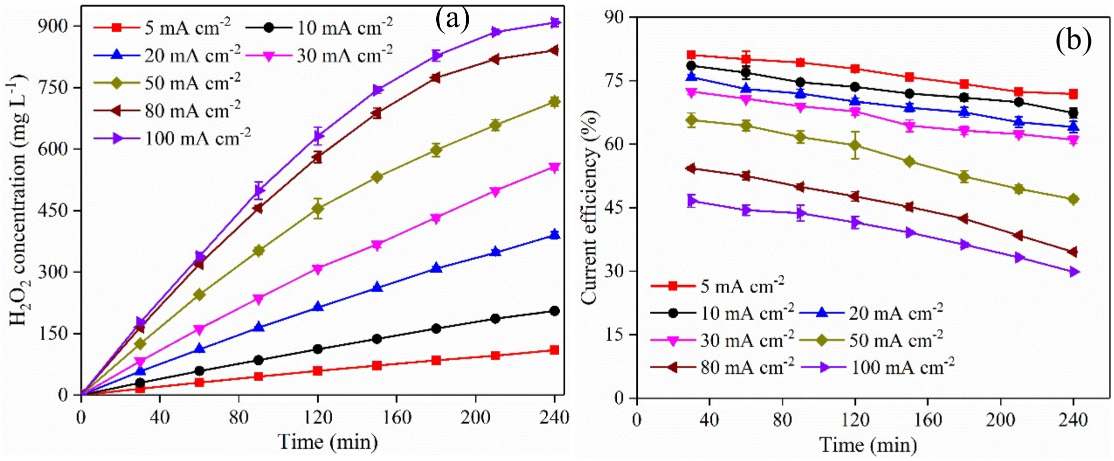


Fig. S9. Influence of current density on H_2O_2 concentration (a) and current efficiency (b) for NO/PC-500-GDE. (NO/PC-500 to PTFE binder ratio of 1:3 and pH 3.0)

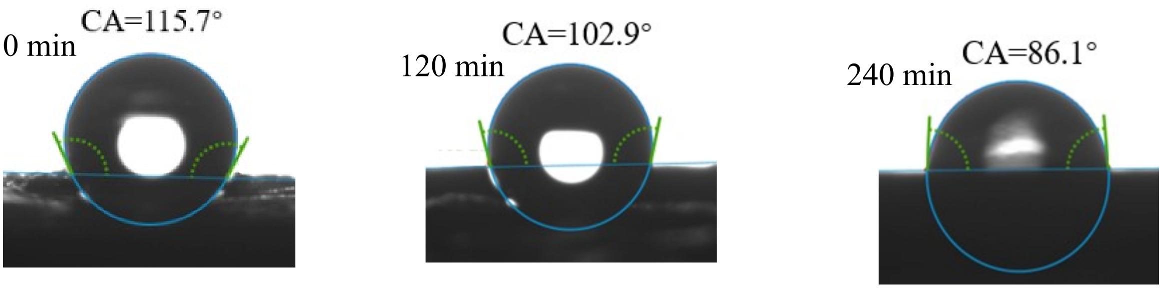


Fig. S10. The contact angle of NO/PC-500-GDE without hydrophobic layer as a function of electrolysis time at 30 mA cm^{-2}.

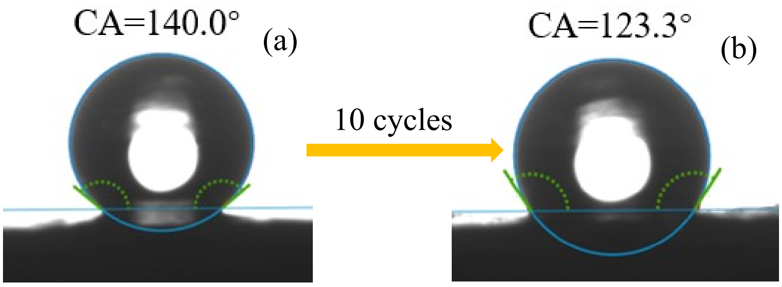


Fig. S11. The contact angle of NO/PC-500-GDE (a) and NO/PC-500-GDE after 10 cycles at 100 mA cm^{-2}at 100 mA cm^{-2} (b).

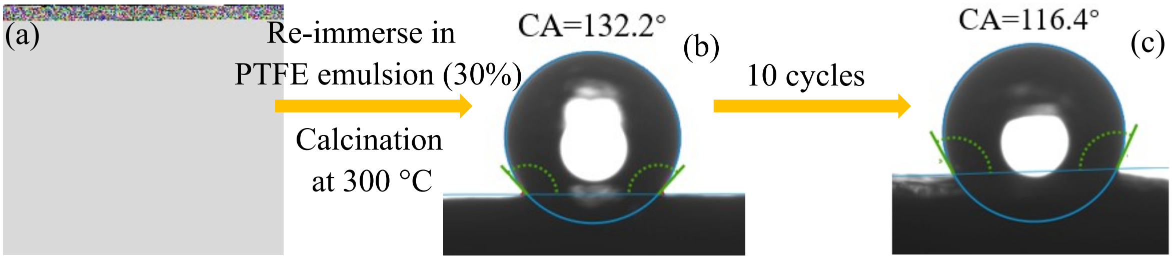


Fig. S12. The contact angle of deactivated cathode (a), the restored cathode (b) and the restored cathode after 10 times consecutive experiments at 100 mA cm^{-2} (c).

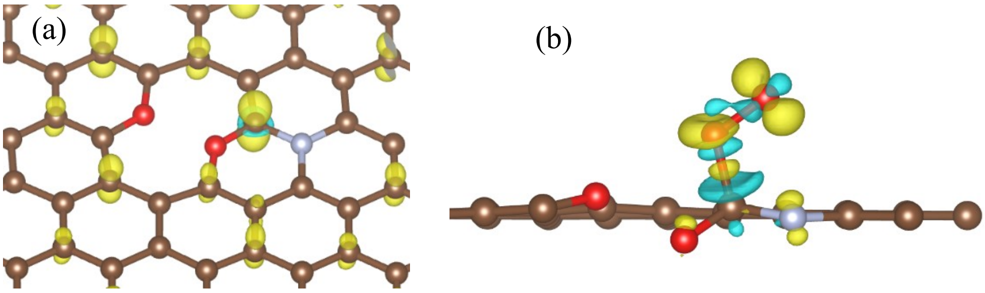


Fig. S13. The extra electron distribution of catalyst surface (a) and the difference electron density of O_2 adsorbed on the catalyst surface (b). (Yellow and Blue are the electron enrichment region and the charge enrichment region, respectively)

Table S1 BET surface area and pore structure properties of the N-O/PC samples.

Samples	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
NO/PC-450	99.6	0.1
NO/PC-500	581.8	0.3
NO/PC-600	1125.8	0.5
NO/PC-700	1860.3	1.3

Table S2 Optimized DFT models for adsorption OOH and H_2O_2 on various types of N/O containing functional groups doping and pure carbon substrate.

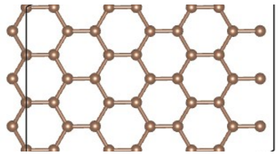
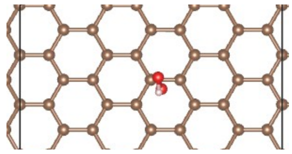
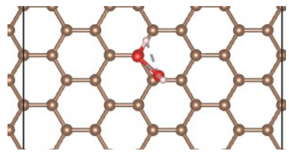
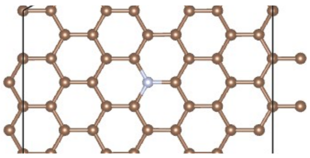
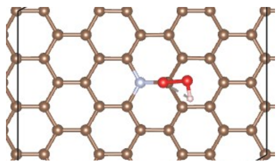
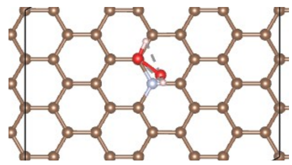
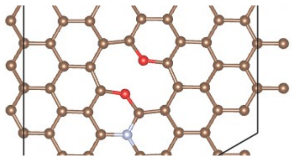
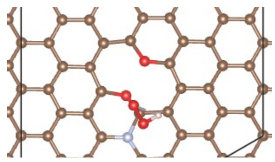
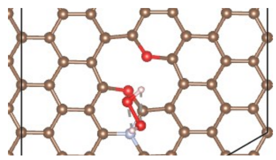
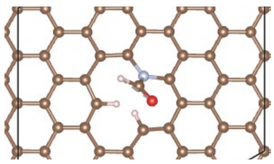
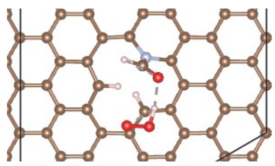
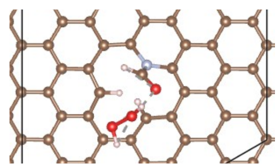
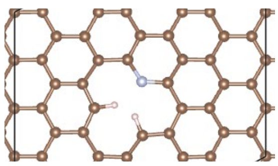
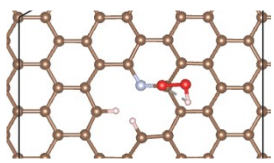
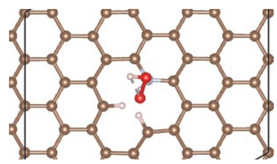
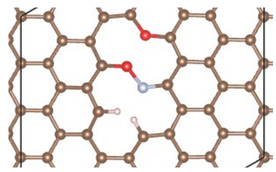
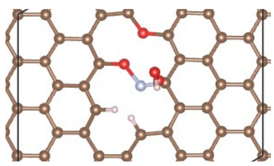
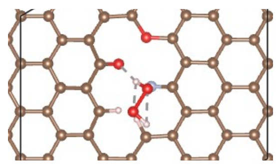
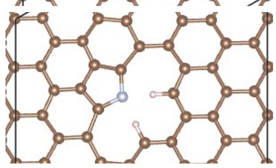
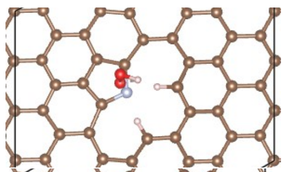
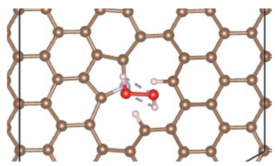
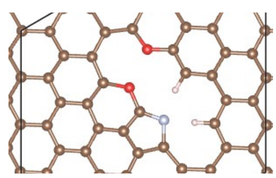
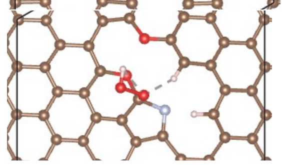
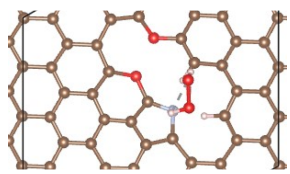
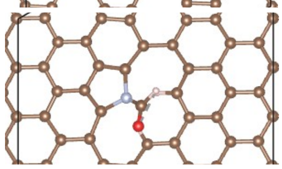
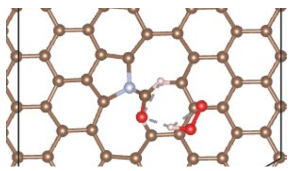
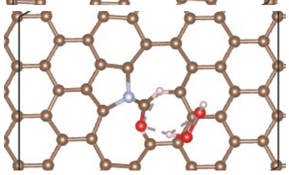
Substrates	Substrates models	OOH adsorbed substrates models	H_2O_2 adsorbed substrates models
Pure carbon			
C-Gr-N			
C-Gr-N-C-O-C			
C- Gr-N(Pyri-N)-C=O			
C-Pyri-N			
C-Pyri-N-C-O-C			
C-Pyrr-N			
C-Pyrr-N-C-O-C			
C-Pyrr-N-C=O			

Table S3 Total energy of the clear substrates surface and OOH molecule adsorbed substrates, and adsorption energy of OOH molecule on various substrates

Substrates	Total energy of the clear substrates surface (eV)	Total energy of OOH molecule adsorbed substrates (eV)	Adsorption energy (eV)
Pure carbon	-660.09	-673.20	-0.35
C-Gr-N	-658.67	-672.50	-1.07
C-Gr-N-C-O-C	-650.45	-665.36	-2.15
C- Gr-N(Pyri-N)-C=O	-674.07	-687.45	-0.62
C-Pyri-N	-654.89	-668.59	-0.94
C-Pyri-N-C-O-C	-645.85	-658.87	-0.26
C-Pyrr-N	-652.41	-665.78	-0.61
C-Pyrr-N-C-O-C	-645.15	-659.55	-1.64
C-Pyrr-N-C=O	-672.43	-685.73	-0.54

The free energy of isolated OOH molecule is -12.76 eV

Table S4 Total energy of the clear substrates surface and OOH molecule adsorbed substrates, and adsorption energy of H_2O_2 molecule on various substrates.

Substrates	Total energy of the clear substrates surface (eV)	Total energy of H_2O_2 molecule adsorbed substrates (eV)	Adsorption energy (eV)
Pure carbon	-660.09	-678.26	-0.03
C-Gr-N	-658.67	-676.87	-0.06
C-Gr-N-C-O-C	-650.45	-668.94	-0.35
C- Gr-N(Pyri-N)-C=O	-674.07	-692.50	-0.29
C-Pyri-N	-654.89	-673.45	-0.42
C-Pyri-N-C-O-C	-645.85	-665.06	-1.07
C-Pyrr-N	-652.41	-670.75	-0.2
C-Pyrr-N-C-O-C	-645.15	-663.86	-0.57
C-Pyrr-N-C=O	-672.43	-690.90	-0.33

The free energy of isolated H_2O_2 molecule is -18.14 eV.