

Supporting Information

Atomically dispersed metal sites stabilized on nitrogen doped carbon carrier via N₂ glow-discharge plasma

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1. Experimental section

Chemicals. Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, 98%, Adamas), palladium nitrate ($\text{Pd}(\text{NO}_3)_2$, 98%, Adamas), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Mclean), copper nitrate nonahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, 98%, Mclean), silver nitrate (AgNO_3 , 98%, Mclean), ethanol (EtOH, Mclean), Nafion (Dupont, 5 wt%, Mclean), acetylene black (Mclean), commercial 20 wt% Pt/C (20 wt% metal, Mclean), sulphuric acid (H_2SO_4 , 98%, Beijing Chemical Reagents). The distilled water used in all experiments was obtained through filtration.

The adjustable synthesis of Pt/C-N. The Pt/C-N samples were prepared by a simple impregnated-plasma method. Briefly, 100 mg acetylene black was dispersed in 5 ml ethanol. Then 0.05 ml, 0.25 ml, 0.5 ml, 1 ml $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ solution (0.01 M) were added into above solution, respectively, followed by ultrasound for 2 h. Subsequently, the impregnated suspension dried in an oven at 60 °C for 12 h. After that, the sample placed in a porcelain boat was treated by N_2 glow discharge plasma for 2 h. The power of nitrogen plasma and the flow rate of nitrogen gas were fixed at 80 W and 20 ml/min. And the vacuum for nitrogen plasma was 10 Pa. At last, Pt/C-N with different theoretical loading of about 0.1, 0.5, 1, 2 wt% were obtained (marked as 0.1Pt/C-N, 0.5Pt/C-N, 1Pt/C-N, 2Pt/C-N).

The preparation of M/C-N. The synthesis of Pd/C-N, Ag/C-N, Co/C-N and Cu/C-N followed the preparation of Pt/C-N, replacing the precursor with 0.1 ml $\text{Pd}(\text{NO}_3)_2$ (0.01 M), 0.5 ml AgNO_3 (0.01 M), 0.8 ml $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.01 M), 0.8 ml $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively.

The synthesis of 2Pt/C-800. 100 mg acetylene black placed in a porcelain boat was treated by N_2 glow discharge plasma for 2 h with power of 80 W and pressure of 10 Pa. And the flow rate of N_2 was fixed at 20 ml/min. Then acetylene black was dispersed in 5 ml ethanol. 1 ml $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ solution (0.01 M) was added into the above solution under ultrasound for 2 h. Subsequently, the impregnated suspension

dried in an oven at 60 °C for 12 h. After that, the sample was placed in a porcelain boat and heated to 800 °C for 1 h at heating rate 5 °C/min under flowing N₂. The black powder was obtained when the temperature was cooled to room temperature.

The synthesis of 2Pt/C-Ar. The preparation of 2Pt/C-Ar was similar to that of 2Pt/C-N except using Ar plasma for the treatment of drying samples.

Physicochemical characterization. The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) elemental mapping were recorded on an FEI Titan 80-300 microscope equipped with a monochromator and a probe Cs corrector operated at 300 kV. XPS measurement was carried out on an Escalab 250Xi (XPS). All the elemental spectra were corrected with respect to C1s peaks at 284.8 eV and analyzed by the XPSPEAK 4.1 software. Powder X-ray diffraction pattern (XRD) was obtained using a Bruker D8. Advance instrument with Cu K α radiation ($\lambda = 0.1542$ nm) operated at 40 kV and 40 mA. The inductively coupled plasma optical emission spectrometer (ICP-OES) was conducted to determine the Pt content of catalysts, such as 1Pt/C-N, 2Pt/C-Ar.

XAFS measurement and analysis. The X-ray absorption spectra were collected at the beamline BL01C1 in NSRRC provided technical support by Ceshigo Research Service “www.ceshigo.com“. The radiation was monochromatized by a Si (111) double-crystal monochromator. The samples were pressed into pellets that with certain thickness for optimum signal-noise-ratio based on the adsorption length calculation. A Pt foil was placed downstream of the sample cell, as a reference to calibrate the photon energy of each spectrum. The obtained XAFS data was processed in Athena (version 0.9.25) for background removal, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.25). As Pt is a high Z metal, in order to highlight the possible existence of Pt-Pt scattering, the k^3 weighting, k -range of 3 - 13 Å⁻¹ and R range of 1 - 5 Å were used for the fitting. The computed coordinates were used to generate the primary input for the

ab initio EXAFS scattering code (FEFF9). The model of bulk Pt, PtO and PtO₂ were used to calculate the simulated scattering paths and to calibrate the multielectron effects (S_0^2) and reference energy value (E_0). We also modified the crystalline structure of PtO by replacing O with N and C atoms to provide the optimized coordinates with the ab initio EXAFS scattering code (FEFF9) for the sample fitting. For Wavelet Transform analysis, the $\chi(k)$ exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 1 - 4 Å, k range, 0 - 13 Å⁻¹; k weight, 2; and Morlet function with $\kappa=10$, $\sigma=1$ was used as the mother wavelet to provide the overall distribution.

Electrochemical measurements. All the electrochemical experiments were conducted on electrochemical workstation (CHI 660E) in a three-electrode system in 0.5 M H₂SO₄ solution (degassed with N₂) at room temperature. A graphite rod and an Ag/AgCl (3 M KCl) electrode were used as the counter and reference electrode, respectively. The working electrode was fabricated as follows: 5 mg of catalyst was dispersed ultrasonically in a mixed solution of 950 μ l of ethanol and 50 μ l of nafion (Dupont, 5 wt%). Then 10 μ l of fresh catalyst ink was dropped onto a glassy-carbon electrode (GC; 5 mm in diameter.) and dried at room temperature. The HER was conducted in N₂-saturated 0.5 M H₂SO₄ solution with a scan rate of 5 mV s⁻¹. The potential vs. Ag/AgCl was converted to the reversible hydrogen electrode (RHE) by the equation ($E_{\text{RHE}}=E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{PH}$). The durability of catalysts was evaluated by 1000 cyclic voltammetry sweeps between 0.2 and -0.1 V in 0.5 M H₂SO₄.

2. Supplementary Figures

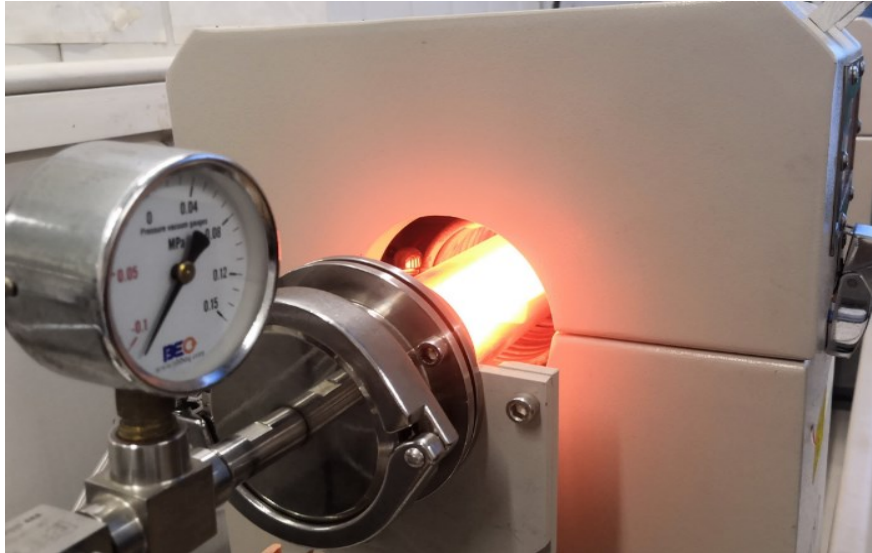


Fig. S1. The photograph of the low-temperature plasma appliance emitting N₂ plasma in orange glow.

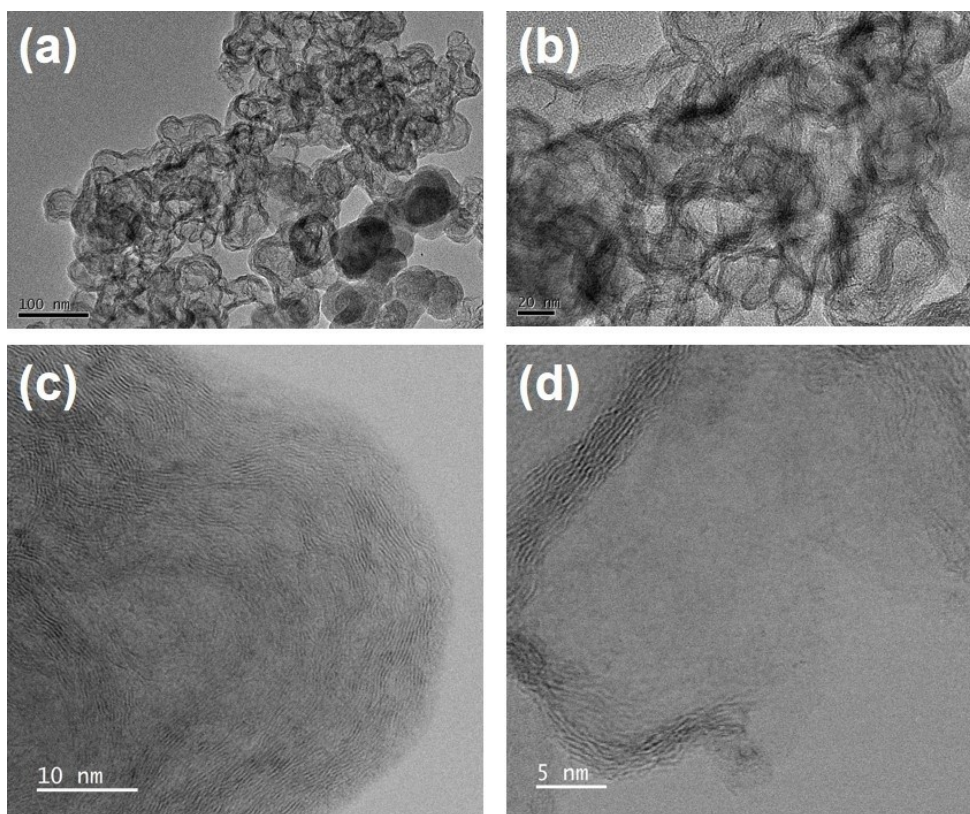


Fig. S2. (a) TEM of 2Pt/C-N. (b) HRTEM of 2Pt/C-N. (c)-(d) STEM of 2Pt/C-N.

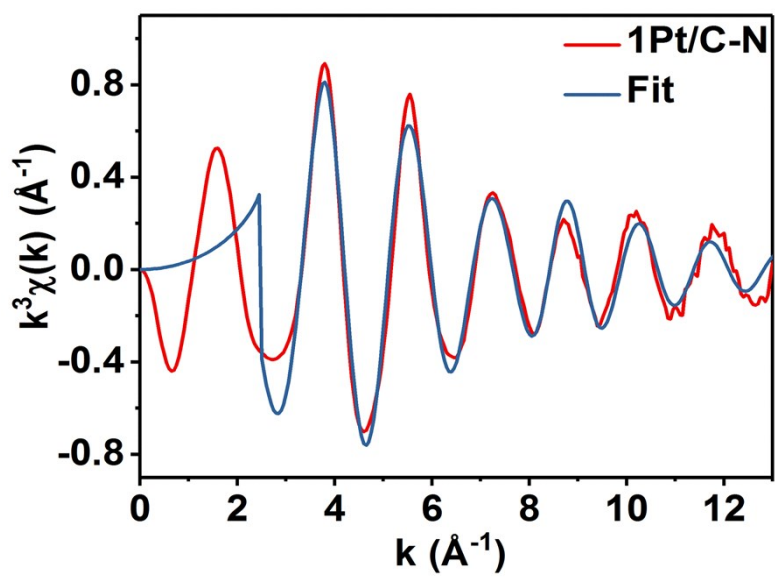


Fig. S3. Fourier-transformed magnitude of 1Pt/C-N K-edge EXAFS spectra in K space.

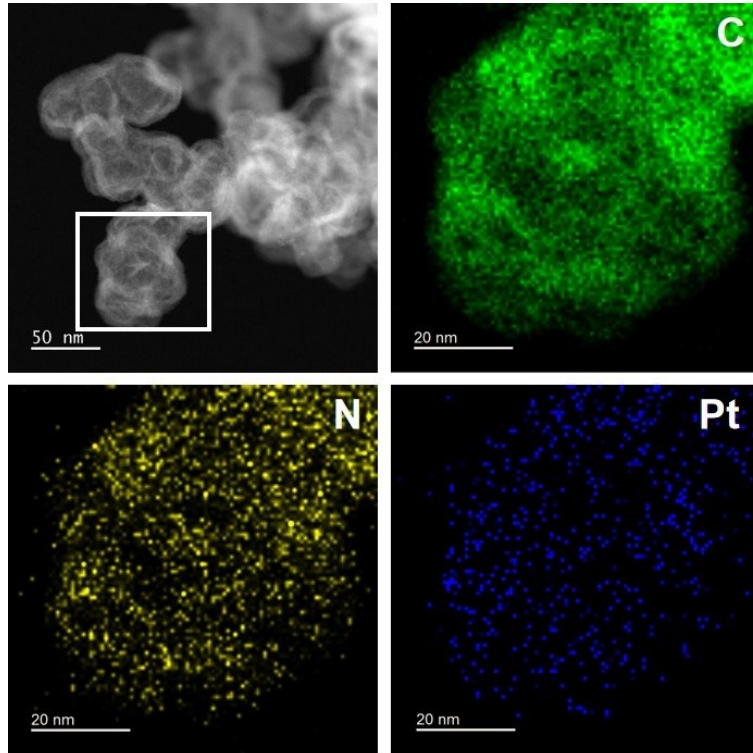


Fig. S4. EDS mapping of 2Pt/C-N.

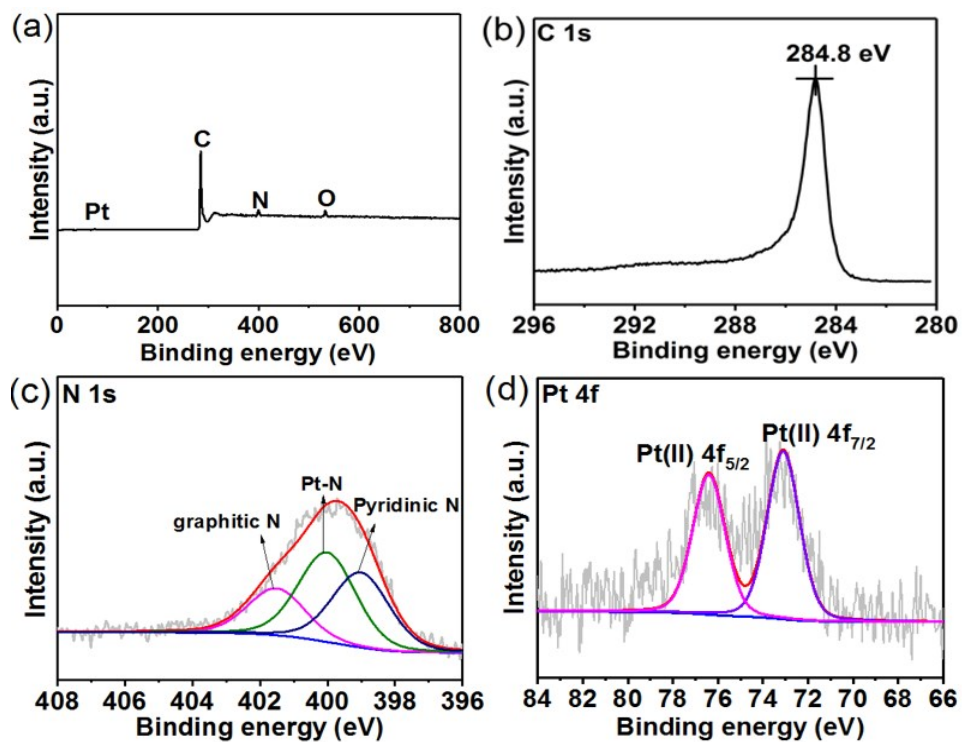


Fig. S5. Compositional characterizations on the 1Pt/C-N. (a) XPS survey spectrum. (b) C 1s XPS spectrum of 1Pt/C-N. (c) N 1s XPS spectrum of 1Pt/C-N and (d) Pt 4f XPS spectra of 1Pt/C-N.

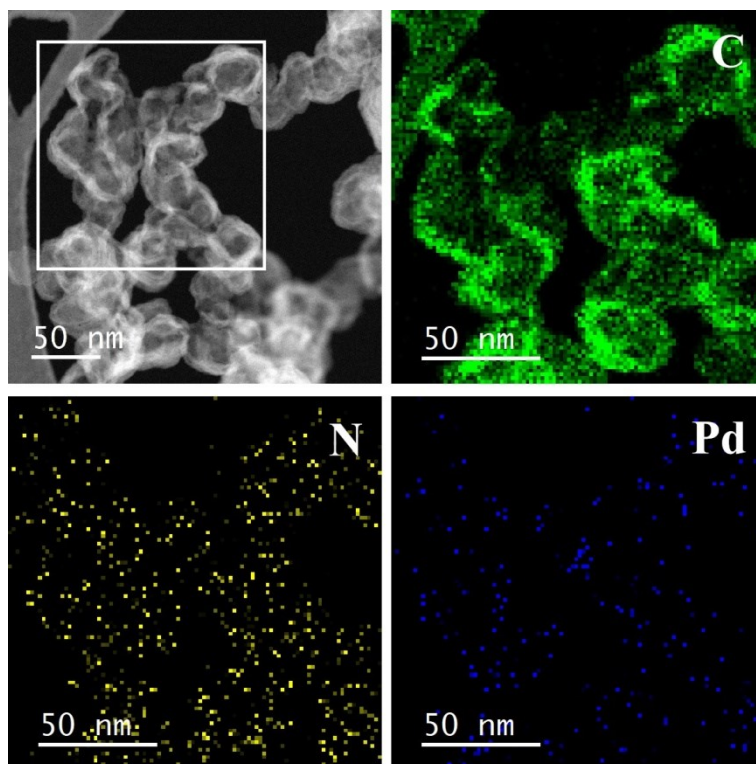


Fig. S6. HAADF-STEM image of Pd/C-N and corresponding element maps showing the distribution of C, N and Pd.

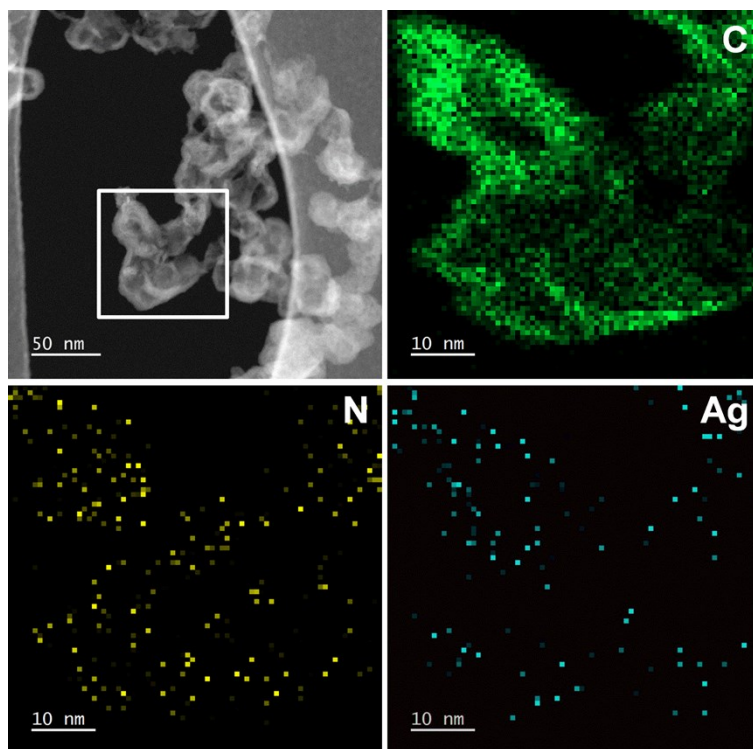


Fig. S7. HAADF-STEM image of Ag/C-N and corresponding element maps showing the distribution of C, N and Ag.

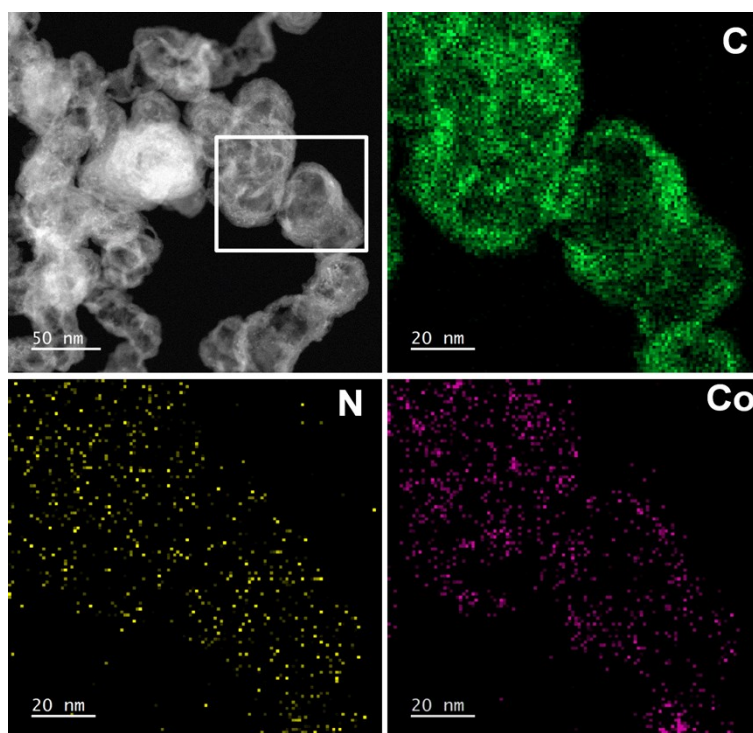


Fig. S8. HAADF-STEM image of Co/C-N and corresponding element maps showing the distribution of C, N and Co.

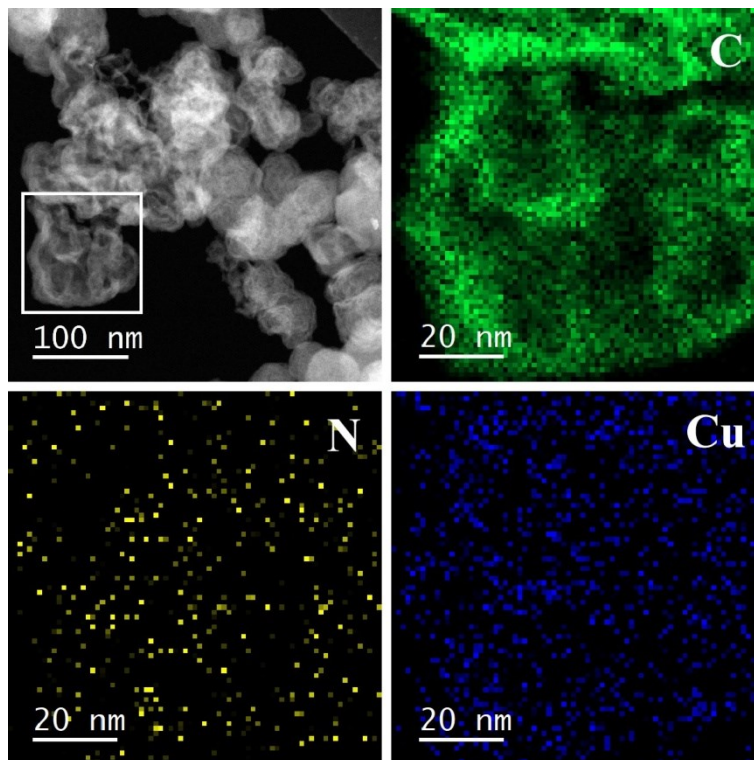


Fig. S9. HAADF-STEM image of Cu/C-N and corresponding element maps showing the distribution of C, N and Cu.

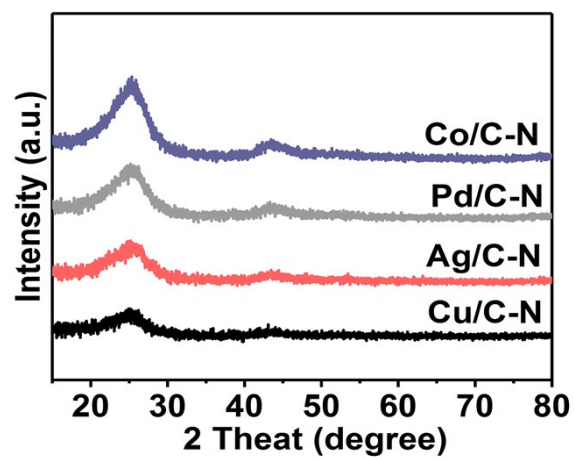


Fig. S10. XRD pattern of Pd/C-N, Ag/C-N, Co/C-N, Cu/C-N.

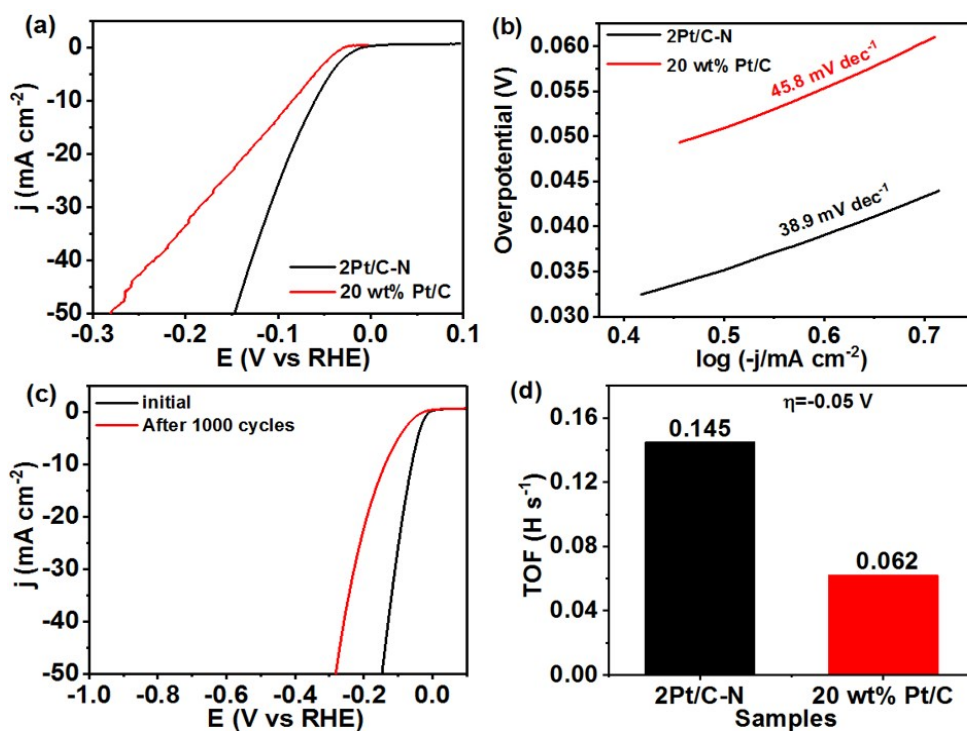


Fig. S11. HER performance of samples after IR-compensation. (a) Polarization curves. (b) Tafel plots. (c) LSV curves of 2Pt/C-N before and after 1000 CV cycles. (d) TOF values of 2Pt/C-N and 20 wt% Pt/C.

3. Supplementary Tables

Table S1. Structural parameters of 1Pt/C-N, the reference PtO₂ and Pt foil extracted from quantitative EXAFS fitting curves.

Sample	Path	CN	R (Å)	DWF	R factor
Pt foil	Pt-Pt	12*	2.761±0.011	0.0044+0.0006	0.01
	Pt-Pt	6*	3.912±0.014	0.0060+0.0021	
PtO ₂	Pt-O	6*	1.998±0.030	0.0029+0.0008	0.01
	Pt-Pt	6*	3.103±0.021	0.0021+0.0012	
1Pt/C-N	Pt-N	1.9±0.8	1.821±0.031	0.0129+0.0038	0.02
	Pt-C	3.8±1.4	2.515±0.043	0.0071+0.0029	

* Parameter set to the theoretical model; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); DWF is a measure of thermal and static disorder in absorber-scatterer distances; R factor is goodness of fitting.

Table S2. Collected data of HER activity in electrolyte solution.

Samples	Electrolyte	Overpotential (mV/mA cm ⁻²)	Loading (mg cm ⁻²)	TOF (H ₂ s ⁻¹ /mV)	References
PtSAS/AG	0.5 M H ₂ SO ₄	12/10	7.07	0.325/12	1
W-SAC	0.1 M KOH	85/10	0.204	1.16/20	2
Mo-Co ₉ S ₈ @C	0.5 M H ₂ SO ₄	98/10	1.0	0.5/98	3
Pt ₁ /OLC	0.5 M H ₂ SO ₄	38/10	0.51	40.78/100	4

Pt ₁ /hNCN C-2.92	0.5 M H ₂ SO ₄	15/10	0.09	7.67/20	5
ALDPt/50 NGN	0.5 M H ₂ SO ₄	24/10	0.0764	6.3/24	6
RuSAs@P N	0.5 M H ₂ SO ₄	24/10	1	2.18/30	7
Mo ₂ TiC _{2x} - PtSA	0.5 M H ₂ SO ₄	30/10	1	0.84/30	8
Mo-SAC	0.1 M KOH	132/10	0.408	0.148/50	9
Co ₁ /PCN	1.0 M KOH	89/10	0.5	0.22/50	10
Ni/GD	0.5 M H ₂ SO ₄	88/10	0.896	1.59/100	11
2Pt/C-N	0.5 M H ₂ SO ₄	60/10	0.255	0.145/50	This work

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