

Supplementary Information for

**Rigid Anchoring Highly-Crystallized and Uniformly-Dispersed Pd
Nanocrystals on Carbon Fibers for Ambient Electrocatalytic
Reduction of Nitrogen to Ammonia**

Yingchao Wang,^a Zizai Ma,^b Kai Liu,^a Xiaowei Yang,^c Jianxing Wang^{*d} and Xiaoguang Wang^{*a,b}

^a Laboratory of Advanced Materials and Energy Electrochemistry, Institute of New Carbon Materials, School of Materials Science & Engineering, Taiyuan University of Technology, Taiyuan, 030024, China.

^b Shanxi Key Laboratory of Gas Energy Efficient and Clean Utilization, Taiyuan, 030024, China.

^c Yancheng Teachers University, Yancheng, 224000, China.

^d State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science & Engineering, Sun Yat-sen University, Guangzhou, 510275, China.

Chemicals and materials

N, N-dimethylformamide (DMF), Polyacrylonitrile (PAN, average Mw 250000), salicylic acid ($C_7H_6O_3$), sodium citrate ($C_6H_5Na_3O_7$), sodium hypochlorite (NaClO) and sodium nitroprusside ($C_5H_4FeN_6Na_2O_3$) were purchased from Macklin. Sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), p-dimethylaminobenzaldehyde ($C_9H_{11}NO$) were purchased from Aladdin. Palladium chloride ($PdCl_2$), sodium borohydride ($NaBH_4$), ammonium chloride (NH_4Cl), hydrazine hydrate ($N_2H_4 \cdot H_2O$) and ethyl alcohol ($C_2H_6O_4$) were obtained from Sinopharm group. Carbon paper, 115 Nafion membrane and Nafion solution (5%) were purchased from Shanghai Hesen Electric Co., LTD. All the reagents are analytically grade and were used without further purification. Deionized water (DI, 18.25 M Ω -cm) was purified by Ultrapure pure water system.

Preparation of the working electrode

5 mg of the catalyst powder and 40 μ L 5 wt % Nafion solution were dispersed in 340 μ L ethanol and 120 μ L DI water followed by 1 hour sonication to form a homogeneous catalyst ink. Then, 20 μ L of the catalyst suspension was loaded onto single side (1.0 cm², effective area exposed to the electrolyte) of carbon paper, and dried at room temperature. The catalyst loading of the prepared electrode is \sim 0.2 mg cm⁻².

NRR test details

Prior to the NRR tests, nitrogen is pumped into the cathode side with a flow rate of 20 mL min⁻¹ for 30 min to saturate the 0.1 M Na_2SO_4 electrolyte. During the tests, the gas flow rate was fixed at 15 mL min⁻¹. All the polarization curves were obtained when reaching a steady state after several CV cycles. After the test, a certain amount of electrolyte was taken from the cathode chamber for quantitative analysis of the product. The product was quantified by an Ultraviolet-visible spectrophotometer (UV-9000S).

Quantification of NH_3

Concentration of produced NH_3 was spectrophotometrically determined by the indophenol blue method.¹ In detail, 2 mL electrolyte was taken from the cathodic chamber, then 2 mL NaOH (1 M) solution containing 5 wt. % sodium citrate and salicylic acid, 1 mL NaClO (0.05 M) and 200 μ L sodium nitroprusside (1 wt. %) were added into the above solution. After two hours reaction, the absorption spectrum of the solution in the wavelength range of 600-700 nm was collected, and the peak appears at 655 nm. The concentration-absorbance curve was calibrated using standard NH_4Cl solution with concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 μ g mL⁻¹ in 0.1 M Na_2SO_4 . The fitting curve ($y = 0.60097x - 0.0286$, $R^2 = 0.9994$) depicts a good linear relationship of absorbance value with NH_4^+ concentration by taking the mean value of three measurements.

The yield rate of product (r_{NH_3}) was calculated by the following equation:

$$r_{NH_3} = (c \times v) / (t \times m) \quad (1)$$

Where c is the measured ammonia mass concentration, v is the volume of the electrolyte, t is the duration of electrochemical reduction reaction, and m is the loading mass of the electrocatalysts.

The Faradaic efficiency (FE_{NH_3}) can be calculated as follow:

$$FE_{NH_3} = (n \times F \times c \times v) / (M \times Q) \quad (2)$$

Where F is the Faraday constant, M is relative molecular mass of product, n is the number of electrons transferred to form a product molecule and Q is the total charge passed through the working electrode during electrolysis.

Determination of N_2H_4

N_2H_4 was determined by Watt and Chrisp colorimetric method.² In brief, the color reagent was obtained by mixing concentrated HCl (30 mL), C_2H_5OH (300 mL) and $C_9H_{11}NO$ (5.99 g). And 5 mL electrolyte was taken from the cathodic chamber and added into 5 mL above as-prepared color reagent. After standing for 15 minutes, the absorption spectrum of the solution was collected in the wavelength range of 420-500 nm, and the peak appears at 455 nm. The calibration curve was measured using the absorbance of N_2H_4 solution with different concentrations. Calibration curve displays good linear relationship of absorbance with N_2H_4 concentrations ($y = 0.58138x + 0.01859$, $R^2 = 0.9998$) by taking the mean of three times independent calibration.

DFT calculation method

DFT calculations were performed by the Vienna Ab initio Simulation Package (VASP), using the planewave basis set with energy cutoff of 450 eV, the projector augmented wave (PAW) potentials, and the generalized gradient approximation proposed by Perdew, Burke and Ernzerhof (GGA-PBE) for the exchange-correlation functional. A slab model consisting of 2×2 super-cells was adopted with a vacuum region of 15 Å, including 98 carbon atoms and 72 Pd atoms. $2 \times 2 \times 1$ Monkhorst-Pack grid k-points are employed for geometric optimization, and the convergence threshold is set as 10^{-5} eV in energy and 0.02 eV/Å in force, respectively.

The free energy (G) for adsorptions were determined as follows:

$$G = E_{\text{DFT}} + E_{\text{ZPE}} - TS \quad (3)$$

where E_{DFT} is the total energy, E_{ZPE} is the zero-point energy, T is the temperature (T = 298.15 K) and S stands for the vibration entropy.



Fig. S1 Digital image of the precursor solution ($\text{PdCl}_2/\text{PAN}/\text{DMF}$).

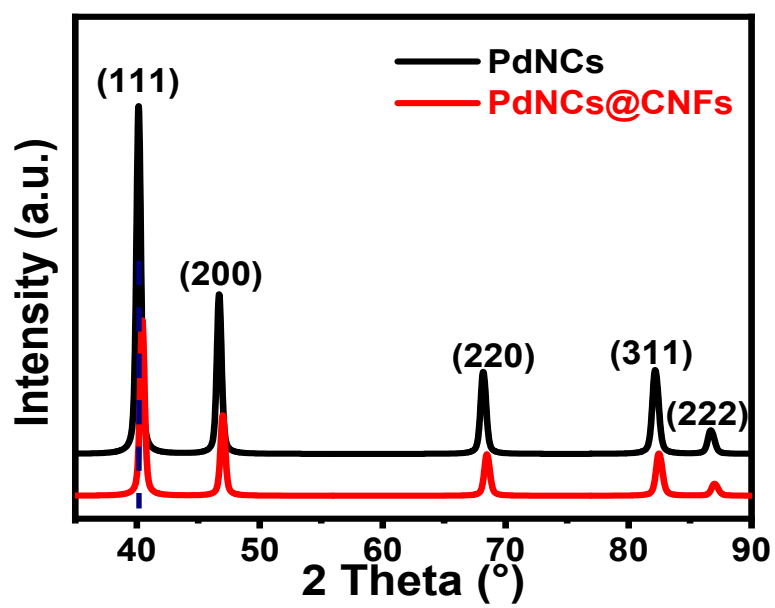


Fig. S2 Refinement XRD pattern of PdNCs and PdNCs@CNFs.

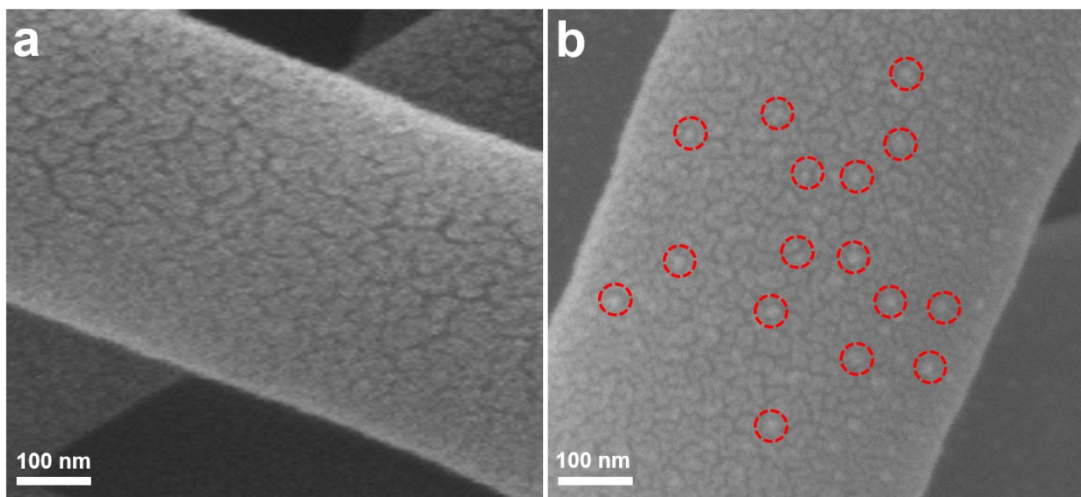


Fig. S3 SEM images of (a) CNFs and (b) PdNCs@CNFs.

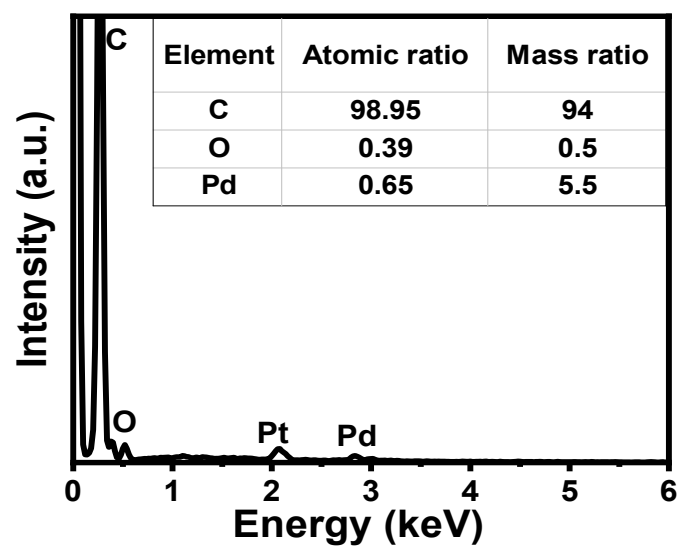


Fig. S4 EDX spectrum of PdNCs@CNFs.

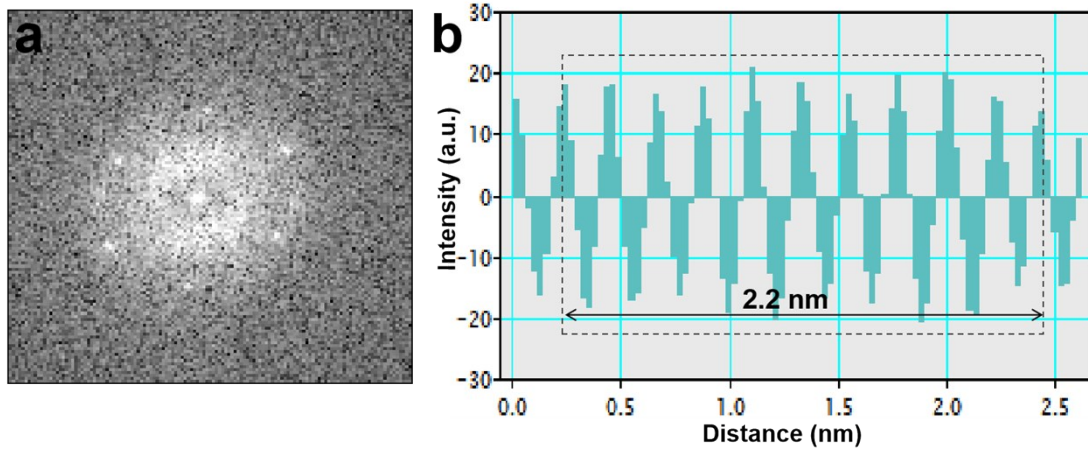


Fig. S5 (a) Fast Fourier transform (FFT) pattern. (b) Integrated pixel intensities of PdNCs in catalyst along with the Pd (111) spacing direction.

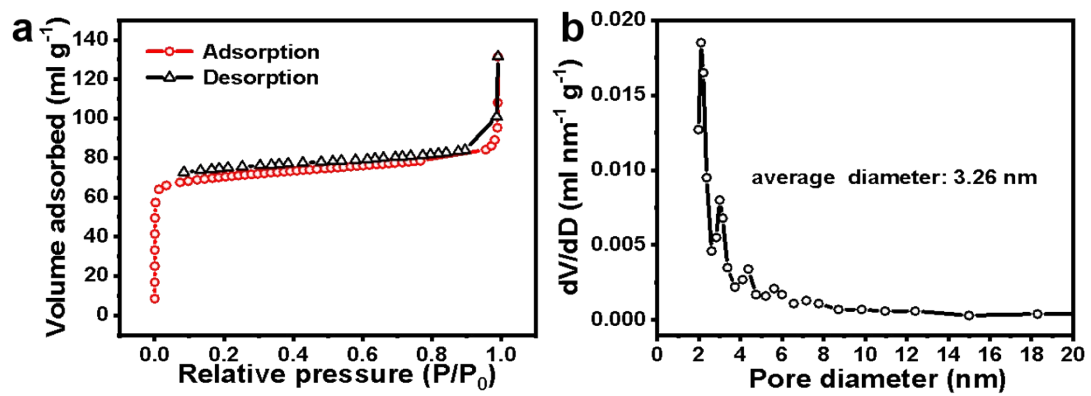


Fig. S6 (a) N_2 adsorption-desorption isotherms and (b) BJH differential pore volume and diameter distribution for PdNCs@CNFs.

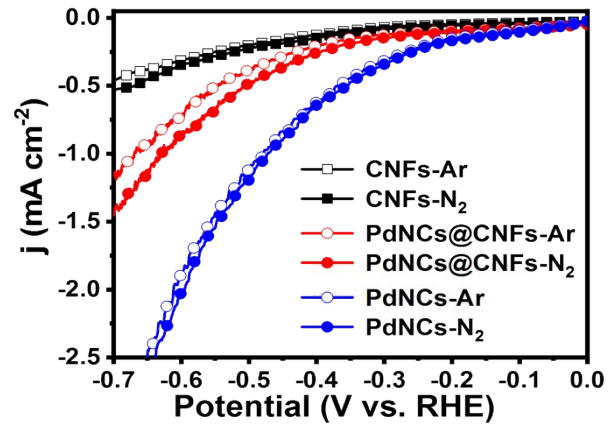


Fig. S7 LSV curves of different catalysts in N₂- and Ar- saturated electrolyte.

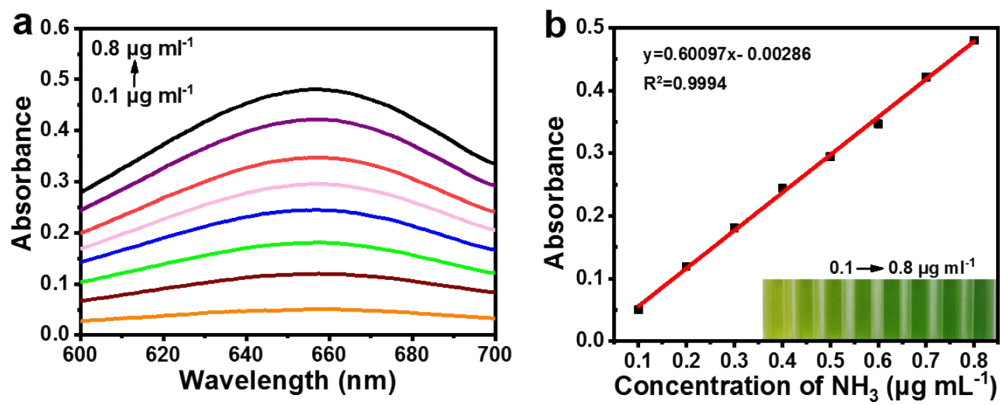


Fig. S8 (a) UV-Vis spectra of indophenol assays with NH_4^+ after incubated for 2 hours at room temperature. (b) Calibration curve used for estimation of concentration of NH_4Cl .

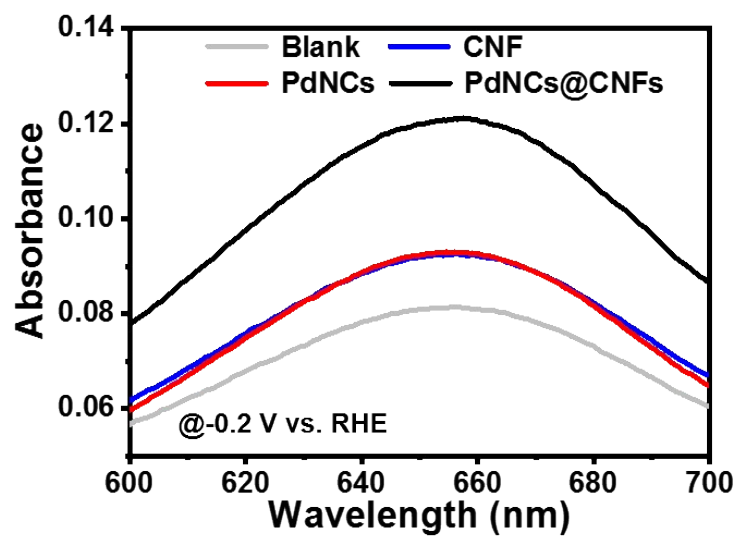


Fig. S9 UV-Vis absorption spectra of electrolytes after 2 hours electrolysis for the different samples.

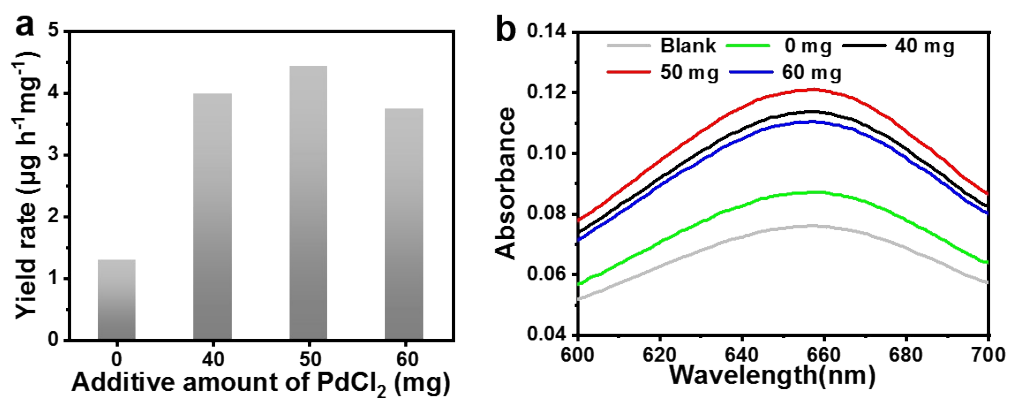


Fig. S10 (a) NH_3 yields of the catalysts prepared from different additive amounts of the PdCl_2 at -0.2 V vs. RHE. (b) UV-Vis absorption spectra of the corresponding solutions after NRR electrolysis.

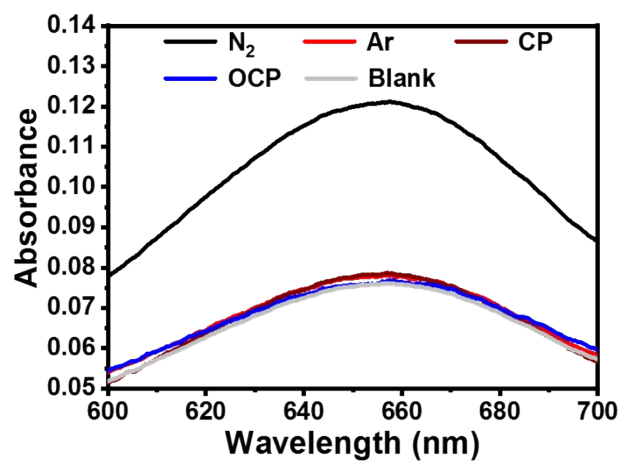


Fig. S11 UV-Vis absorption spectra of electrolytes after 2 hours electrolysis under different conditions.

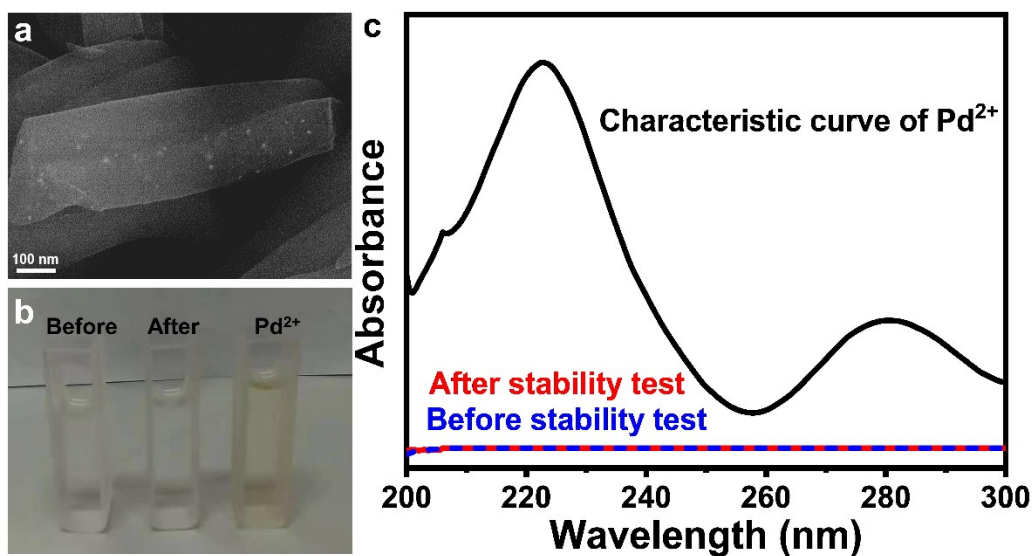


Fig. S12 (a) Electron back scattered SEM image of PdNCs@CNFs after stability test. (b) The digital images of the electrolytes before and after the stability test and standard solution of Pd²⁺. (c) The absorbance curves of the solutions in (b).

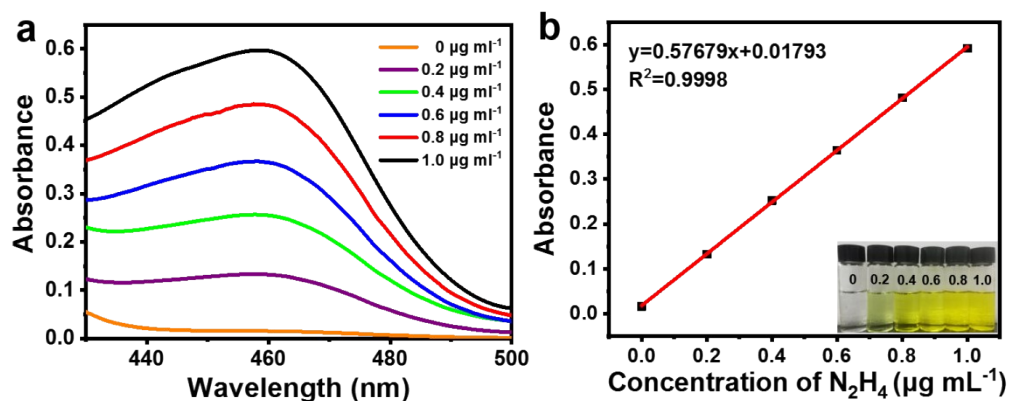


Fig. S13 (a) UV-Vis spectra of various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.

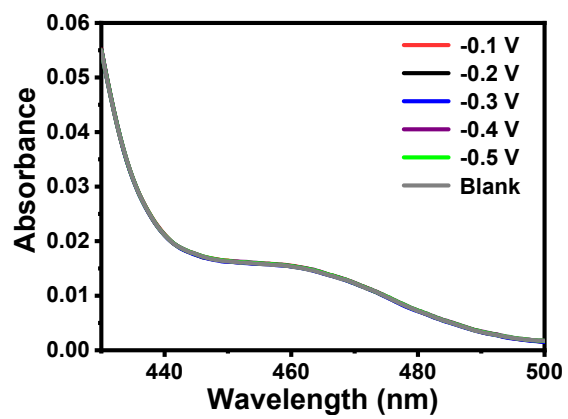


Fig. S14 UV-Vis spectra of the electrolytes stained with Watt and Chrisp indicator at various potentials for 2 hours.

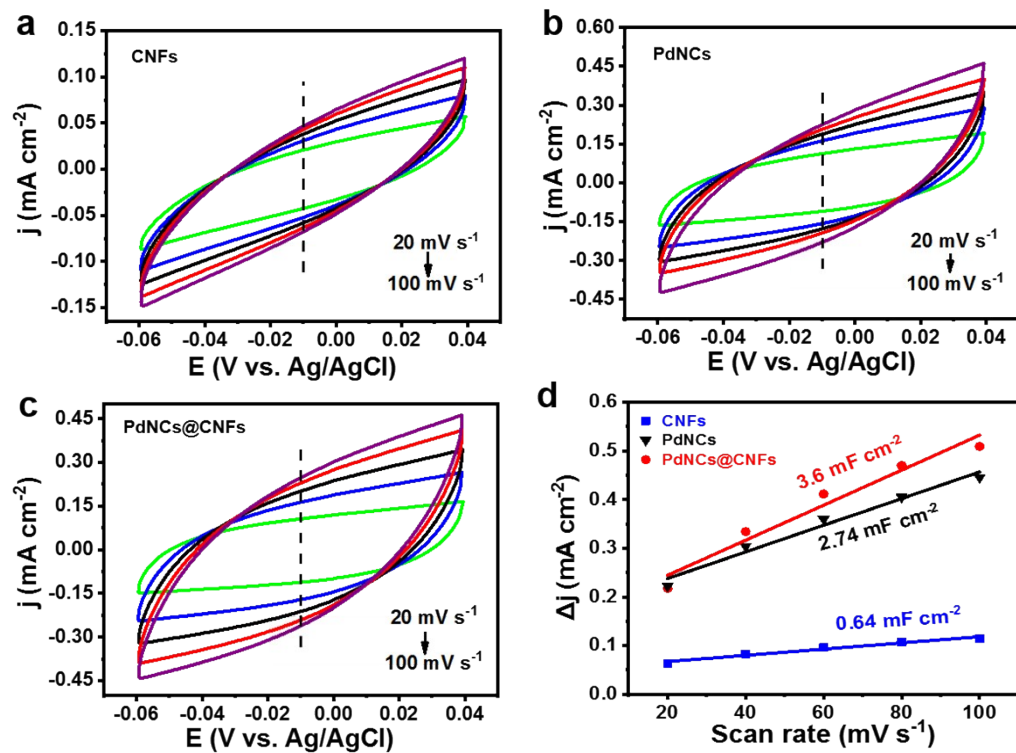


Fig. S15 Cyclic voltammetry curves of (a) CNFs, (b) PdNCs and (c) PdNCs@CNFs at different scan rates. (d) Charging current density differences plot against scan rates.

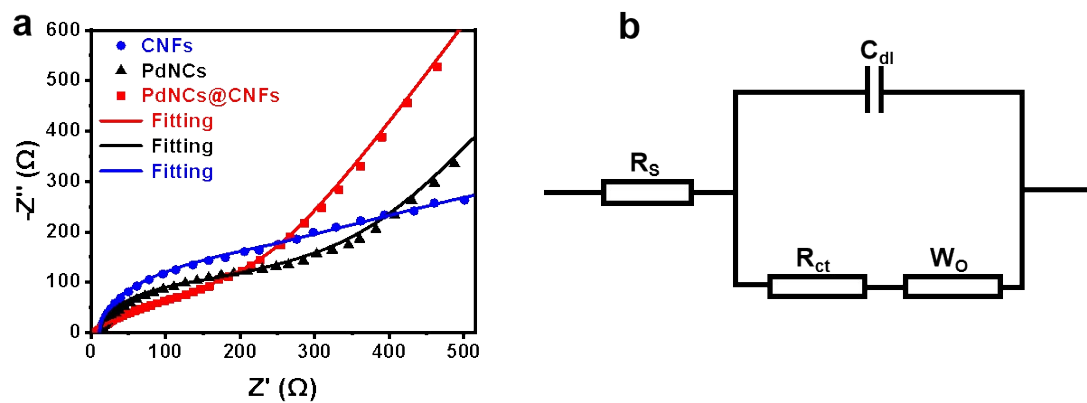


Fig. S16 (a) Electrochemical impedance spectroscopy of the samples at -0.2 V vs. RHE. (b) The equivalent circuit.

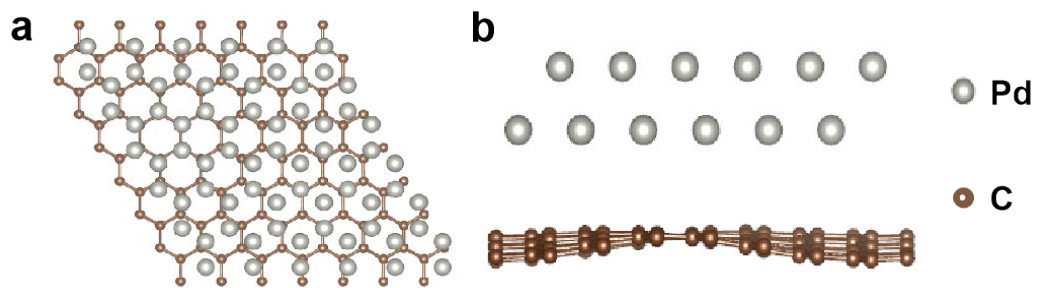


Fig. S17 Theoretical models used in DFT calculations. (a) Top and (b) side view.

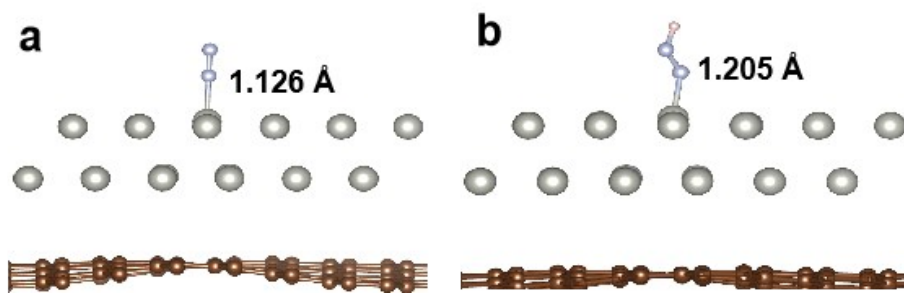


Fig. S18 Optimized model. (a) Nitrogen adsorption. (b) First protonation.

Table. S1 Comparison for the NRR electrocatalytic activity of PdNPs@CNFs with other reported catalysts.

Catalyst	Electrolytes	Yield rate	FE	Ref.
PdNCs@CNFs	0.1 M Na ₂ SO ₄	4.4 μg mg ⁻¹ h ⁻¹	14.4%	This work
Pd _{0.2} Cu _{0.8} /rGO	0.1 M KOH	2.8 μg mg ⁻¹ h ⁻¹	0.71%	3
α-Fe ₂ O ₃	0.1 M KOH	0.46 μg cm ⁻² h ⁻¹	6.04%	4
CN/C ₆₀₀	0.1 M HCl	2.9 μg mg ⁻¹ h ⁻¹	16.8%	5
AuNPs/CeO _x -RGO	0.1 M HCl	8.3 μg mg ⁻¹ h ⁻¹	10.1%	6
Pd/C	0.1 M PBS	4.5 μg mg ⁻¹ h ⁻¹	8.2%	7
NPC	0.1 M HCl	0.97 μg mg ⁻¹ h ⁻¹	4.2%	8
AuHNCS	0.5 M LiClO ₄	2.3 μg mg ⁻¹ h ⁻¹	30.2%	9
Vo-TiO ₂	0.1 M HCl	3.0 μg mg ⁻¹ h ⁻¹	6.5%	10
Mo ₂ S/CC	0.1 M Na ₂ SO ₄	4.9 μg cm ⁻² h ⁻¹	1.7%	11
CoxFe-MOF	0.1 M KOH	8.79 μg mg ⁻¹ h ⁻¹	25.6%	12
CoFe ₂ O ₄ /rGO	0.1 M Na ₂ SO ₄	2.57 μg mg ⁻¹ cm ⁻²	6.2%	13
NbO ₂	0.05 M H ₂ SO ₄	4 μg mg ⁻¹ h ⁻¹	32%	14
Bi (110) nanoplates	0.2 M Na ₂ SO ₄	5.453 μg mg ⁻¹ h ⁻¹	11.7%	15

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