Electronic Supplementary Information for

Interfacial engineering of hydrophobic octadecanethiol/Pd metallene toward electrocatalytic nitrogen reduction

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Experimental

Materials and chemicals

Sodium tetrachloropalladate (II) (Na_2PdCl_4), octadecanethiol ($CH_3(CH_2)_{17}SH$, C18), potassium hydroxide (KOH), N,N-dimethylformamide (DMF), ethylene glycol (EG), diethylenetriamine (DETA), sodium hydroxide (NaOH), *p*-dimethylaminobenzaldehyde (p-$C_9H_{11}NO$), sodium salicylate ($C_7H_5O_3Na$), sodium hypochlorite solution (NaClO), sodium sulfate (Na_2SO_4), concentrated hydrochloric acid, ethanol (C_2H_5OH), acetone (CH_3COCH_3), and hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 80%) were purchased from Aladdin. VC-X72 carbon was obtained from Suzhou yilongsheng Energy Technology Co. Ltd. Ammonium chloride (NH_4Cl, 99.99%) and sodium nitroferricyanide dihydrate ($Na_2[Fe(CN)_5NO] \cdot 2H_2O$, 99%) were provided by MACKLIN Inc. Nafion (5wt%) was obtained from Sigma-Aldrich.

Synthesis of the Pdene@C18

Pdene was first synthesized by solvothermal method.[1] Typically, 1 g of KOH, 6 mL of DMF, and 4 mL of EG were successively added to a 50 mL glass bottle for dissolution under sonication, followed by mixing with 1 mL of Na_2PdCl_4 in DMF (0.1 M) and 10 mL of DETA. The resulting solution was transferred to a 50 mL Teflon-lined autoclave, which was heated to 200 ^{o}C and reacted for 8 h. After cooling to room temperature, the product was washed and centrifuged with ethanol and acetone for several cycles. For surface modification, the 5 mg of Pdene powder was dispersed in 0.05 M octadecanethiol in ethanol under sonication for 10 min, and then the mixture solution was further stirred for 24 h. Finally, the product was washed with ethanol and centrifuged twice before drying. Under typical synthesis conditions, Pdene modified by octadecanethiol with different concentrations (0.01 and 0.1 M) was also prepared.

Characterizations

The microstructure of the catalyst was analyzed by scanning electron microscopy (SEM, Zeiss Gemini 500) and transmission electron microscopy (TEM, Hitachi HT 7700) and atomic force microscopy (AFM, MFP-3D Infinity). Moreover, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), selected area electron diffraction (SAED), high-resolution TEM (HRTEM) and element mapping analysis tests were also performed. The crystal structure and chemical state of the catalyst were analyzed by X-ray diffraction (XRD, PANalytical Empyrean) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI), respectively. The functional groups of the samples were analyzed by Fourier transform infrared spectrometer (FTIR) using Nicolet iN10 instrument. Contact Angle measurements were performed by Datphysics OCA20 instrument.

Electrochemical measurements

All electrochemical tests were conducted at room temperature by CHI 760E electrochemical workstation using a conventional three-electrode cell system, consisting of catalyst loaded carbon paper, Ag/AgCl (3 M KCl) electrode and carbon rod as working, reference and counter electrodes, respectively. Nafion 117 membrane was treated with 5% H_2O_2 and deionized water successively for 1 h at 80 °C. In order to reduce the consumption of precious metals, the catalyst was mixed with VC-X72 carbon powder before electrochemical test. Specifically, the sample (2 mg) was mixed with VC-X72 carbon powder (8 mg) in 10 mL cyclohexane, and continuous ultrasound for 2 h made Pdene@C18 deposit on C powder. Before the electrochemical test, N_2 was introduced into the catholyte until it was saturated, and N_2 was continuously injected into the electrolyte solution during tests. All potentials were converted to RHE scale according to the following formula: $E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + \varphi^{\theta}_{\mathrm{Ag/AgCl}} + 0.059 \times \mathrm{pH}$.

Product Analysis

The published indophenol blue method was used to determine ammonia in electrolyte.[2] Briefly, 0.256 g NaOH and 1.28 g $C_7H_5NaO_3$ were dissolved in deionized water (20 mL) as coloring solution, 0.3 g NaOH, NaClO (0.325 mL) and deionized water (9.675 mL) were mixed as oxidation solution, and 0.1 g $C_5FeN_6Na_2O \cdot 2H_2O$ was dissolved in deionized water (10 mL) as catalyst solution. For ammonia detection, 500 μL coloring solution, 50 μL oxidation solution and 50 μL catalyst solution were mixed with 4 mL electrolyte for 1 h, which was measured by ultraviolet–visible (UV–vis) spectrophotometer at 680 nm. The following formula was used to calculate the ammonia production rate and Faraday efficiency, where c_{NH3} (μg mL^{-1}) is the measured NH_3 concentration, V (mL) is electrolyte volume, t (h) is the electrolytic time, and m (mg) means the catalyst mass, F (96485 C mol^{-1}) is Faraday's constant, and Q is the total electric quantity.

$$\mathrm{r}_{\mathrm{NH3}} = (\mathrm{c}_{\mathrm{NH3}} \times \mathrm{V})/(\mathrm{t} \times \mathrm{m}) \qquad (1)$$

$$\mathrm{FE} = 3 \times \mathrm{F} \times (\mathrm{c}_{\mathrm{NH3}} \times \mathrm{V})/(17 \times \mathrm{Q}) \times 100\% \qquad (2)$$

The byproduct N_2H_4 in the electrolyte was determined by watt and Chrisp method.[3] In brief, 5.99 g p-$C_9H_{11}NO$ was mixed with hydrochloric acid (30 mL) and ethanol (300 mL) as chromogenic agent. Then, 5 mL electrolyte and 5 mL color developing agent were mixed and stirred for 15 min, the absorbance of the peak at 455 nm was measured by UV-vis spectroscopy. The absorbance-concentration curve was obtained by N_2H_4 standard solution with a certain concentration difference, and the content of by-product N_2H_4 in electrolyte was calculated by this curve.

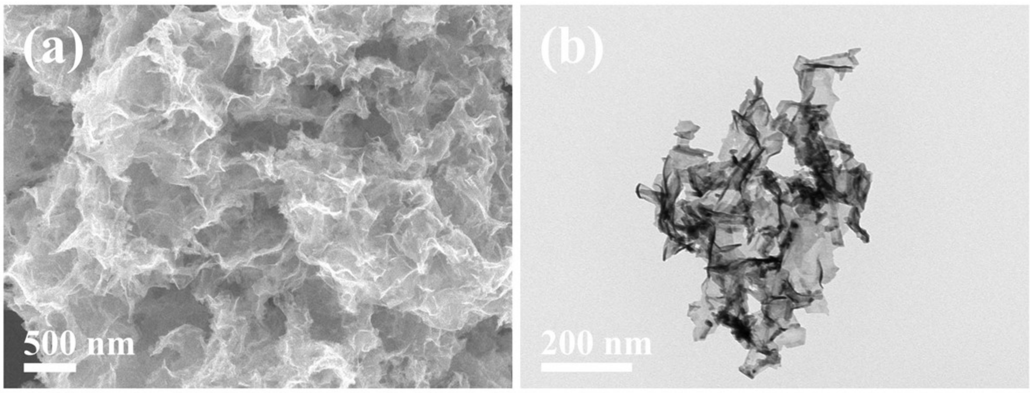

Fig. S1 (a) SEM and (b) TEM images of Pdene.

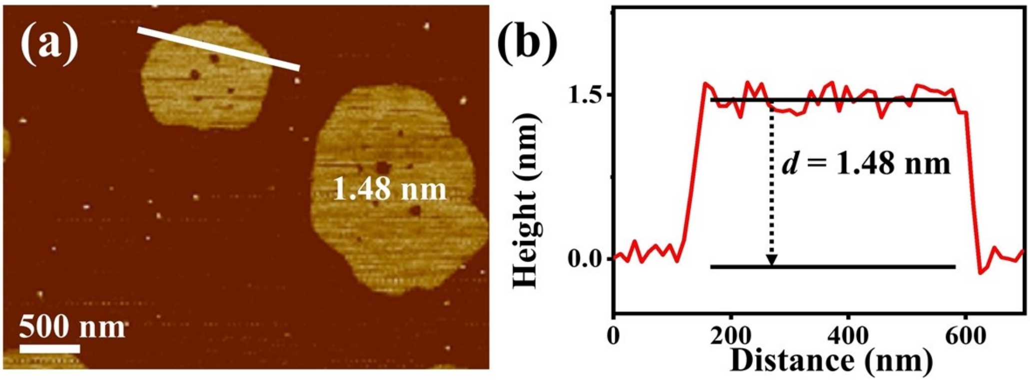

Fig. S2 (a) AFM image and (b) corresponding height profile of Pdene.

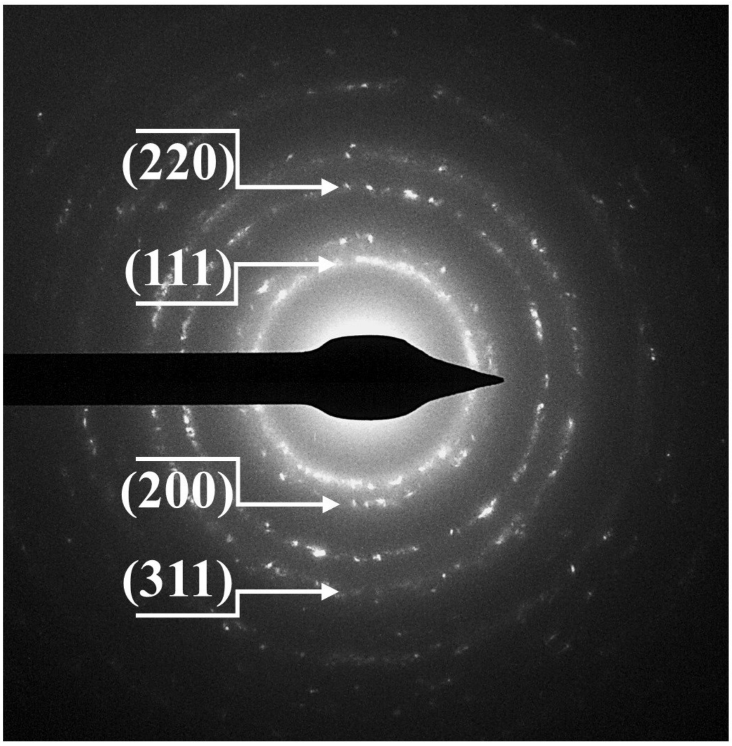

Fig. S3 SAED pattern of Pdene@C18.

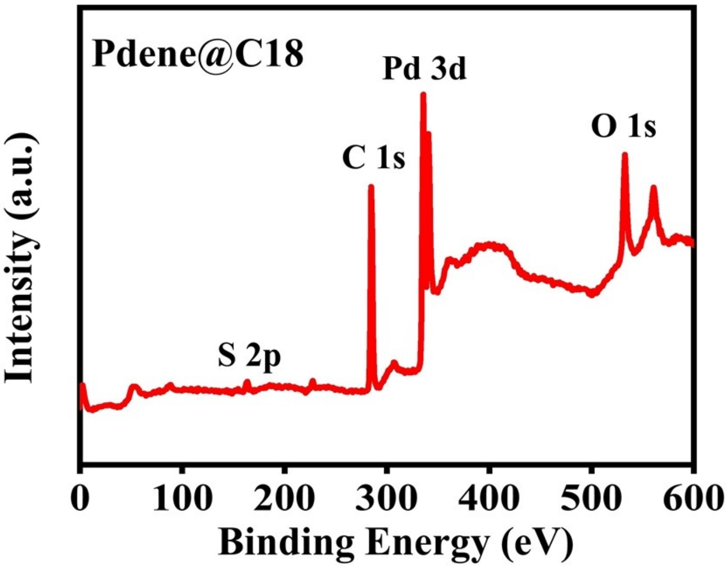

Fig. S4 XPS survey spectrum of Pdene@C18.

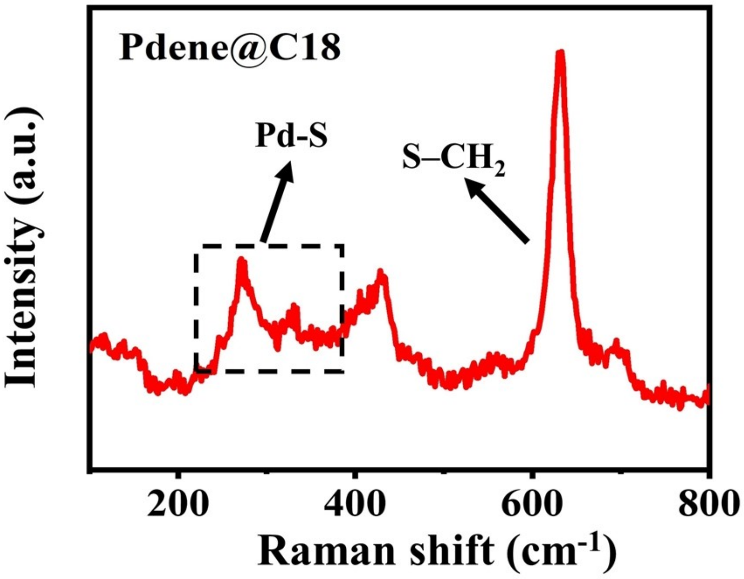

Fig. S5 Raman spectrum of Pdene@C18.

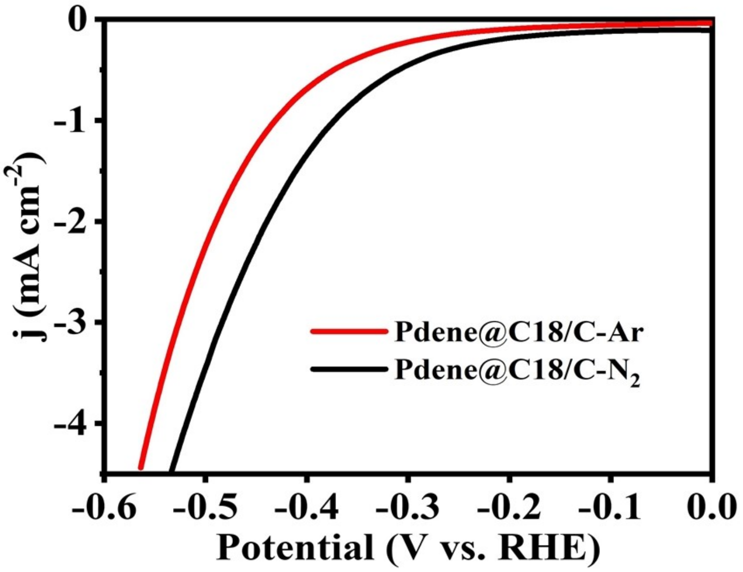

Fig. S6 LSV curves of Pdene@C18/C in Ar- and N_2-saturated 0.1 M Na_2SO_4 with a scan rate of 10 mV s^{-1}.

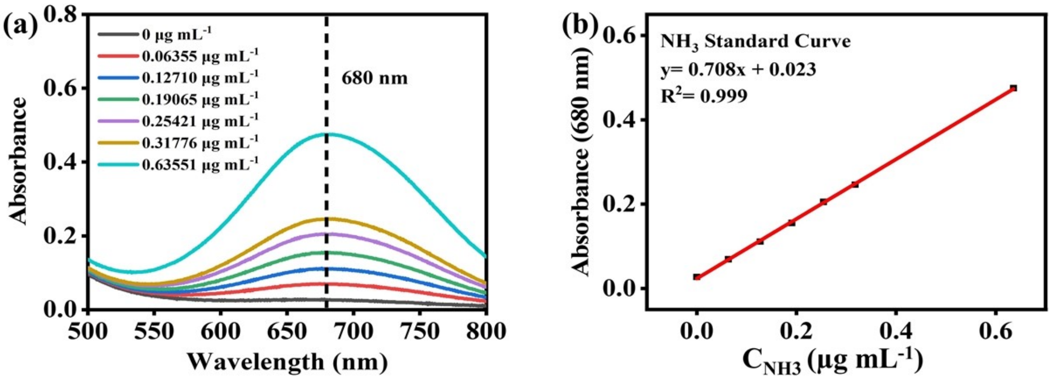

Fig. S7 (a) The UV-vis spectra of various NH_4^+ concentrations with the color reagent at room temperature for 1 h. (b) Calibration curve used for calculation of NH_3 concentration.

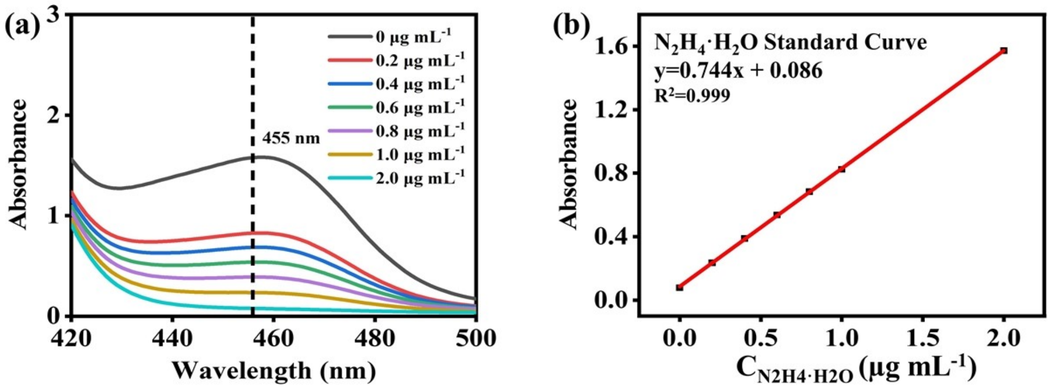

Fig. S8 (a) UV-vis spectra of $N_2H_4 \cdot H_2O$ with different concentrations incubated at room temperature for 15 min. (b) Calibration curve used for calculation of N_2H_4 concentrations.

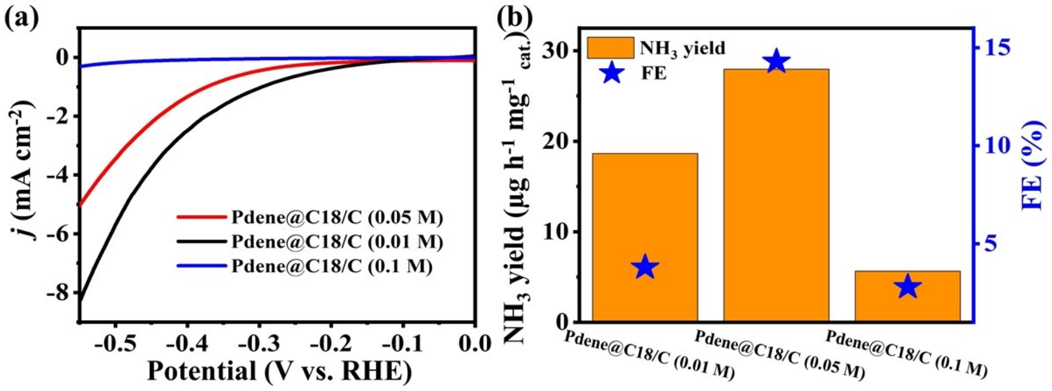

Fig. S9 (a) LSV curves of Pdene modified with different concentrations of octadecanethiol in N_2-saturated 0.1 M Na_2SO_4 with a scan rate of 10 mV s $^{-1}$. (b) Corresponding NH_3 yields and FEs of Pdene modified with different concentrations of octadecanethiol.

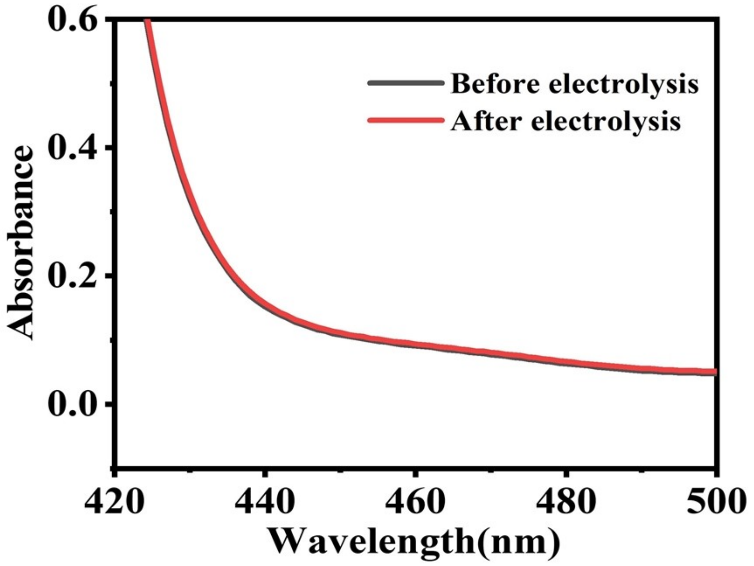

Fig. S10 UV-vis absorption spectra of the electrolytes stained with $C_9H_{11}NO$ indicator before and after NRR electrolysis.

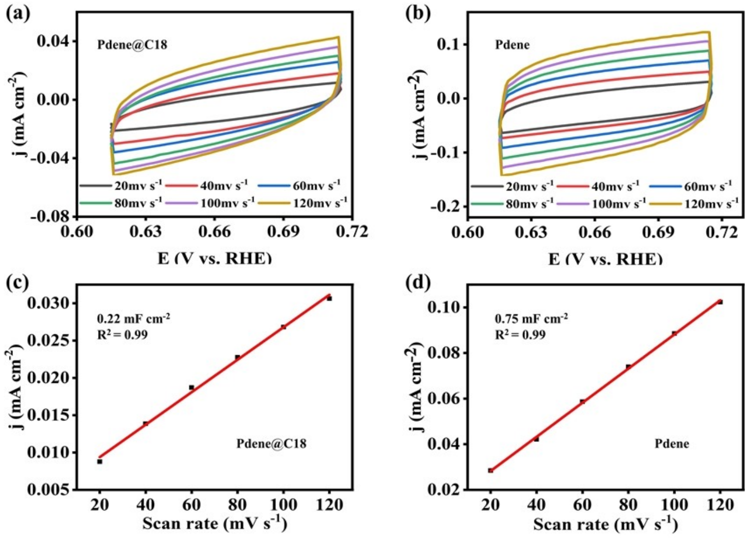

Fig. S11 Double layer capacitance measurements at various scan rate ranging from 20-120 mV s^{-1} (a) Pdene@C18 and (b) Pdene. The capacitive current densities at 0.665 V vs. RHE as a function of scan rates for (c) Pdene@C18 and (d) Pdene.

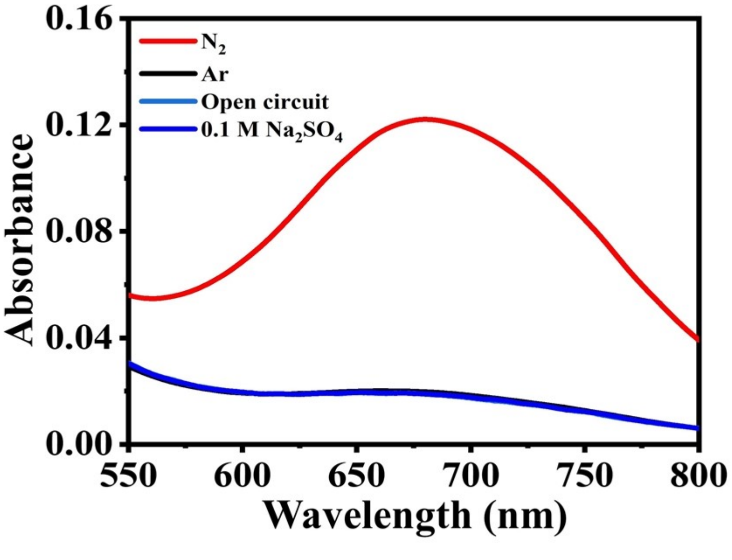

Fig. S12 UV-vis absorption spectra of electrolysis solutions for 2 h under different conditions.

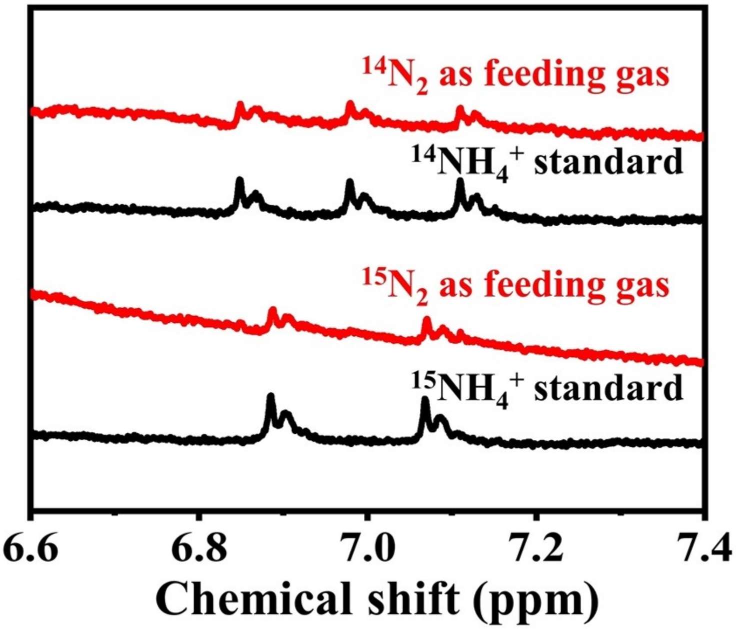

Fig. S13 ^{1}H-NMR spectra of both $^{15}NH_4^+$ and $^{14}NH_4^+$ produced from NRR process using $^{15}N_2$ and $^{14}N_2$ as the feeding gas, respectively.

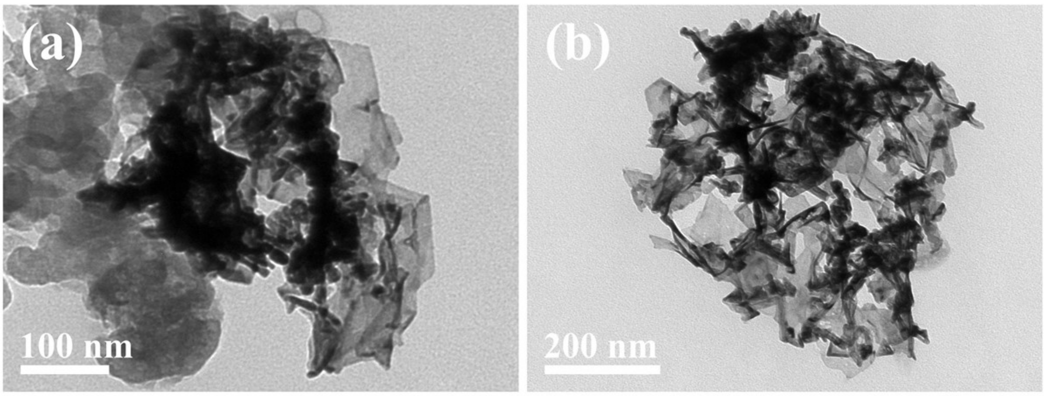

Fig. S14 TEM images of Pdene@C18/C after stability test.

Table S1. Comparison of NRR performance between Pdene@C18/C and other Pd-based electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH_3 yield	FE	Ref.
Pdene@C18/C	**0.1 M Na_2SO_4**	**27.97 μg h^{-1} mg^{-1} cat.**	**14.29%**	**This work**
PdNCs@CNFs	0.1 M Na_2SO_4	4.4 μg h^{-1} mg^{-1} cat.	14.4%	[4]
mPd-PdO/NF	0.1 M Na_2SO_4	24.8 μg h^{-1} mg^{-1} cat.	16.64%	[5]
mAu_3Pd/NF	0.1 M Na_2SO_4	24.02 μg h^{-1} mg^{-1} cat.	18.16%	[6]
PdCuIr-LS	0.1 M Na_2SO_4	13.43 μg h^{-1} mg^{-1} cat.	5.29%	[7]
Pd-TA	0.1 M Na_2SO_4	24.12 μg h^{-1} mg^{-1} cat.	9.49%	[8]
Pd/C	0.1 M Na_2SO_4	4.4 μg h^{-1} mg^{-1} cat.	8.2%	[9]
nPd/NF	0.1 M Na_2SO_4	18.27 μg h^{-1} mg^{-1} cat.	10.36%	[10]
$PdH_{0.43}$ NRs	0.1 M Na_2SO_4	17.53 μg h^{-1} mg^{-1} cat.	18.56%	[11]
AuPd NSs	0.1M Na_2SO_4	16.9 μg h^{-1} mg^{-1} cat.	15.9%	[12]
AuPdP NWs	0.1M Na_2SO_4	18.78 μg h^{-1} mg^{-1} cat.	15.44%	[13]

References

1. Q. Yang, L. Shi, B. Yu, J. Xu, C. Wei, Y. Wang and H. Chen, *J. Mater. Chem. A*, 2019, **7**, 18846-18851.
2. D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, **12**, 836-841.
3. G.W. Watt, J.D. Chrisp, *Anal. Chem., 2002,**24,*** 2006-2008.
4. Y. Wang, Z. Ma, K. Liu, X. Yang, J. Wang and X. Wang, *Dalton Trans*, 2021, **50**, 6975-6981.
5. M. Zhang, L. Cui, Q. Mao, Z. Wang, H. Yu, Y. Xu, X. Li, L. Wang and H. Wang, *Nanotechnology*, 2022, **33**. 385703.
6. H. Yu, Z. Wang, S. Yin, C. Li, Y. Xu, X. Li, L. Wang and H. Wang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 436-442.
7. R. D. Kumar, Z. Wang, C. Li, A. V. Narendra Kumar, H. Xue, Y. Xu, X. Li, L. Wang and H. Wang, *J. Mater. Chem. A*, 2019, **7**, 3190-3196.
8. G. Deng, T. Wang, A. A. Alshehri, K. A. Alzahrani, Y. Wang, H. Ye, Y. Luo and X. Sun, *J. Mater. Chem. A*, 2019, **7**, 21674-21677.
9. J. Wang, L. Yu, L. Hu, G. Chen, H. Xin and X. Feng, *Nat. Commun.*, 2018, **9**, 1795.
10. Z. Wang, Z. Dai, H. Yu, H. Zhang, W. Tian, Y. Xu, X. Li, L. Wang and H. Wang, *ACS Sustainable Chem. Eng.*, 2020, **8**, 11827-11833.
11. Z. Wang, Z. Dai, S. Wang, H. Zhang, W. Tian, Y. Xu, X. Li, L. Wang and H. Wang, *Chem. Eng. J.*, 2021, **416**, 129105.
12. S. Yin, S. Liu, H. Zhang, S. Jiao, Y. Xu, Z. Wang, X. Li, L. Wang and H. Wang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 20233-20239.
13. H. Wang, D. Yang, S. Liu, S. Yin, Y. Xu, X. Li, Z. Wang and L. Wang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 15772-15777.