Supporting Information

Rapid-heating-assisted metal-support interaction formation: Pd nanoparticles on boron nitride nanotube electrocatalyst towards high N₂-to-ammonia yield

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Fig. S1 Structural optimization for the DFT simulation of (a). Pd on plane and (b). Pd on defect of BN for Fig. 2a.

Energy calculations were performed to find the most stable state for the *z*-axis distance between the Pd atoms and BNNT supports. In case of Pd/C-BNNT (Fig. S8a), when the distance is 2.5 Å between Pd and C-BNNT layer is mostly stable showing the highest energy. In case of Pd/D-BNNT (Fig. S8b), when the distance is 3.0 Å between Pd and C-BNNT layer is mostly stable.



Fig. S2 Optimized electronic state of Pd for the calculation of eNRR and HER pathways.



Fig. S3 Adsorption structures of reaction intermediates on Pd (111) surface.



Fig. S4 (a) Temperature profile during RRJH and (b) thermogravimetric analyzer (TGA) profile under nitrogen gas flow.

Defective BNNT (D-BNNT) for improving NRR performance was synthesized using the plasma jet process. Rich nitrogen vacancies are generated on the surface of BNNT during its growth due to the decomposition of -BNH composites from hexagonal boron nitride (hBN) by plasma, which combine to form large segments on the B droplets.¹⁻³ Given the insulating nature of BNNT, characterized by a high bandgap of approximately 6 eV,⁴ we employed the RRJH method to synthesize Pd nanoparticles (NPs) on BNNT.⁵ Initially, PdCl₂ as the catalyst precursor was drop-casted onto the BNNT/CP substrate and fully dried in a vacuum oven. Subsequently, a high current of 2.8 A was applied for 0.5 seconds to rapidly increase the temperature up to 1,030 K (see Fig. 2a and S4). The subsequent color change of the BNNT layer from dark orange to dark gray indirectly indicates the reduction of PdCl₂ to Pd metal (Fig. S5).



Fig. S5 The photographs of (a) PdCl₂/EtOH solution, (b) PdCl₂/BNNT/CP (before RRJH), and (c) Pd/BNNT/CP after RRJH.



Fig. S6 (a) Electron energy loss spectroscopy (EELS) spectra from STEM of Pd/BNNT layer and (b) SEM EDS spectrum of Fig. 2c.

The chemical composition of BNNT layer where Pd NPs were formed was determined by electron energy loss spectroscopy (EELS). The distinct peaks of characteristic K-edge absorptions were observed corresponding to B- and N-atoms around 185-220 eV and 395-420 eV, respectively. The sharp peak followed by a wider band corresponding to 1s π^* and 1s σ^* transitions, respectively, is the characteristics of sp² hybridization, indicating the hexagonal arrangements of BNNT. Additionally, B, N and Pd atoms were obviously detected by EDS elemental compositions in Fig. 2d.





Fig. S8 X-ray spectroscopic study of Pd/D-BNNT electrocatalyst. (a) XRD patterns and (b) XPS survey scan spectra of D-BNNT and Pd/D-BNNT.



Fig. S9 Selected area electron diffraction (SAED) pattern of Pd/D-BNNT electrocatalyst. Inset shows a bright image of corresponding area of SAED pattern. Yellow and red dashed lines indicate diffraction pattern of BNNT and Pd, respectively.



Fig. S10 XPS high resolution of (a) N1s and (b) O1s of D- and C-BNNTs and (c) defect concentration of C- and D-BNNT layer from Fig. 2f.



990 993 996 999 1002 Energy Loss (eV) Fig. S11 REELS spectra of (top) C- and D-BNNT and (bottom) Pd loaded C- and D-BNNT layer prepared *via* RRJS method.



Fig. S12 (a) SEM image of Pd/C-BNNT and (b) corresponding size distribution of Pd NPs.



Fig. S13 Experimental protocol for elimination of false-positive eNRR. (a) Experimental protocol. (b) Schematic illustration of N_2 gas purification process.



Fig. S14 Purity confirmation of N₂ gas fed into the electrolysis system. The protocol includes (A) N₂ bubbling (2 hours, 10 ml min⁻¹), followed by (B) Ar gas bubbling (2 hours), then (C) cyclic voltammetry measurement at a potential window of $0.2 \sim -0.3$ V, and (D) investigate the NH₃ concentration based on the indophenol protocol.



Fig. S15 eNRR activity of Pd/BNNT catalysts under 0.25 M H_2SO_4 electrolyte. (a) Linear sweep voltammetry (LSV) trajectories and (b) corresponding Tafel plot of respective electrocatalyst at scan rate of 2 mV s⁻¹



Fig. S16 Chronoamperometry (CA) profiles of Pd/D-BNNT catalyst at various potential range.



Fig. S17 Quantification of NH_3 by salicylic acid-assisted indophenol blue method. (a-c) Indophenol blue test results of standard solution. (a) Photograph of color evolution of standard solution. (b) UV-vis spectra and (c) calibration curve plotted by absorbance values at 655 nm against the NH_3 concentration.



Fig. S18 Quantification of the resulting electrolysis electrolyte at various potentials. (a) UV-vis spectra with indophenol blue indication and (b) plot of concentration with calibration curve. The sample at -0.10 V was diluted twice to reduce the concentration. Observed NH₃ concentrations in -0.10 V with three repeated measurements were 177.69, 176.67, and 179.92 μ M, respectively.



Fig. S19 ¹H NMR results for ¹⁴NH₃. (a) NMR spectra of standard solution and (b) electrolyte obtained from electrolysis at different potential held. (c) Plot of calibration and resulting concentration of ¹⁴NH₃ product.



Fig. S20 H_2 gas evolution detection through *in-situ* DEMS measurement. (a) Time- and voltagedependent H_2 gas evolution results of Pd/D-BNNT. (b) Accumulation plot of H_2 at various electrolysis voltage held. (c) Plot of Faradaic efficiency of HER and eNRR at various electrolysis potential. The electrolyte used in DEMS measurement was additionally investigated with colorimetric assay to determine the NH₃ efficiency in (c).



Fig. S21 Partial current density of Pd/D-BNNT under various eNRR electrolysis.



Fig. S22 Optimization of Pd/D-BNNT as a function of BNNT thickness with fixed loading amount of Pd NPs. Thickness of BNNT was controlled by adjusting the amount of supernatant poured onto the carbon paper, ranging from 10.0 to 100 mL. (a-c) TEM image of various thickness of BNNT layer with fixed amount of Pd NPs. (d) LSV profile. eNRR performance of Pd/D-BNNT electrocatalyst as a function of thickness of BNNT layer. (e) UV-vis spectra and (f) corresponding Faradaic efficiency and yield of NH₃ after electrolysis at -0.1 V for two hours under N₂ bubbling.



Fig. S23 Optimization of Pd/D-BNNT as a function of loading amount of Pd NPs. (a) and (b) Top-view of Pd/D-BNNT with different loading level of Pd NPs. (a) 0.5 Pd and (b) 1.0 Pd. (c) LSV profile and (d) corresponding Faradaic efficiency and yield of NH₃ after electrolysis at - 0.1 V for two hours under N₂ bubbling.



Fig. S24 eNRR measurement results with Pd/C-BNNT electrocatalyst at various electrolysis potential range. (a) Plot of current density response, (b) UV-vis results of electrolyte obtained from electrolyte used in (a) and (c) digital photograph of indophenol blue colorimetric test at various electrolysis potential held.



Fig. S25 Electrocatalytic performance of defective BNNT. (a) H_2 gas evolution profile of BNNT under LSV measurement. (b) Faradaic efficiency and yield of NH₃ of BNNT/CP sample at various electrolysis potential.



Fig. S26 eNRR performance of Pd/D-BNNT under 0.1 M PBS neutral solution. (a) LSV profile comparison under 0.25 M H_2SO_4 and 0.1 M PBS as electrolyte. (b) CA profile under 0.1 M PBS electrolyte with saturated N_2 gas.



Fig. S27 Tafel plot of Pd/D-BNNT electrocatalyst under 0.1 M PBS solution at scan rate of 2 mV s⁻¹



Fig. S28 Indophenol blue test of NH_3 product in 0.1 M PBS solution. (a) nitrate contamination investigation in 0.1 M PBS solution. (b) Plot of NH_4Cl standard solution. (c) Faradaic efficiency and yield of NH_3 and (d) partial current density of Pd/D-BNNT electrocatalyst under 0.1 M PBS at various electrolysis potential. All experiments are repeated for three times and new electrode was used for each trial.



Fig. S29 Watt and Chrisp test results for possible hydrazine byproduct detection.



Fig. S30 Griess test results for possible contamination of (b and c) nitrite (NO_2^{-}) and (d and e) nitrate (NO_3^{-}) in electrolyte used in this work. NO_3^{-} concentration was measured using the modified Griess reagent where the VCl₃ as a reducing agent for NO_3^{-} to NO_2^{-} .



Fig. S31 Quantification of ¹⁵NH₃ product from ¹⁵N₂ electrolysis test. (a) and (b) Plot of calibration using ¹⁵NH₄Cl as standard solution. (c) CA profile of Pd/D-BNNT under ¹⁵N₂ bubbling. (d) and (e) Plot of quantification of ¹⁵NH₃ using indophenol blue method.



Fig. S32 ¹H NMR spectra of ¹⁵NH₄Cl solution and electrolyte extracted from ¹⁵N₂ experiments. (a) ¹H NMR spectra of standard solution of ¹⁵NH₄Cl and (b) electrolyte obtained from ¹⁵N₂ experiments. (c) Plot of calibration and resulting concentration of ¹⁵N₂ experiments. Raw NMR plot can be found in Fig. S40–S42.



Fig. S33 ADT test results of Pd/CP and PD/D-BNNT electrocatalyst. (a) LSV curve comparison of Pd/CP (up) and PD/D-BNNT (down) electrocatalyst before and after ADT test. (b) CA profile of Pd/D-BNNT before (solid line) and after (dashed line) ADT test. (c) UV-vis absorption spectrum of electrolyte obtained from the two hours CA using Pd/D-BNNT after ADT test.



Fig. S34 TEM image of Pd/D-BNNT electrocatalyst. (a) Before and (b) after ADT. Scale bars for both images are 50 nm.



Fig. S35 Calibration of Ag/AgCl reference electrode. (a) 0.25 M H_2SO_4 and (b) 0.1 M PBS solution.

Free energy (eV)	Pd	Pd on plane	Pd on defect
H*	-0.738	-0.727	-0.711
2H*	-1.076	-1.066	-1.065
 H ₂ *	-0.162	-0.23	-0.537

 Table S1 Gibbs free energy for HER process (Heyrovsky step)

Electrocatalysts	Substrate	FE	YR (× 10 ⁻¹⁰ mol cm ⁻² s ⁻¹)	Electrolyt e	Potential	ref.
Pd@D_BNNT	Carbon paper	58.90	4.58	0.25 M H ₂ SO ₄	-0.10 V	This
I d@D-DI4141		68.00	8.69	0.1 M PBS	-0.10 V	work
Pd/C		8.20	0.221	0.1 M PBS	0.10 V	6
Pd nanothorn	Ni foam	20.00	0.889	0.1 M Na ₂ SO ₄	-0.15 V	7
Pd cubes	Carbon paper	36.60	3.96	0.1 M Li ₂ SO ₄	0.00 V	8
Pd hydride (PdH _{0.43})	Glassy carbon	43.60	0.965	0.1 M PBS	-0.15 V	9
PdCu/C	Carbon paper	24.80	5.64	0.05 M H ₂ SO ₄	-0.45 V	10
ם וחו		5.79	0.838	0.1 M HCl	0.05 V	11
Pupp nanosponge		-	1.23	0.1 M HCl	-0.05 V	
PdO/Pd/CNT		11.50	0.27	0.1 M NaOH	-0.05 V	12
Tannic acid- modified Pd NPs		9.49	0.787	0.1 M Na ₂ SO ₄	-0.45 V	13
PdAg		1.70	1.57	1 M KOH	-0.20 V	14
Pd ₃ Bi	Glassy carbon	21.50	2.311	0.05 M H ₂ SO ₄	–0.20 V	15
PdCu/TiO _{2-x}		49.10	4.736	0.1 M HCl	-0.10 V	16
Co-SA/N-SCF	A/N-SCF SA on Pd etallene Carbon efective paper $-66-NH_2$ S_2/TiO_2 u/SnS_2	56.90	3.314	0.01 M HCl	-0.10 V	17
Fe SA on Pd metallene		37.80	3.657	0.5 M LiClO4	-0.20 V	18
Defective UiO-66-NH ₂		85.20	2.071	0.1 M Na2SO4	-0.40 V	19
ReS ₂ /TiO ₂		49.80	0.866	0.1 M Na2SO4	-0.20 V	20
Au/SnS ₂		49.30	3.386	0.1 M Na2SO4	-0.50 V	21

 Table S2 Performance comparison with previously reported eNRR electrocatalysts



Fig. S36 ¹H NMR spectra of NH₄Cl standard solution.



Fig. S37 ¹H NMR spectra of electrolyte after CA at -0.05 V.



Fig. S38 ¹H NMR spectra of electrolyte after CA at -0.10 V.



Fig. S39 ¹H NMR spectra of electrolyte after CA at -0.15 V.



Fig. S40 ¹H NMR spectra of ¹⁵NH₄Cl standard solution.



Fig. S41 ¹H NMR spectra of electrolyte after one hour CA at -0.1 V under ${}^{15}N_2$ gas environment.



Fig. S42 1 H NMR spectra of electrolyte after two hours CA at -0.1 V under $^{15}N_{2}$ gas environment.

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