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Electronic Supplementary Information

Construction of PdO-Pd interface assisted by laser irradiation for

enhanced electrocatalytic N₂ reduction reaction

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Preparation of working electrodes

1.27 mg each catalyst was dispersed into a mixture, which contained 1 mL absolute ethyl alcohol and 40 μ L of Nafion solution (0.05 wt%), with ultrasonic for 30 min to form a homogeneous ink. After then, 100 μ L homogeneous ink was carefully dropped onto a carbon paper with area of 1 × 1 cm² and dried under ambient condition.

Pretreatment of Nafion 115 membranes

Prior to NRR tests, Nafion 115 membranes were heat-treated in 5% H_2O_2 , 0.5 M H_2SO_4 , and water for 1 h, respectively. After be rinsed in water thoroughly, the membranes were immersed in distilled water for future use.

Calculation of potential values

The reported potential values were referenced to that of a reversible hydrogen electrode, according to the following equation:¹

E (vs. RHE) = E (vs. Ag/AgCl) + 0.059pH + E⁰(vs. Ag/AgCl) Where, E⁰(vs. Ag/AgCl) = 0.1976 V at 25 °C, and pH=13 in 0.1 M NaOH in this paper.

Determination of ammonia

Concentration of produced NH₃ was spectrophotometrically determined by the indophenol blue method.² Specifically, 2 mL aliquot of the solution was removed from the electrochemical reaction container. Then, 2 mL of a 1 M NaOH solution contained 5 wt% sodium salicylate ($C_7H_5NaO_3$) and 5 wt% sodium citrate (Na₃C₆H₅O₇·2H₂O), 1 mL of 0.05 M sodium hypochlorite (NaClO) and 0.2 mL of 1 wt% sodium nitroferricyanide ($C_5FeN_6Na_2O$) solution were added subsequently. After standing 2 h at room temperature, the absorption spectrum of the result solution was measured using an UV-Vis spectrophotometer as shown in Fig. S5a. The formed indophenol blue was measured using the absorbance at a wavelength of 678 nm. Fig. S5b displayed the concentration-absorbance curves, which were calibrated using standard ammonia chloride solutions to quantify the produced NH₃, and the same concentrations of NaOH as used in all electrolysis experiments. Furthermore, the measurements with the background solutions (no NH₃) were also performed for all experiments, and the background peak was subtracted from the measured peaks of NRR experiments to calculate the NH₃ concentrations and the Faradaic efficiencies.

Determination of hydrazine

A color reagent developed upon the addition of 2 g para-(dimethylamino) benzaldehyde, 5 mL HCI (80% concentrated) and 50 mL ethanol was used as the basis for the spectrophotometric method to quantify the N_2H_4 concentration.³ Typically, 5 mL of the electrolyte solution was taken out and then mixed with 5mL of the color reagent, after 15 min standing at room temperature, the absorption spectra of the resulting solution were measured at 456 nm, and the yields of hydrazine were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent in the same way using hydrazine monohydrate solutions of known concentration as standards, as shown in Fig. S5c and S5d. It's worth mentioning that no apparent NH₃ was detected in the acid trap under our experimental conditions.

Faradaic efficiency

The Faradaic efficiency for NRR was defined as the quantity of electric charge used for synthesizing ammonia divided the total charge passed through the electrodes during the electrolysis. The total amount of NH₃ produced was measured using colorimetric methods.⁴ Assuming three electrons were needed to produce one NH₃ molecule, the Faradaic efficiency can be calculated as follows:

Faradaic efficiency =
$$\frac{3F \times c_{NH3} \times V}{Q}$$

The rate of ammonia formation was calculated using the following equation:

Yield rate =
$$\frac{17c_{NH3} \times V}{t \times m}$$

Where F is the Faraday constant, c_{NH3} is the measured NH₃ concentration, V is the volume of electrolyte, t is the reduction reaction time and m is the catalyst mass.



Fig. S1 Photograph of the electrochemical cell setup used for the NRR electrolysis.



Fig. S2 XRD patterns of pure PdO synthesized by chemical method⁵ before and after laser irradiation.



Fig. S3 HRTEM-EDX elemental mapping (Pd, C, and O elements) of PdO/CNTs.



Fig. S4 XPS spectra of C 1s for PdO/Pd/CNTs composites with 10 min irradiation.



Fig. S5 Raman spectra of CNTs, PdO/CNTs and PdO/Pd/CNTs.



Fig. S6 (a) The UV-Vis absorption spectra and (b) corresponding calibration curves for the colorimetric NH_3 quantification using the indophenol blue method in 0.1 M NaOH; (c) The UV-Vis absorption spectra and (d) corresponding calibration curves for the colorimetric N_2H_4 assay in 0.1 M NaOH.



Fig. S7 Chronoamperometry curves of commercial Pd/C, PdO/CNTs and PdO/Pd/CNTs catalysts on the carbon-paper support in N₂-saturated 0.1 M NaOH at -0.05 V (vs. RHE). The current density of every catalyst has not presented significant difference.



Fig. S8 UV-Vis absorption spectra of the electrolytes after electrolysis at -0.05 V vs. RHE for 3 h under different conditions. (a) No apparent NH_3 was detected for the control experiments with Ar-saturated electrolyte (CP-Cat.-Ar) or without catalyst catalyst (CP-N₂), indicating that NH_3 was produced by PdO/Pd/CNTs electroreduction of N₂, and (b) no N₂H₄ was detected with N₂-saturated electrolyte (CP-Cat.-N₂) throughout the system.



Fig. S9 Stability of 10 min irradiated PdO/Pd/CNTs for NH₃ synthesis at the potentials of -0.05 V versus RHE. There is no any distinct variation in the NH₃ yield and Faradaic efficiency during the recycling tests for 4 times, indicating this ternary composite catalyst excellent stability for NRR.

Catalysts	Irradiation time	Content of PdO	Content of Pd
PdO/CNTs	0 min	100 %	0 %
PdO/Pd/CNTs	10 min	82 %	18 %
PdO/Pd/CNTs	30 min	58 %	42 %
PdO/Pd/CNTs	60 min	50 %	50 %
PdO/Pd/CNTs	120 min	41 %	58 %

Table S1. The contents of PdO and Pd in PdO/Pd/CNTs with different irradiation time.

Catalysts	Electrolytes	NH ₃ yield rate	Faradaic efficience	cy Ref.
Pd/C	0.1 M PBS	$4.5 \ \mu g \ m g^{-1}{}_{Pd} \ h^{-1}$	8.2 %	6
PdRu BPNs	0.1 M HCl	$25.92 \ \mu g \ m g^{-1} \ h^{-1}$	1.53 %	7
Pd _{0.2} Cu _{0.8} /rGO	0.1 M KOH	$2.8 \ \mu g \ m g^{-1} \ h^{-1}$	0.71 %	8
Pd ₃ Cu ₁	1 M KOH	39.9 µg mg ⁻¹ h ⁻¹	1.22 %	9
PdRu NRAs	0.1 M HCl	34.2 $\mu g m g^{-1} h^{-1}$	2.4 %	10
PdRu TPs	0.1 M KOH	$37.23 \mu g m g^{-1} h^{-1}$	1.85 %	11
PdO/Pd/CNTs	0.1 M NaOH	18.2 $\mu g m g^{-1} h^{-1}$	11.5 %	This work

 Table S2. Comparison of the NRR performance for the PdO/Pd/CNTs and other Pd-based NRR
 electrocatalysts reported recently.

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