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Electronic Supplementary Information

Surfactant-free atomically ultrathin rhodium nanosheets nanoassemblies for efficient nitrogen electroreduction

Hui-Min Liu,‡[a] Shu-He Han,‡[a] Yue-Zhao,[a] Ying-Ying Zhu,[a] Xin-Long Tian,[b] Jing-Hui Zeng,[a] Jia-Xing Jiang,[a] Bao Yu Xia*[bc] and Yu Chen*[a]

[a] Key Laboratory of Macromolecular Science of Shaanxi Province, Key Laboratory of Applied Surface and Colloid Chemistry (MOE), Shaanxi Key Laboratory for Advanced Energy Devices, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, PR China. E-mail: ndchenyu@gmail.com

[b] Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, Wuhan National Laboratory for Optoelectronics, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China. E-mail: byxia@hust.edu.cn

[c] Shenzhen Institute of Huazhong University of Science and Technology, Shenzhen 518000, PR China

‡ These two authors made an equal contribution to this work.

Experimental Section

Determination of the NRR products:

Determination of NH_3[1]

Stock Reagents:

1) Phenol-alcohol reagent: 10 g phenol was dissolved in 100 mL 95% ethanol;

2) Sodium nitroprusside (nitroferricyanide): 1 g nitroferricyanide was dissolved in 200 mL Millipore water;

3) Alkaline complexing reagent: 50 g trisodium citrate and 2.5 g sodium hydroxide were dissolved in 250 mL Millipore water;

4) Sodium hypochlorite

5) Oxidizing solution: 200 mL alkaline solution (3) was added in 50 mL sodium hypochlorite (4)

Calibration curve of NH_3 in 0.1 KOH solution[1]

Stock Solution A-1000 ppm NH_4-N stock: After drying $(NH_4)_2SO_4$ at 100 ^oC for 24 h, 4.7168 g of $(NH_4)_2SO_4$ and two drops of chloroform were added in 1000 mL 0.1M KOH solution.

Stock Solution B-100 ppm NH_4-N stock: 10 mL of Stock solution A was added in a 100 mL volumetric flask, and constant volumed to 100 mL with 0.1M KOH.

Working standards. A series of working standards were prepared using 100 mL volumetric flasks. Analysis:

1. Adding 10 mL standard or sample to test tube.

2. To all tubes, adding 400 µL of phenol solution (1), 400 µL nitroferricyanide (2) and 1000 µL oxidizing reagent (5)

3. Mixing well. Let mixture store for at least 1 h (3 h is better) in darkness. Mix samples periodically while development is occurring.

4. using a spectrophotometer set to 630 nm and reading the absorbance of standards and samples

5. Using absorbance values of standards to draw a standard curve. Calculate concentrations of samples from standard curve (Fig. S3).

Volume of Stock B	Volume of standard	Concentration
1 mL NH_4-N/L	100 mL	1000 µg
750 µL NH_4-N/L	100 mL	750 µg
500 µL NH_4-N/L	100 mL	500 µg
200 µL NH_4-N/L	100 mL	200 µg
100 µL NH_4-N/L	100 mL	100 µg
50 µL NH_4-N/L	100 mL	50 µg
0 µL NH_4-N/L	100 mL	0 µg

Calibration curve of NH_3 in 0.001M H_2SO_4 solution[1]

Stock Solution A-1000 ppm NH_4-N stock: After drying $(NH_4)_2SO_4$ at 100 °C for 24 h. 4.7168 g $(NH_4)_2SO_4$and two drops of chloroform were added in 1000 mL of 0.001M H_2SO_4.

Stock Solution B-100 ppm NH_4-N stock: 10 mL of Stock solution A was added to a 100 mL volumetric flask, and constant volumed to 100 mLwith 1 mM H_2SO_4.

Working standards. 100 mL volummetric flask was used to prepare the following series of working standards.

Analysis:

1. Adding 10 mLstandard or sample to test tube.

2. To all tubes, adding 400 μL of phenol solution (1), 400 μL nitroferricyanide (2) and 1000 μL oxidizing reagent (5)

3. Mixing well. Let mixture store for at least 1 h (3 h is better) in darkness. Mix samples periodically while development is occurring.

4. Using a spectrophotometer set to 630 nm and reading the absorbance of standards and samples

5. Using absorbance values of standards to draw a standard curve. Calculate concentrations of samples from standard curve (Fig. S4).

Volume of Stock B	Vol. of standard	Concentration
1 mL NH_4-N/L	100 mL	1000 μg
750 μL NH_4-N/L	100 mL	750 μg
500 μL NH_4-N/L	100 mL	500 μg
200 μL NH_4-N/L	100 mL	200 μg
100 μL NH_4-N/L	100 mL	100 μg
50 μL NH_4-N/L	100 mL	50 μg
0 μL NH_4-N/L	100 mL	0 μg

Determination of N_2H_4[2, 3]

Calibration curves of N_2H_4 in 0.1 M KOH solution[2, 3]

The production of N_2H_4 in the experiment was estimated using the Watt and Chrisp method.[3] The mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Calibration curve was plotted as follow: First, preparing a series of reference solutions, by pipetting suitable volumes of the hydrazine hydrate-nitrogen 0.1 M KOH solution in colorimetric tubes; Second, making up to 5 mL with 0.1 M KOH solution; Third, adding 5 mL above prepared color reagent and stirring 15 min at room temperature. Fourth, an absorbance of resulting solution was measured at 460 nm, and the yields of N_2H_4 were calculated from the standard curve using 5 mL residual electrolyte and 5 mL color reagent (Fig. S5).

Calibration curves of N_2H_4 in 1 mM H_2SO_4 solution.[2, 3]

The production of N_2H_4 in the experiment was estimated using the Watt and Chrisp method.[3] The mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Calibration curve was plotted as follow: First, preparing a series of reference solutions, by pipetting suitable volumes of the hydrazine hydrate-nitrogen 0.001 M H_2SO_4 solution in colorimetric tubes; Second, making up to 5 mL with 0.001 M H_2SO_4 solution; Third, adding 5 mL above prepared color reagent and stirring 15 min at room temperature. Fourth, an absorbance of resulting solution was measured at 460 nm, and the yields of N_2H_4 were calculated from the standard curve using 5 mL residual electrolyte and 5 mL color reagent (Fig. S6).

The calculation method of activation energy (*Ea*) [4]

Activation energy was calculated by the Arrhenius equation as equation 1, the reduction rate grows exponentially with the temperature, where v was reaction rate, A was Arrhenius constants, Ea was activation energy, R was gas constant, and T was reaction temperature under the absolute scale. Then by converting the Equation 1 and we can obtain Equation 2, Ea could be calculated from fitting curve that revealed the linear relation of ln(rate) with temperature.

$$v = Ae\text{-}Ea/RT \qquad \text{(equation 1)}$$

$$lnv = lnA - Ea/RT \qquad \text{(equation 2)}$$

Fig. S1 Digital photograph of $RhCl_3$-$K_3Co(CN)_6$ cyanogel.

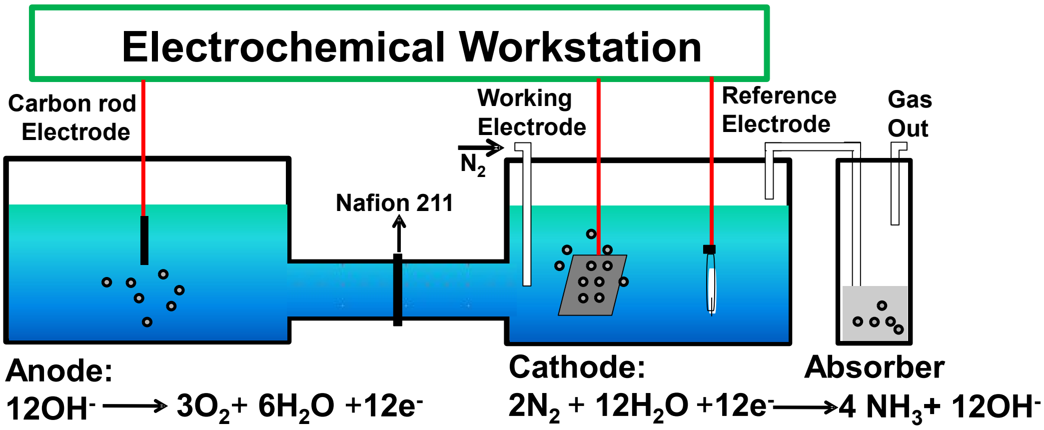

Fig. S2 Schematic illustration for the NRR.

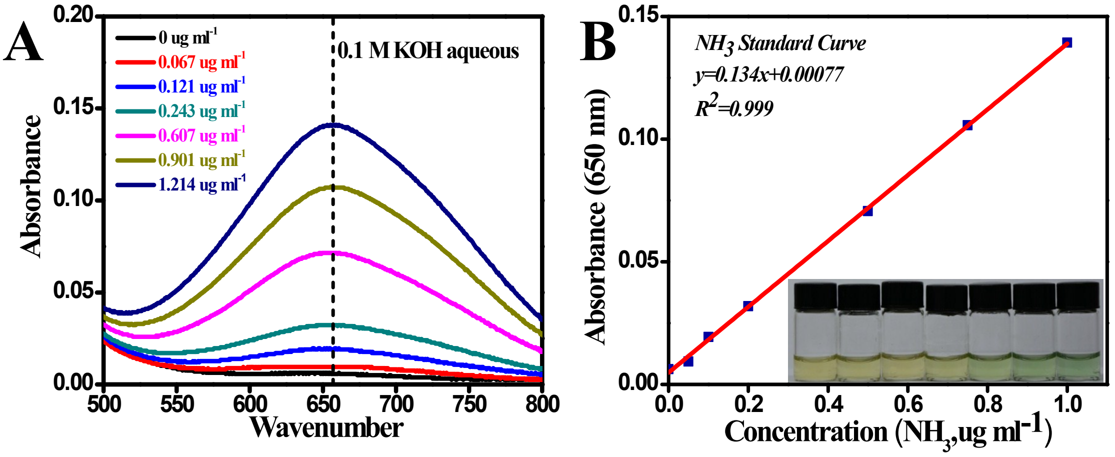

Figure S3 Absolute calibration of the phenate method using ammonium solutions of known concentration as standards. (A) UV-Vis curves of phenate assays after in darkness for 3 hours at room temperature, (B) calibration curve used for estimation of NH_3 by NH_4^+ ion concentration. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH_4^+ ion concentration (y =0.134x + 0.00077, R^2=0.999) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of phenate indicator with NH_4^+ ions.

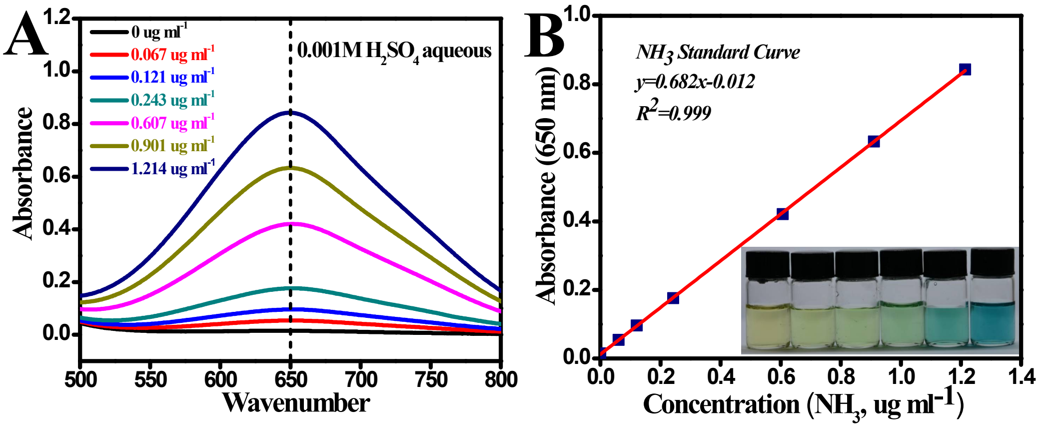

Fig. S4 Absolute calibration of the phenate method using ammonium solutions of known concentration as standards. (A) UV-Vis curves of phenate assays after in darkness for 3 hours at room temperature, (B) calibration curve used for estimation of NH_3 by NH_4^+ ion concentration. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH_4^+ ion concentration (y =0.682x−0.012, R^2=0.999) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of phenate indicator with NH_4^+ ions.

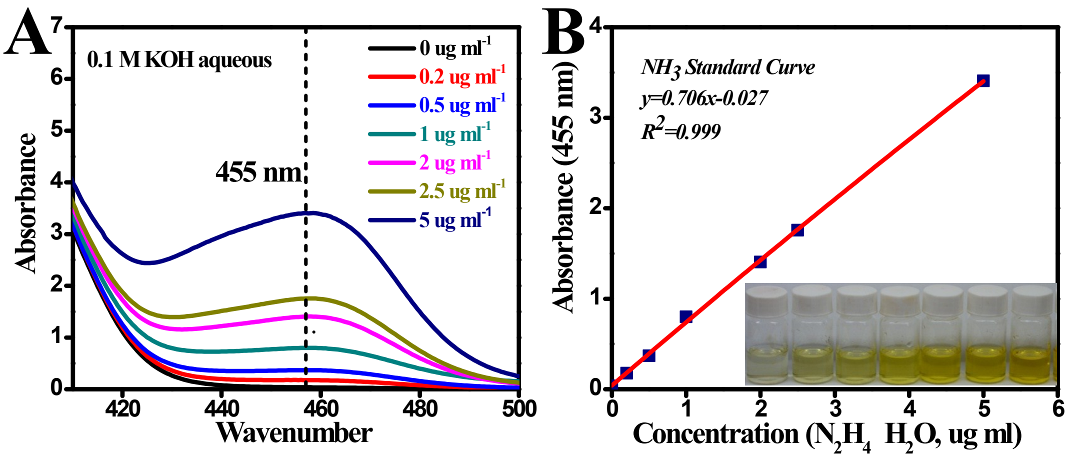

Fig. S5 Absolute calibration of the Watt and Chrisp (para-dimethylamino-benzaldehyde) method for estimating $N_2H_4 \cdot H_2O$ concentration, using $N_2H_4 \cdot H_2O$ solutions of known concentration as standards. (A) UV-Vis curves of various $N_2H_4 \cdot H_2O$ concentration after incubated for 10 min at room temperature, (B) calibration curve used for estimation of $N_2H_4 \cdot H_2O$ concentration. The absorbance at 455 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with $N_2H_4 \cdot H_2O$ concentration ($y = 0.706x - 0.027$, $R^2=0.998$) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of para-dimethylamino-benzaldehyde indicator with $N_2H_4 \cdot H_2O$.

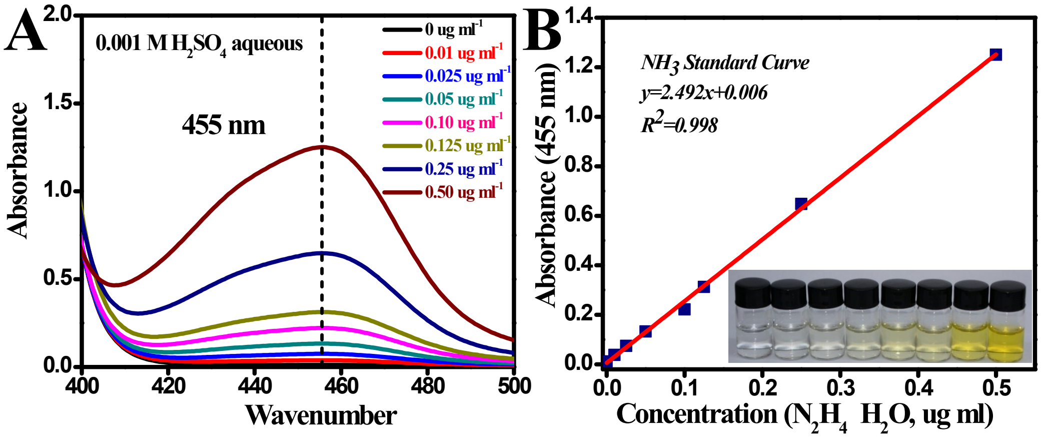

Fig. S6 Absolute calibration of the Watt and Chrisp (para-dimethylamino-benzaldehyde) method for estimating $N_2H_4 \cdot H_2O$ concentration, using $N_2H_4 \cdot H_2O$ solutions of known concentration as standards. (A) UV-Vis curves of various $N_2H_4 \cdot H_2O$ concentration after incubated for 10 min at room temperature, (B) calibration curve used for estimation of $N_2H_4 \cdot H_2O$ concentration. The absorbance at 455 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with $N_2H_4 \cdot H_2O$ concentration ($y = 2.492x + 0.006$, $R^2=0.998$) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of para-dimethylamino-benzaldehyde indicator with $N_2H_4 \cdot H_2O$.

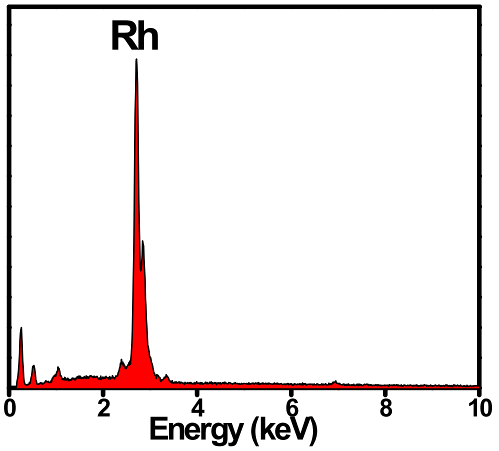

Fig. S7 EDX spectrum of Rh NNs.

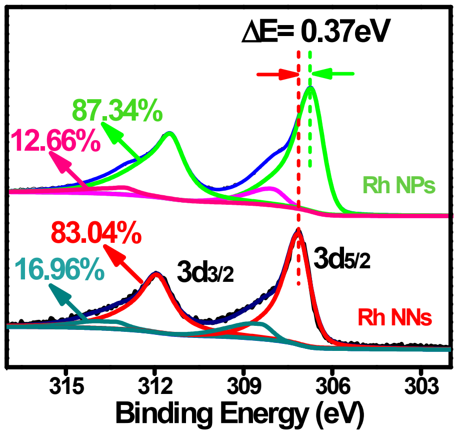

Fig. S8 XPS spectra of Rh NNs and Rh NPs. The Rh NPs were obtained by using $RhCl_3$ solution as the reaction precursors and HCHO as reducing agent.

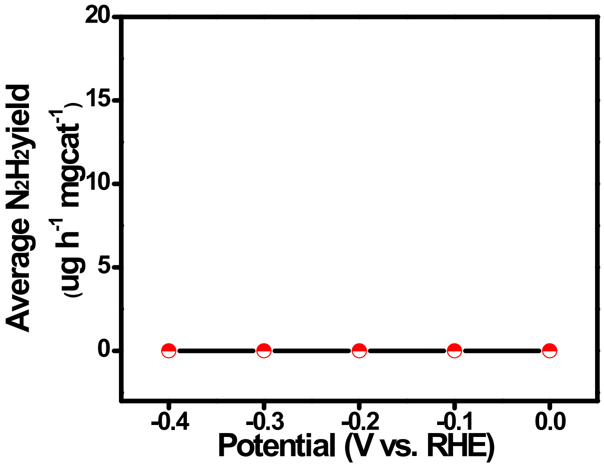

Fig. S9 Yield rate of $N_2H_4 \cdot H_2O$ formation at each given potentials.

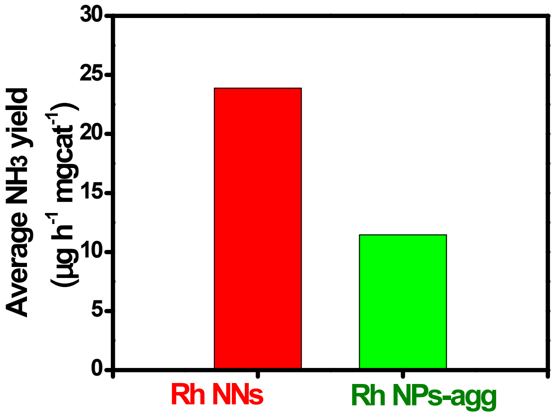

Fig. S10 Yield of NH_3 against Rh NNs and Rh NPs with severe aggregation at -0.2 V vs RHE at room temperature and ambient pressure.

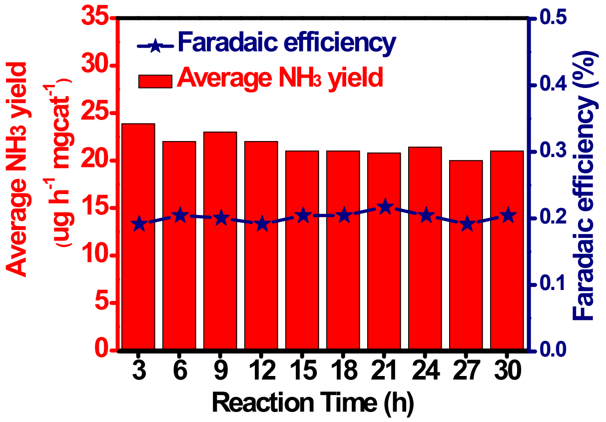

Fig. S11 Cycling stability results of yield of NH_3 (cyan) and Faradic efficiency of NH_3 at Rh NNs.

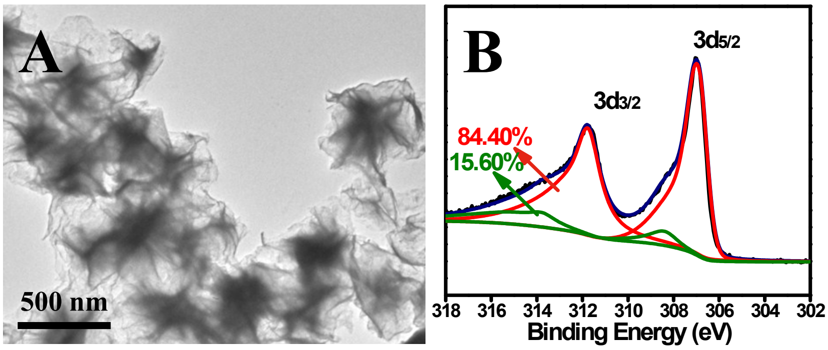

Fig. S12 (A) TEM image and (B) Rh 3d XPS spectrum of Rh NNs after 5th consecutive chronoamperometry running.

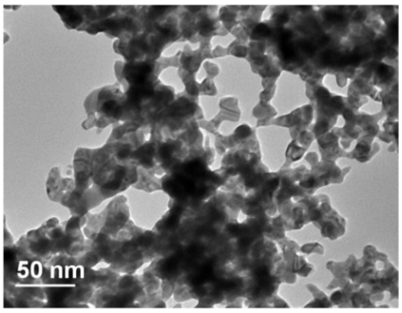

Fig. S13 TEM image of Au nanoparticles.

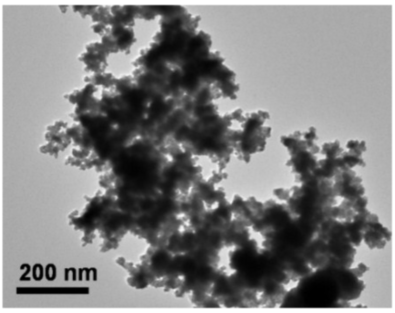

Fig. S14 TEM image of Pt nanoparticles.

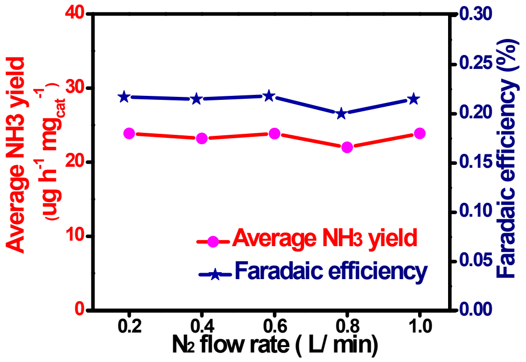

Fig. S15 Faradic efficiency (blue) and yield of NH_3 (red) against N_2 flow rate under atmospheric pressure at -0.2 V vs RHE.

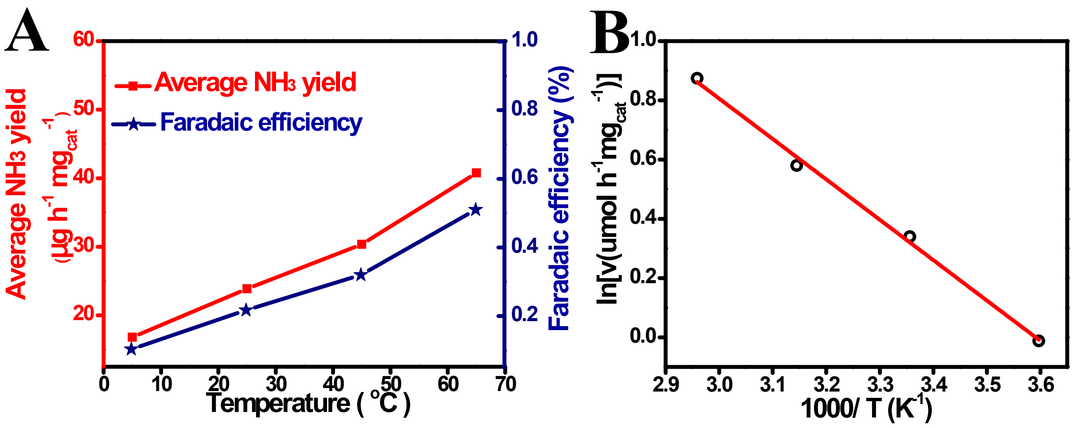

Fig. S16 (a) Faradic efficiency (blue) and yield of NH_3 (red) against catalytic temperature under atmospheric pressure at -0.2 V vs RHE, (b) Arrhenius plot of the NRR rate over Rh NNs. The fitting curve shows the linear relation of ln(rate) with temperature.

Table S1. The average yields (μg h^{-1} mg_{cat}^{-1}.) and corresponding Faradaic efficiencies (%) under different electrode potentials.

Potential(vs. RHE)	AverageNH$_3$ Yield (μg $h^{-1}mg_{cat}^{-1}$)	Faradaic efficiency (%)
0	7.64	0.671
-0.1	15.33	0.239
-0.2	23.88	0.217
-0.3	9.93	0.049
-0.4	4.75	0.016

Table S2. Summary of the representative reports on artificially N_2 fixation at high temperature and /or pressure.

Process	System/Catalyst	Conditions	Yield	NH_4^+-N Testing Method	Ref.
high temperature and /or pressure	Ag	550 °C	0.0018 μg h^{-1} cm^{-2}	Indophenols blue method	Ref. [5]
	H_2, Ag-Pd |LCC| Ag-Pd, N_2, NH_3	520 °C	79.56 μg h^{-1} cm^{-2}	Nessler's reagent	Ref. [6]
	Fe_2O_3/AC (Molten hydroxide)	523 K, atmospheric pressure	506.12 μg h^{-1} cm^{-2}	Salicylic method	Ref. [7]
	Rh NNs	**Room temperature, atmospheric pressure**	**3.82 μg h^{-1} cm^{-2}**	**phenolhypochlorite method**	**This work**
	Ru (7.8 wt%)-loaded Y_5Si_3	400 °C	32.3μg $h^{-1}mg_{cat}^{-1}$	Ion chromatography	Ref. [8]
	Rh NNs	**Room temperature, atmospheric pressure**	**23.88 μg $h^{-1}mg_{cat}^{-1}$**	**phenolhypochlorite method**	**This work**

Table S3. Summary of the representative reports on artificially N_2 fixation at ambient conditions.

Process	System/Catalyst	Yield	NH_4^+-N Testing Method	Ref.
Near -ambient conditions (Room temperature and atmospheric pressure)	Li^+ incorporation intopoly(N-ethyl-benzene-1,2,4,5-tetracarboxylic diimide)(PEBCD)	2.01×10^{-4} μg h^{-1} cm^{-2}	Nessler's reagent	Ref. [**9**]
	Au Nanorods (electrocatalysis)	6.042 μg h^{-1}cm^{-2} (NH_3) 0.374 μg h^{-1} cm^{-2} ($N_2H_2\cdot H_2O$)	Nessler's reagent and Ammonia colorimetric assay kit	Ref. [**2**]
	Carbon nanotubes	0.218μg h^{-1}cm^{-2}	indophenol blue method.	Ref. [**10**]
	Rh NNs	**3.82 μg h^{-1} cm^{-2}**	**phenolhypochlorite method**	**This work**
	Au Sub-Nanoclusters on TiO_2	21.4 μg h^{-1} mg$_{cat}^{-1}$	indophenol blue method	Ref. [**4**]
	Au Nanoparticles by CeOx-RGO HybridSupport	8.3 μg h^{-1} mg$_{cat}^{-1}$	indophenol blue method	Ref. [**11**]
	Rh NNs	**23.88 μg h^{-1}mg$_{cat}^{-1}$**	**phenolhypochlorite method**	**This work**

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