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Supporting Information

Solar-powered plasmon-boosted graphene towards enhanced ammonia production

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Table S1. Inductively coupled plasma mass spectrometry (ICP−MS) analysis of Pt and Ru loading on TiN/NG

Sample	Pt	Ru
PtRu@TiN/NG	1.10 Wt.%	1.0 Wt.%
Pt@TiN/NG	2.05 Wt.%	xx
Ru@TiN/NG	xx	2.1 Wt.%

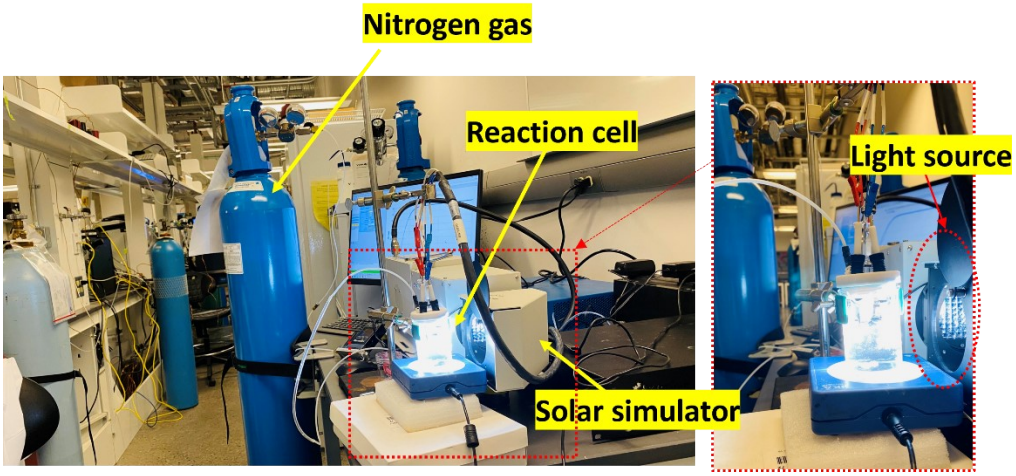

Figure S1. Photograph capturing the experimental arrangement.

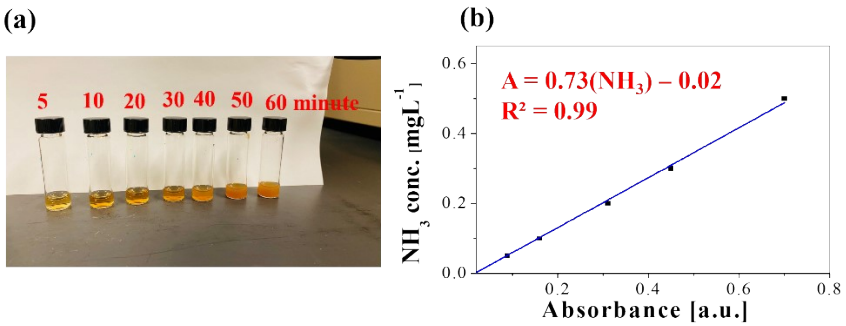

Figure S2. (a) Reaction product collection using Nessler reagent from PtRu@TiN/NG, (b) calibration curve used for estimation of NH_3 concentration. The absorbance at 420 nm was measured by UV-vis spectrophotometer.

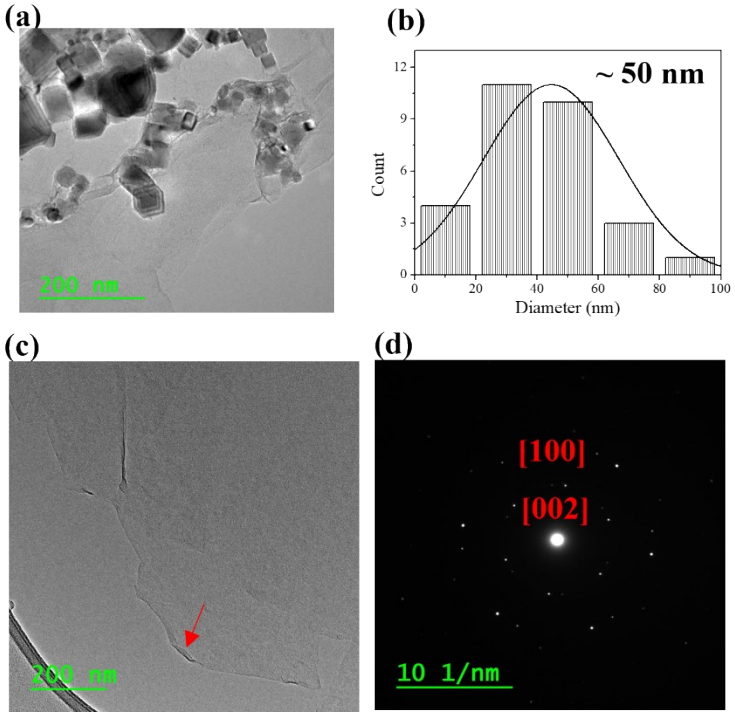

Figure S3. TEM image of (a-b) TiN NPs and its histogram illustrating the size distribution (c) pure monolayer N doped graphene i.e., NG indicated by arrow, (d) corresponding SAED pattern.

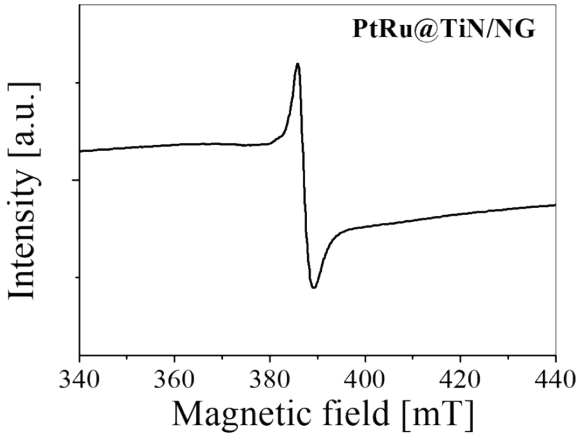

Figure S4. EPR spectra of PtRu@TiN/NG sample at room temperature.

Conditions	H_2	O_2	N_2	NH_3 (μmol $h^{-1}.mg^{-1}_{cat}$)
-0.5V	ND	0.8%	99.2%	198
-1V	0.08	0.82%	99.1%	316
-1.5V	0.21%	0.78%	99.01%	301

Figure S5. Micro-GC of NRR gas products collected after the 60 min reaction.

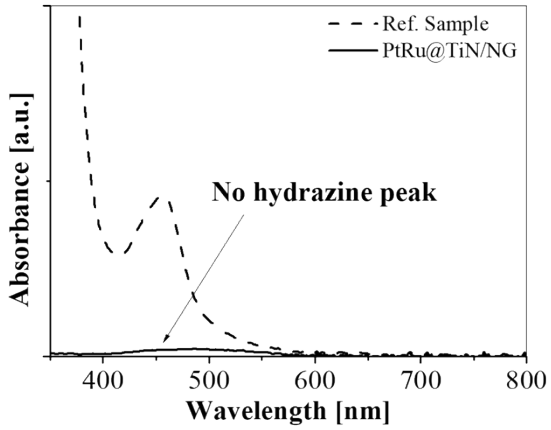

Figure S6. Hydrazine detection using a para-(dimethylamino) benzaldehyde color reagent, with absorbance measured at 455 nm. PtRu@TiN/NG exhibited no detectable hydrazine signal.

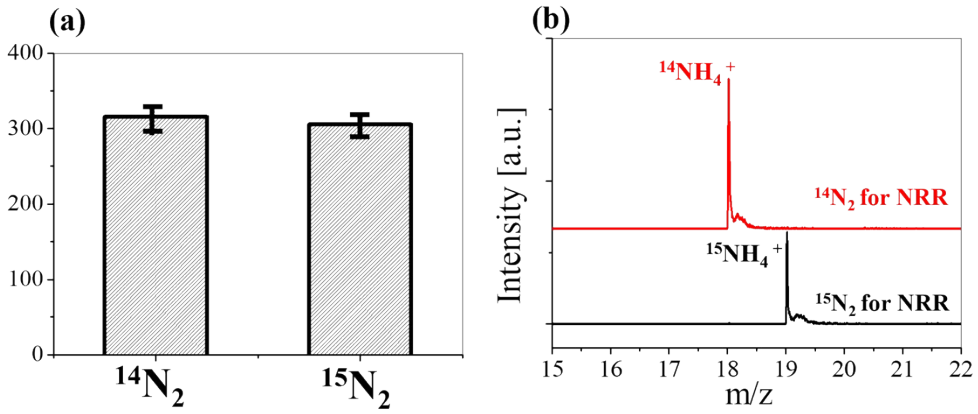

Figure S7. (a) $^{15}N_2$ isotope labelling experiment for the NRR, (b) MALDI-MS spectra for the qualitative isotope labelling test.

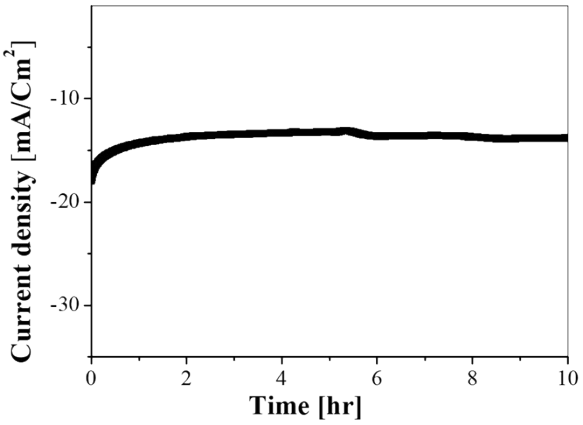

Figure S8. Plot depicting the current-time profile of the PtRu@TiN/NG electrode, recorded at -1 V in an N_2 environment with light exposure for a duration of 10 hours.

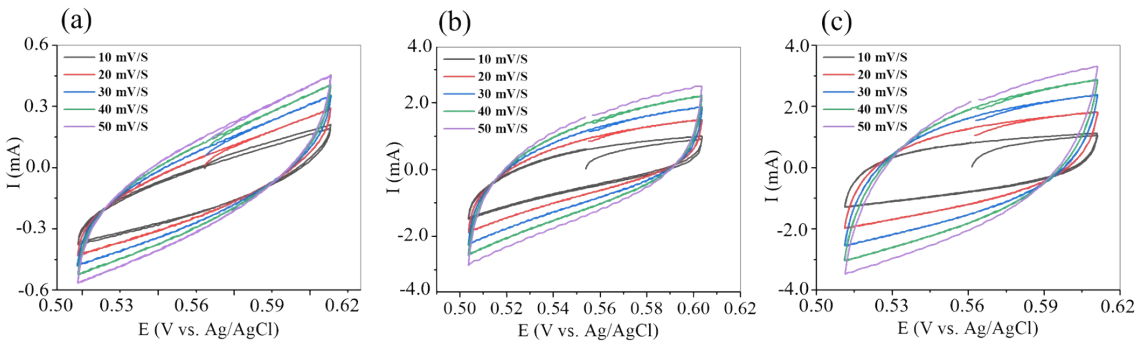

Figure S9. Effective electrochemical active surface area tests (ECSA) of (a) PtRu@TiN, (b) PtRu@NG, and (c) PtRu@NG.

Table S2. An overview of the documented research on the photo-electro-catalytic conversion of N_2 to NH_3.

Catalysts	**Light sources**	**Electrolytes**	**NH_3 yield rates**	**Ref.**
PtRu@TiN/NG	2 suns illumination	N_2- saturated H_2SO_4 in H_2O, Scarifical reagent: Methanol	316 $\mu g \cdot h^{-1} \cdot mg_{cat.}^{-1}$	This work
Pt-TiN/C_3N_4	1 sun illumination	N_2- saturated H_2SO_4 in H_2O, -1V Vs. Hg/SO_4	105 $\mu g \cdot h^{-1} \cdot mg_{cata.}^{-1}$	1
Black Silicon	2-sun illumination	N_2 –saturated Na_2SO_3 in H_2O, -1 V Vs. Ag/AgCl	13.3 mg m^{-2} h^{-1}	2
Cs 2O/Os-Au	UV-Visible	N_2/H_2	2685 $\mu mol\ g^{-1}\ h^{-1}$	3
TiO_2-Cu_2O/Ru	150-W Xenon lamp	N_2 -saturated Na_2SO_4 in H_2O	37.4 $\mu g \cdot mg_{cat}^{-1}\ h^{-1}$	4
reduced graphene oxide	N/A	N_2 -saturated HCl in H_2O at -0.1V vs RHE	7.3 $\mu g \cdot mg_{cat}^{-1}\ h^{-1}$	5

NiO-Au-TiO_2	532 nm CW laser, 43.8 mW/cm^2	0.2 M KNO_3 electrolyte, −1.2 V vs Ag/AgCl,	80 μmol· L^{-1}	[6]
Au embedded in hollow carbon nitride sphere	Xenon lamp at 420 nm cutoff filter	N_2 -saturated in H_2O	783.4 μmol g^{-1} h^{-1}	[7]
BaONCS-TNS		KNO_3 Scarifical reagent: ethylene glycol, −1.0 to 1.5 V vs. RHE	11.97 mol g_{metal}^{-1} h^{-1}	[8]
Au nanoparticles		0.1M Li_2SO_4 ,-0.3 V vs. RHE	9.2 μg $h^{-1}cm^{-2}$	[9]

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