

Supporting Information

Pd doped Carbonitride (Pd-g-C₃N₄): An efficient Photocatalyst for Hydrogenation *via* Al-H₂O system & Electrocatalyst towards Overall Water Splitting

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ES1: Experimental: Chemical Used in Protocol

The material used in the experiments such as Urea, olefins, Nitro group compounds, Palladium chloride (PdCl_2), Deionized water, Al, Aluminium oxide (Al_2O_3), chemicals were purchased from commercial firms (Sigma Aldrich and reliable resources) and used without further purification. Aluminium foil is purchased from glossary store. GC analyses were performed using Focus GC from Thermo Electron Corporation, equipped with low polarity ZB-5 column. GC analyses were performed using Trace 1300 Gas Chromatograph model from Thermo Scientific, equipped with the Rxi-1ms (crossbond 100% dimethyl polysiloxane) column. Conversion based on GC area. The Palladium (Pd) content of product was determined by an Inductively Coupled Plasma Mass Spectrometry (ICPMS) spectrometer (Agilent 7500 cx).

ES2: Characterization Instrumentation

FTIR spectra were obtained by using a Bruker (Alpha-T). Sample morphology was observed by extra high-resolution scanning electron microscopy (MagellanTM 400 L). XPS analysis was conducted using an XPS Kratos AXIs Ultra (Kratos Analytical Ltd, UK) high resolution photoelectron spectroscopy instrument. X-ray diffraction patterns were collected by using a Bruker AXS D8 Advance. XRD measurements were performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm, Göbel Mirror parallel-beam optics, 2° Soller slits, and 0.2 mm receiving slit. A low background quartz sample holder was carefully filled with the powder samples. UV/Vis absorption spectra were monitored by using a Carry 100 Bio and diffuse reflectance analysis was carried out by using an Integrating Sphere (JASCOV-650 Series ISV-722). BET analysis Surface area analysis was performed by means of N_2 adsorption/desorption measurements at 77 K on a volumetric gas adsorption analyzer (Autosorb iQ XR, Anton-Paar Quanta Tec, USA) up to 0.965. Prior the analysis, the sample was degassed under high vacuum (10^{-7} Pa) at 80 °C for 25.1 hrs, while high purity (99.999 %) N_2 and He gases were used for the measurements.

AFM analysis sample are prepared via; The solid sample was dissolved in EtOH, the solution was sonicated and placed at freshly cleaved MICA substrate via drag and drop method and left to dry. For AFM measurement Combined system NTEGRA Spectra (NT-MDT, Russia) was utilized to acquire sample topography (software Nova Px. 3.4.0 rev. 19040). The surface morphology was obtained by the means of semi-contact mode (height) with a ACTA-SS (AppNano, USA) cantilever having a force constant of 13-77 N/m and resonant frequency of 200 – 400 kHz. The scanning rate was 0.5 Hz. During the measurement the humidity was in range of 20-30% and the temperature was RT. The height profile and surface roughness (RMS) was calculated using Gwyddion 2.51 software. HR-TEM Microscopic TEM images were obtained by HRTEM TITAN 60-300 with X-FEG type emission gun, operating at 80 kV. This microscope is equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution is 0.06 nm in TEM mode. The elemental mappings were obtained by STEM-energy dispersive X-ray spectroscopy (EDS) with acquisition time 20 min. For HRTEM analysis, the powder samples were dispersed in ethanol and ultra-sonicated for 5 min. One drop of this solution was placed on a copper grid with holey carbon film. XRD patterns from 5° to 85° 2 θ were recorded at room temperature using Cu K α radiation ($\lambda = 0.15418$ nm) with the following measurement conditions: a tube voltage of 40 kV, a tube current of 40 mA, step scan mode with a step size of 0.02° 2 θ and a counting time of 1 s per step for preliminary study and 12 s per step for structural refinement. The instrumental broadening was determined using LaB6 powder (NIST-660a).

ES3: Photo catalyst Synthesis and Photochemical Reaction Protocol.

i: Photoactive Graphitic Carbon nitride (g-C₃N₄) support & Pd-g-C₃N₄ photo-catalyst Synthesis:

Graphitic carbon nitride (g-C₃N₄) was synthesized by a known established method as reported by J. by Wei Chen using 10 g urea (99 %) as easily available raw material via 550 °C for 3 h (10 °C/min rate) in furnace method yield (1.2 g).^{[1] [1b, 2]}

Calculated amount (8 wt.%) Palladium chloride (PdCl_2) was dissolved in water (10 mL). 2.5 gm $\text{g-C}_3\text{N}_4$ (preheated in oven at 100°C for 1 hour) the treated (2.5 g for 8 weight % $\text{Pd-g-C}_3\text{N}_4$ final) was added into the palladium chloride (PdCl_2) solution and stirring was activated to 700 rpm for 1 h. Later an aqueous solution of potassium formate (HCOOK) was added drop wise for 30 min at 25°C RT (molar ratio between palladium and reducing agent is 10:1, total concentration of formate in vessel maintained 0.008 M) (used as a reduction agent). In addition, the mixture with stirring continued at room temperature for 12 h. After 12 h the mixture was filtered, washed thoroughly with deionized water and left to dry at room temperature. Yield (2.49 g).^[1b, 3]

ii. Optimized protocol for the Photochemical in-situ Hydrogenation Reaction using Aluminum - Water System:

We performed photochemical hydrogen generation reaction at room temperature with 15 cm height distance from the visible light source (15 W LED lamp) to reaction mixture in a closed glass tube to neutralize heating impact (Fig. S2). A typical example a mixture of substrate (10 mmol), Al pieces (10 mmol, 0.27 g), $\text{Pd-g-C}_3\text{N}_4$ 20 mg (0.015 mmol 8 weight % loading), and water (15 mL) under visible light (15 W LED domestic table lamp) was kept in a pressure glass tube equipped with a magnetic stirrer and was degassed by a flow of nitrogen for five minutes. The tube was sealed with stirring for 12 h at room temperature under LED table lamp (15 W visible light sources). After completion of reaction samples were diluted with dichloromethane (DCM) and filtered by Whatman paper before injection into a gas chromatograph.

iii. Recycling Study and heterogeneity Test of Photo catalyst $\text{Pd-g-C}_3\text{N}_4$:

The recycling test was performed under the optimized reaction conditions [room temperature, visible light (15 W LED lamp visible light source), 800 rpm] for hydrogen transfer reaction using substrate (10 mmol, 1.04 g), Al pieces (10 mmol, 0.27 g), $\text{Pd-g-C}_3\text{N}_4$ 20 mg (0.015 mmol 8 wt.% loading), and water (15 mL) under visible light (15 W LED domestic table lamp). After the reaction, the heterogeneous photocatalyst Pd-g-

C_3N_4 was recovered by simple filtration by using Whatman filter paper washed with methanol, acetone (5*20 mL) dried (overnight in an oven at 100°C) and reused in further experiments for next recycle study. No major loss was observed in every recycle study reaction process activity. The observed study [4] confirmed that the photo catalyst is stable and true in heterogeneous nature.[1b, 3, 5]

vi. General Protocol for the Deuterated Photochemical in-situ hydrogenation Reaction using Aluminum Foil-Water System: For the confirmation of hydrogen generation from water source in hydrogenation is actually comes from water. As per optimized reaction condition for hydrogenation reaction, substrate (10 mmol), aluminum foil (10 mmol, 0.27 g), Pd-g- C_3N_4 20 mg (20 mg, 0.015 mmol), and D_2O (10 mL) under visible light (15 W LED domestic table lamp) processed in a closed glass tube with a magnetic stirrer and degassed via purging nitrogen for five minutes. The tube was sealed with stirring for 12 h at room temperature under LED lamp (15 W visible light sources). After completion of reaction mixture was diluted with dichloromethane (DCM) and filtered by Whatman paper before injection into a gas chromatograph. The observed GC-MS chart of deuterated ethyl benzene GC-MS and deuterated 4-amino toluene were included here below in S7 and S8 figures.[6]

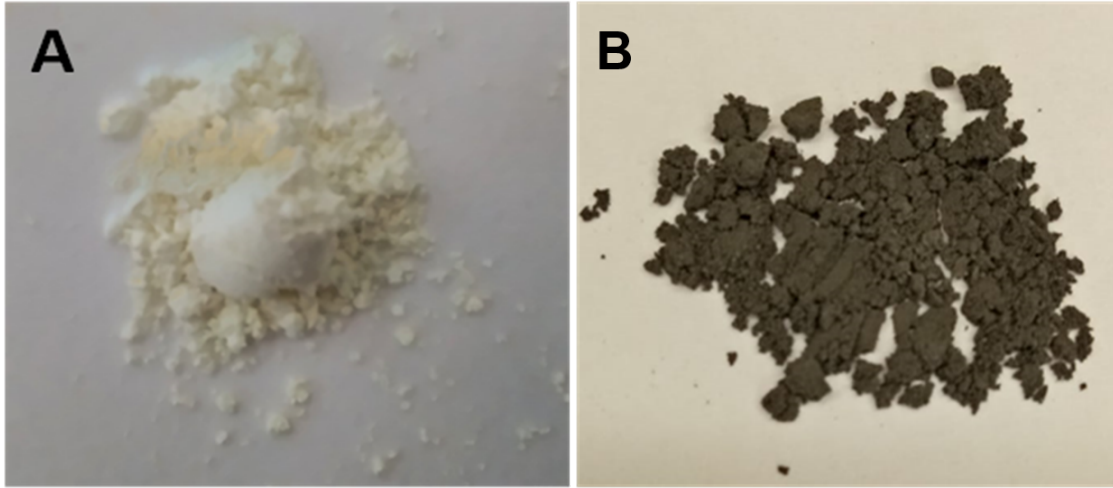


Figure S1. Physical appearance of (A) $g\text{-C}_3\text{N}_4$ and (B) $\text{Pd-}g\text{-C}_3\text{N}_4$.



Figure S2. Photochemical in-situ hydrogenation Reaction Setup under Visible light (15 W LED Lamp).

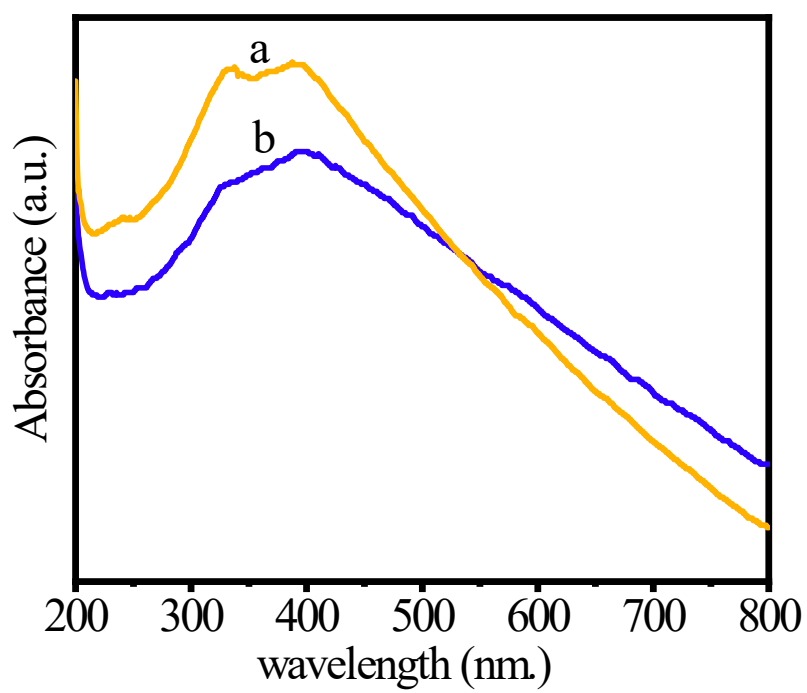


Figure S3. UV-vis spectra: (a) g-C₃N₄, (b) Pd-g-C₃N₄.

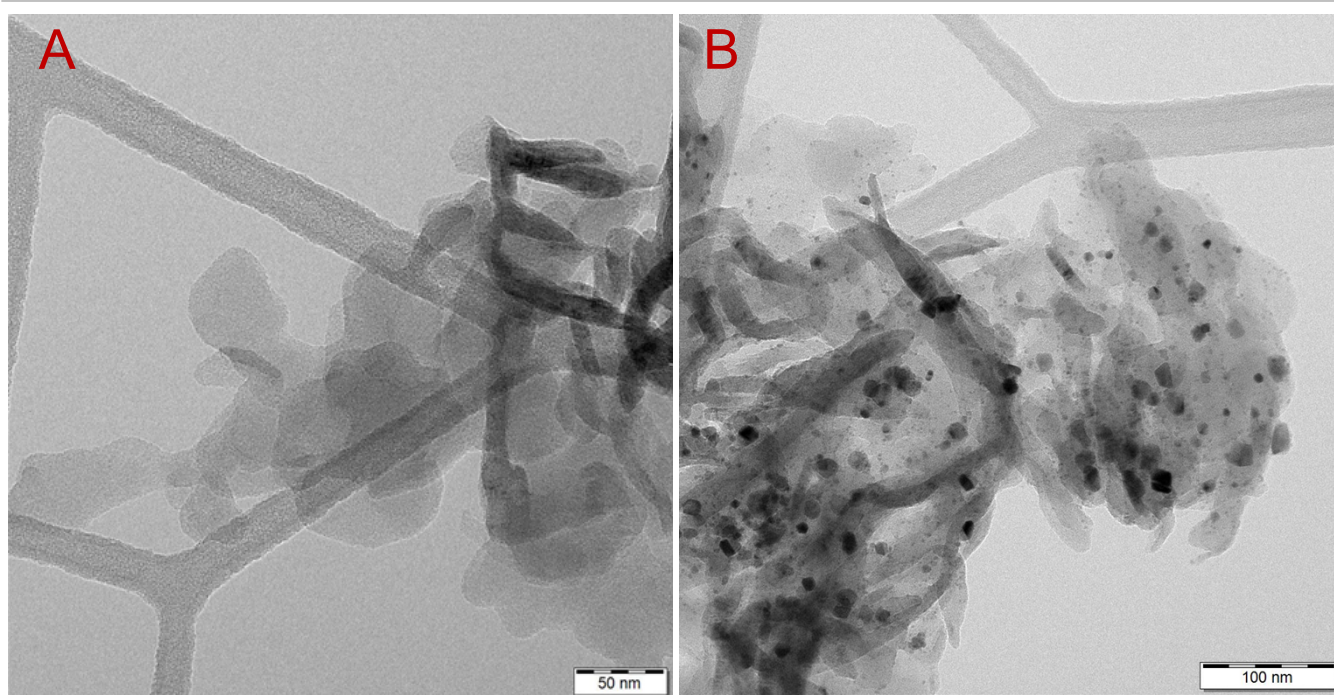


Figure S4. TEM images of (A) g-C₃N₄ and (B) Pd-g-C₃N₄.

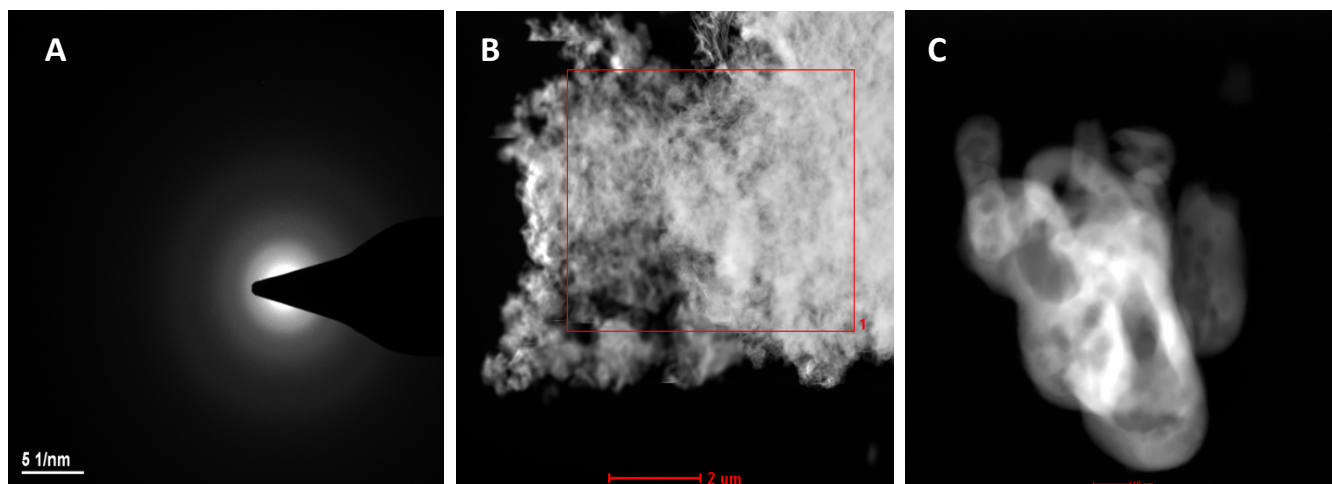


Figure S5 (1). A) SAED pattern g-C₃N₄; B) 2 μm and C) 50 nm STEM images of g-C₃N₄ at different magnifications.

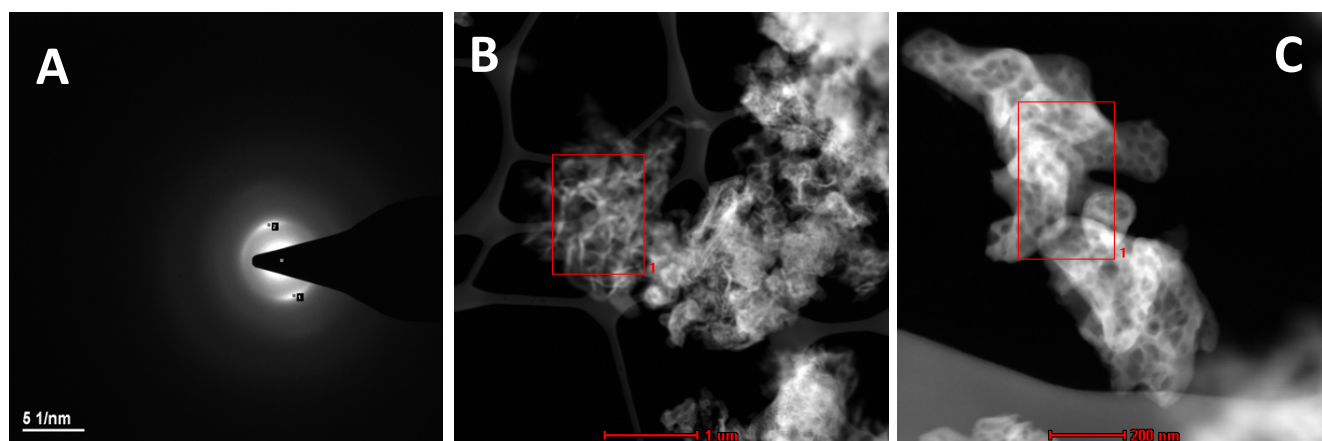


Figure S5 (2). A) SAED pattern Pd-g-C₃N₄; B) and C) STEM images of g-C₃N₄ at different magnifications.

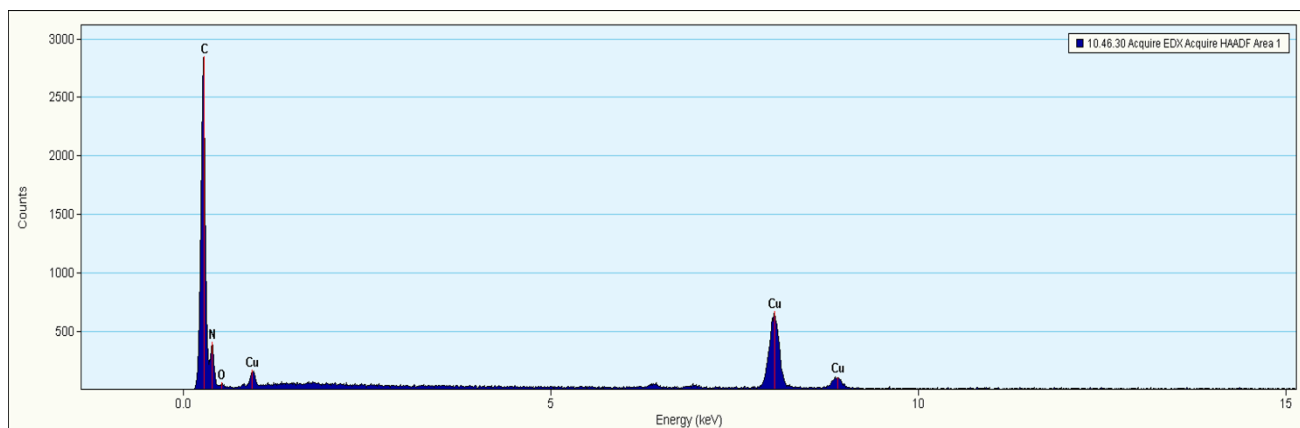


Figure S6 (1). STEM-EDS pattern for the g-C₃N₄.

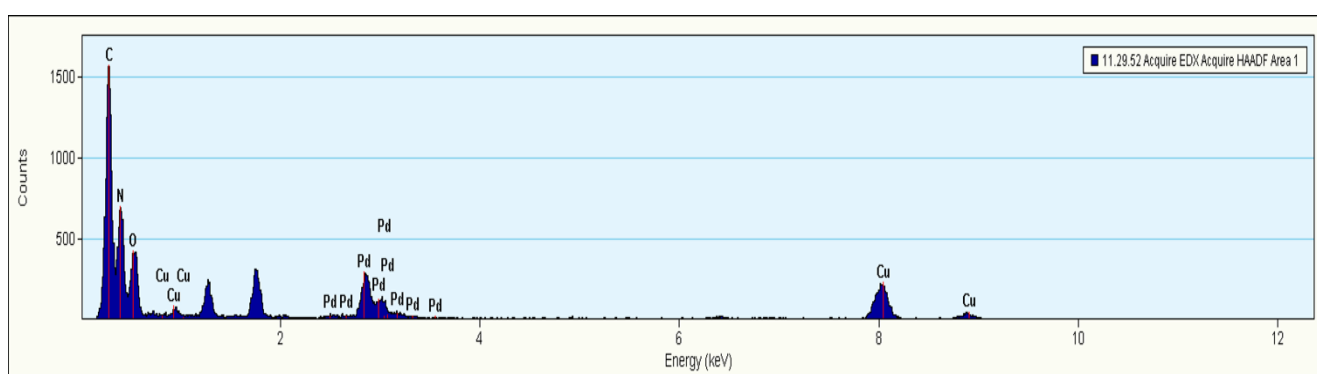


Figure S6 (2). STEM-EDS pattern for Pd-g-C₃N₄.

Quantification Results

Correction method: None

Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor
C (K)	56.19	64.62	0.54	0.26	3.940
N (K)	26.78	26.41	0.37	0.26	3.826
O (K)	9.19	7.93	0.15	0.49	1.974
Pd (K)	7.82	1.01	0.22	0.98	6.031

Figure : S6 (3). Elemental analysis of Pd-g-C₃N₄ obtained from the EDS analysis.

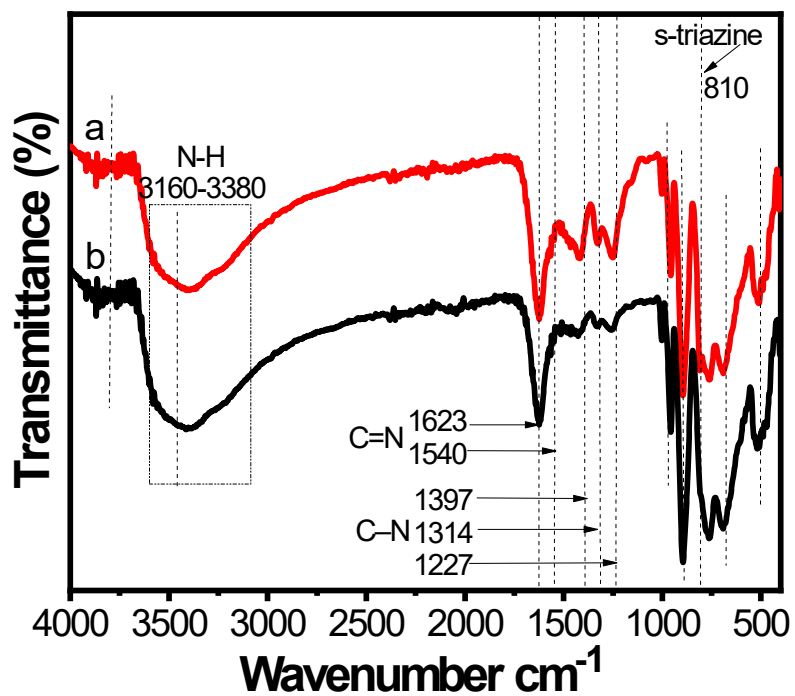


Figure S7. FT-IR spectrum of a) g-C₃N₄, b) Pd-g-C₃N₄.

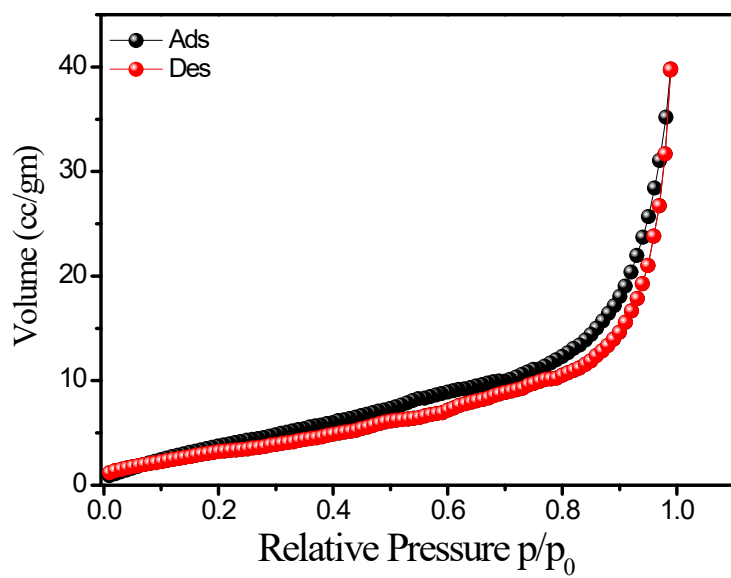


Figure S8. BET surface area plot analysis of Pd-g-C₃N₄.

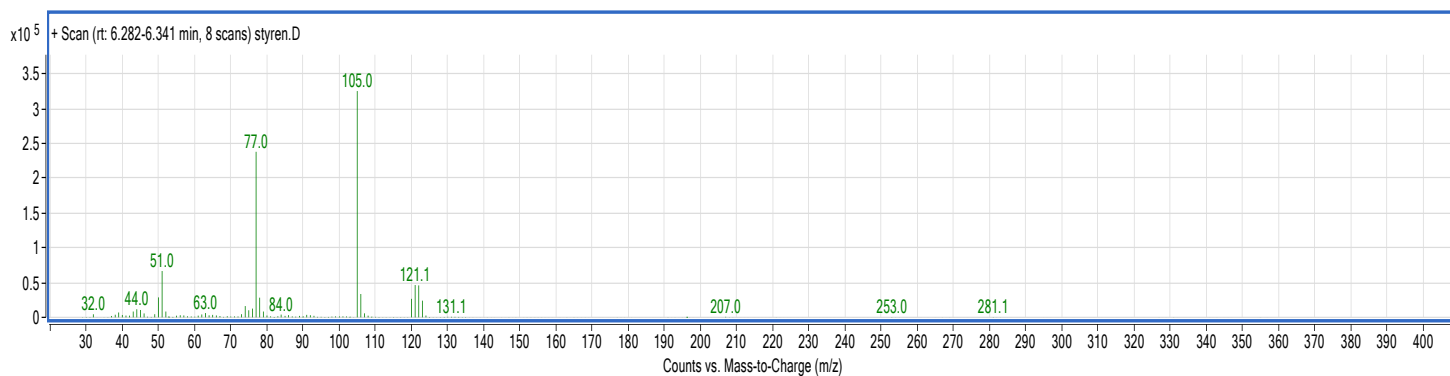


Figure S9(1). Deuterated product ethyl benzene GC-MS profile.

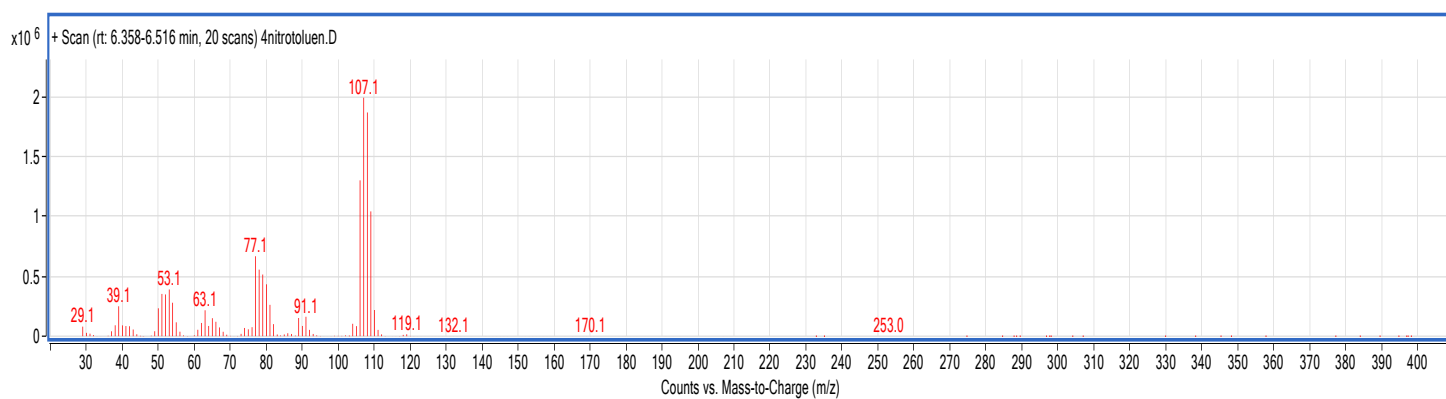


Figure S9(2). Deuterated product 4-amino toluene GC-MS profile.

Table S1: Reaction optimization for aluminum (foil)-water complex for in-situ photochemical hydrogenation reaction.

Entry	Reaction Optimization	Yield (%)	Time (h.)
1.	H ₂ O (Light/ Dark)	0/0	24
2.	Al (foil pieces) (Light/ Dark)	0/0	24
3.	PdCl ₂ (Light/ Dark)	01/01	24
4.	Al ₂ O ₃ (Light/ Dark)	0/0	24
5.	g-C ₃ N ₄ (Light/ Dark)	0/0	24
6.	g-C ₃ N ₄ + Al (Light/ Dark)	02/01	24
7.	g-C ₃ N ₄ + Pd (Light/ Dark)	01/0	24
8.	g-C ₃ N ₄ + Al ₂ O ₃ (Light/ Dark)	0/0	24
9.	Pd + Al ₂ O ₃ (Light/ Dark)	02/01	24
10.	Pd + Al (Light/ Dark)	20/15	24
11.	Pd-g-C ₃ N ₄ + Al ₂ O ₃ (Light/ Dark)	05/01	24
12.	Pd-g-C ₃ N ₄ + Al (Light/ Dark)	99/45	12
13.	Pd/C ((4wt.%) (Light/ Dark/heat-100°C)	03/02/10	24
14.	Pd/C (4wt.%) + Al (Light/Dark/heat-100°C)	10/09/89	12
15.	Pd/C (4wt. %) + Al ₂ O ₃ (Light/ Dark-100°C)	05/03/10	12

Reaction conditions: Styrene (10 mmol, 1.04 g), Al (foil) pieces (25 mg, 0.364 g), Pd-g-C₃N₄ (30 mg, 0.0012 mmol 0.4 % loading) and H₂O (10 mL) under visible light (15 W LED lamp, 15 cm. height).

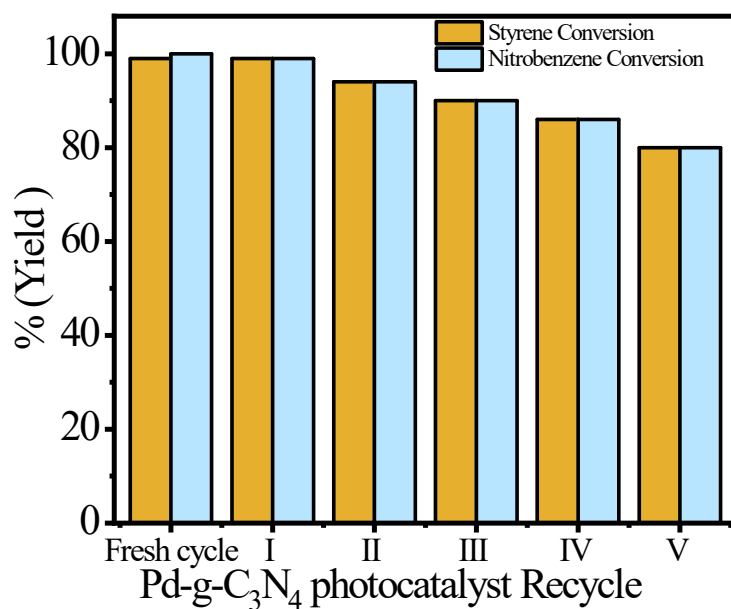


Figure S10. Recycling study of photo catalyst Pd-g-C₃N₄ for (A) olefin (styrene) (B) and nitro group (4-nitro toluene) in-situ hydrogenation.

Materials	Tafel slope (mV dec ⁻¹)	
	Hydrogen Evolution Reaction(HER)	Oxygen Evolution Reaction (OER)
Pd-g-C₃N₄	36	72
g-C₃N₄	149	134
Pd-C	92	90

Table S2: Tafel slopes for overall water splitting (HER and OER) for Pd-g-C₃N₄, g-C₃N₄, and Pd-C.

References

- [1] a) J. Liu, T. Zhang, Z. Wang, G. Dawson, W. Chen, *Journal of Materials Chemistry* **2011**, *21*, 14398-14401; b) P. Sharma, Y. Sasson, *Green Chemistry* **2017**, *19*, 844-852.
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- [4] P. Sharma, Y. Sasson, *RSC Advances* **2018**, *8*, 2824-2828.
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- [6] O. Muhammad, S. U. Sonavane, Y. Sasson, M. Chidambaram, *Catalysis Letters* **2008**, *125*, 46-51.