

Supporting information

Noble metal free naphthylbisimide/TiO₂/graphene: an efficient H₂ evolution photocatalyst

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Experimental Section:

General Information

In the present work, all chemicals used were analytical grade, and were obtained from commercial sources and used without further purification unless otherwise stated. Elemental analysis (C, H and N) were performed using a 2400 Series-II CHN Analyzer, PerkinElmer, USA. FTIR spectra of the samples were recorded in the range of 400–4000 cm⁻¹ on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. ¹H NMR was carried out by Bruker Spectrometer operating at 400 MHz in DMSO-*d*₆ solvent. Mass spectrum was collected by Micromass Q-ToF Micro instrument. UV-visible and UV-vis diffuse reflectance spectra (DRS) were recorded at ambient temperature on a Cary-500 UV-vis Spectrophotometer along with different compartment for DRS. Photoluminescence spectra were measured Cary eclipse fluorescence spectrometer from Agilent technologies. Powder X-ray diffraction (PXRD) measurement was characterized using a Bruker AXS diffractometer (D8 Advance) using Cu-K α radiation (λ = 1.5406 Å), a generator voltage of 40 kV and current 30 mA. Sample was scanned in the range of 2θ = 5-100° with the scan rate 1s/step. The HRTEM micrograph of the sample was prepared by taking acetone dispersion of TiO₂ on the carbon coated copper grid and drying at room temperature in air followed by vacuum. HRTEM were carried out by JEOL 2010 EX operated at an accelerating voltage of 200 kV fitted with a CCD camera. FESEM were carried out using Carl Zeiss microscopy introduce SIGMA HD field emission scanning electron microscope. GC analysis were performed by Perkin Elmer Clarus 580 GC instrument with a thermal conductivity detector (TCD), a 5 Å molecular sieve column (2 mm × 2 mm) and Argon as carrier gas. Atomic force microscopy (AFM) images were obtained using Nanosurf FlexAFM instrument in tapping mode. Raman spectra was collected using J–Y Horiba Confocal Triple Raman Spectrometer (Model: T64000) fitted with gratings of 1800 groove/mm, and a TE cooled Synapse CCD detector from J–Y Horiba. 632.8 nm red line of He–Ne laser made up by Melles Griot. The scattered signals were collected at 180° scattering angle to the excitations from an Olympus open stage microscope.

X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIS 165 with a dual X-ray anode (Mg and Al); all XPS spectra were recorded using the Mg K α line. The pressure in the spectrometer was about 10⁻⁹ Torr. Linear scan voltammetry (LSV) measurement was carried out on a CH electrochemical workstation CHI600E, in a three-electrode cell with a Pt disk counter electrode, a Ag/AgCl reference electrode and a FTO glass coated with photocatalyst as working electrode. All LSV measurements were performed in presence of supporting electrolyte of 2 M Na₂SO₃. The photocatalytic experiments were carried out under external light source using a 450 W Oriol Research Arc lamp Source (Newport, USA, model no: 66924) equipped with xenon (Xe) lamp. Intensity of the light has been measured using optical power/energy meter, Newport, model: 842-PE. The light intensity of solar irradiation was 1.95 W/cm².

Synthesis of graphene oxide (GO) and reduced graphene oxide (rGO)

GO was synthesized from graphite powder according to the modified Hummers' method. Usually graphite powder was gradually added into 24 ml of hot concentrated H₂SO₄ solution (80 °C) containing K₂S₂O₈ (8 g), and P₂O₅ (8 g), followed by stirring for a period of 6 h, and then the resulting dark blue mixture was thermally isolated and slowly cooled to room temperature. The achieved mixture was diluted with MilliQ-H₂O to 300 ml, and then filtrated with a filter membrane of 0.22 μ m and dried overnight at 60 °C. The preoxidized graphite powder (2 g) was added to 2 ml of cold H₂SO₄ (0 °C), then KMnO₄ (12 g) was gradually added under continuous stirring in ice-bath. After 15 min, NaNO₃ (2 g) was introduced into the mixture. The solution was further stirred at 35 °C for 2 h and then MilliQ-H₂O (200 ml) was added. After being stirred for 15 min, the reaction was terminated by addition of MilliQ-H₂O (560 ml) and 10 ml of 30% H₂O₂ (10 ml). The product was washed with HCl (1:10) and then with water, and then suspended in distilled water. The brown dispersion was extensively dialyzed to remove residual metal ions and acids. After the unexploited graphite in the resulting mixture was removed by centrifugation, as-synthesized GO was collected then and dried at 70 °C in air oven.

Reduced graphene oxide (rGO) was prepared by simple chemical method.¹ In a typical procedure, GO (100 mg) was charged in 100 ml of distilled water in a 250 ml round bottle flask, which yielding a brownish yellow inhomogeneous dispersion. Then it was sonicated by using Takashi Ultrasonic cleaner (150 W) until it became a clear solution. Hydrazine hydrate (1.00 ml) was added slowly drop wise into the solution under constant stirring. Then the reaction mixture was refluxed at 100 °C for 24 h over which the reduced GO gradually precipitated out as

a black solid. Then it was filtered, washed with water and methanol 5 times, and then dried under continuous air flow.

Synthesis of platinumized TiO_2 (1 wt %)

Platinumized TiO_2 was prepared by a photochemical reduction method. In a 100 ml round-bottomed flask, 1 g TiO_2 was dispersed in 20 ml methanol with adequate time of ultrasonication. To this solution, H_2PtCl_6 (0.25 ml, 8 wt% aqueous solution) was slowly added. Then, the reaction mixture was irradiated for 1 h under 450 W Xe-lamp. H_2PtCl_6 was reduced to form Pt nanoparticles during the reaction, causing a change in color of the material from pale yellow to grayish. The resultant composites were retrieved by centrifugation, washed five times with excess methanol and dried under vacuum. The as synthesized platinumized samples are designated as Pt/c TiO_2 and Pt/s TiO_2 .

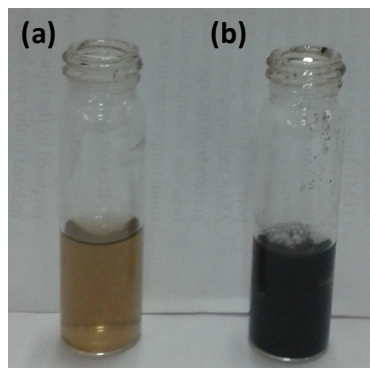


Fig. S1 Aqueous suspension of (a) GO and (b) rGO.

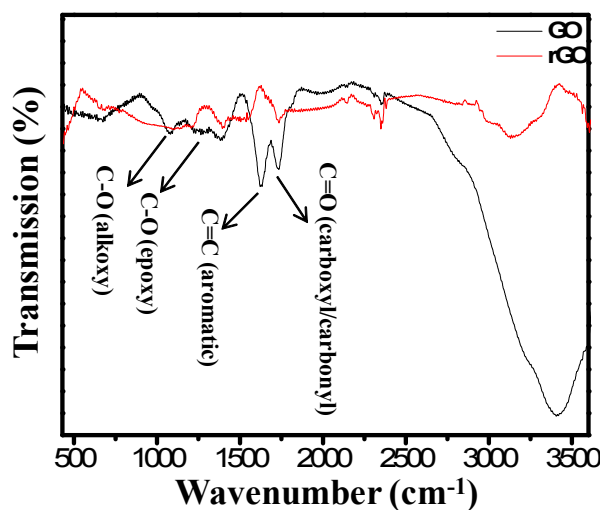


Fig. S2 FTIR spectra of GO and rGO.

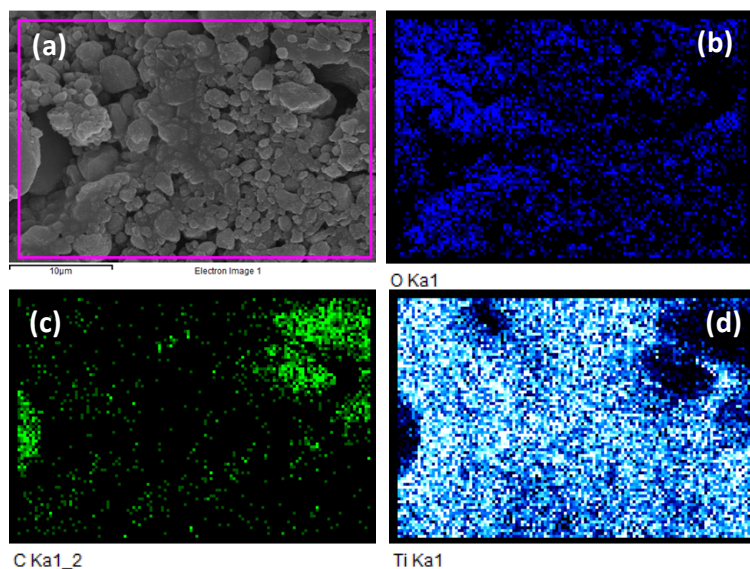


Fig. S3 (a) FESEM image; (b) oxygen; (c) carbon and (d) Ti mapping in composite IV.

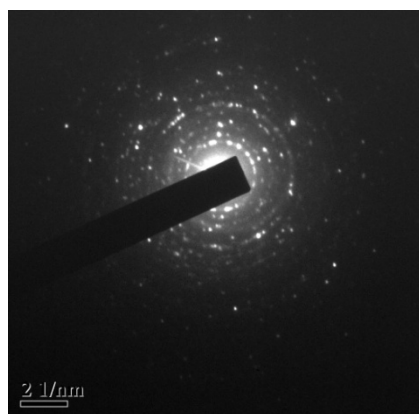


Fig. S4 FFT TEM image of sTiO₂.

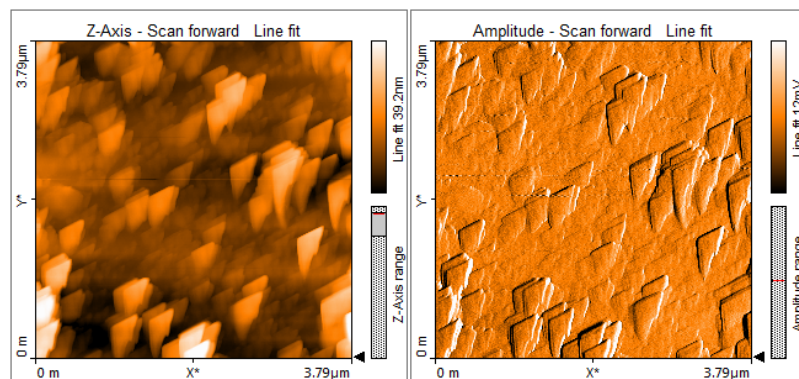


Fig. S5 Tapping mode AFM images of rGO on silicon wafer. Image dimensions are 3.79 µm x 3.79 µm.

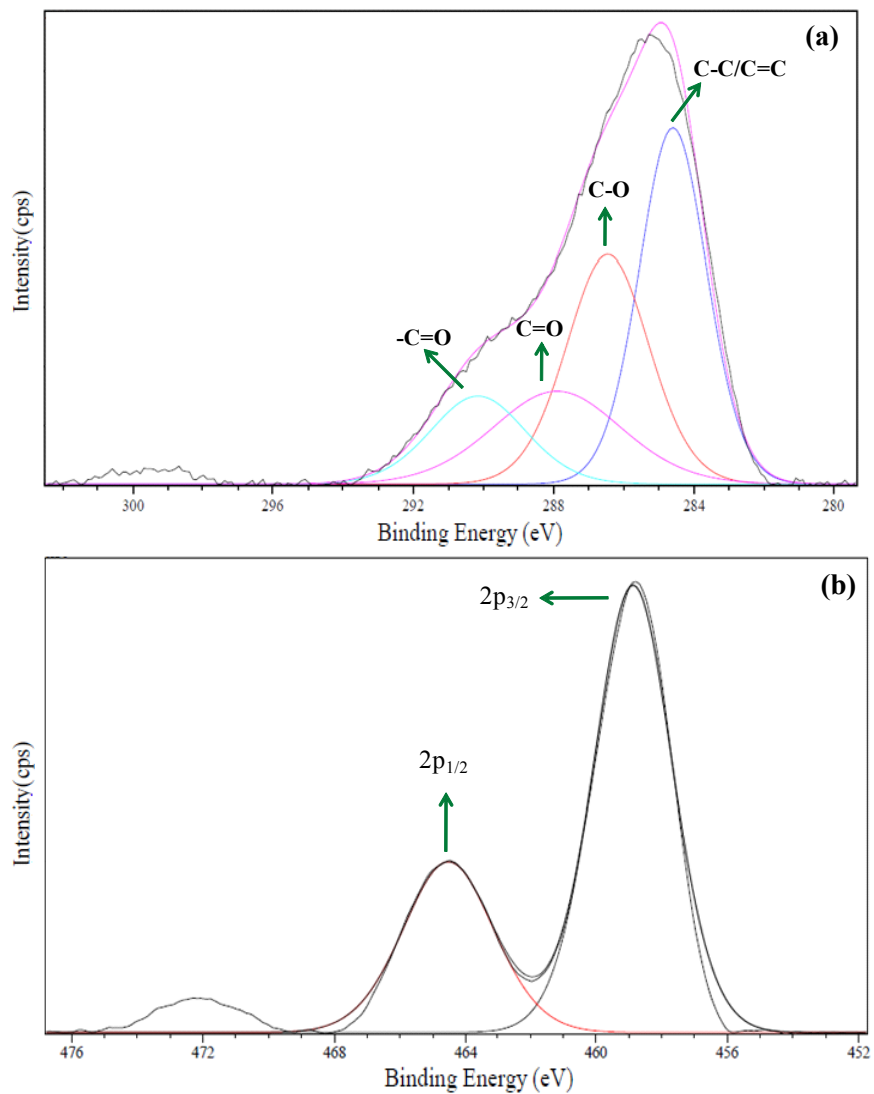


Fig. S6 XPS spectra of (a) C 1s and (b) Ti 2p of NDIPYPZ/sTiO₂-rGO composite

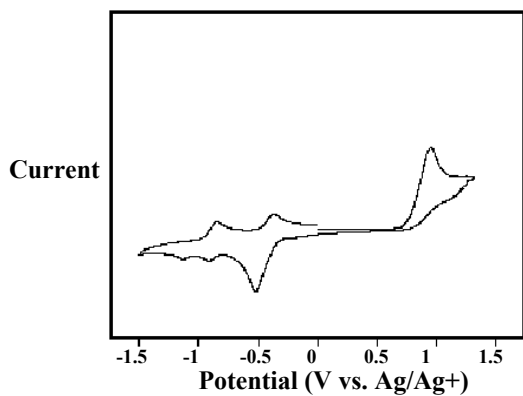


Fig. S7 Cyclic voltammogram of NDIPYPZ. Oxidation potential were measured using Fc/Fc+ as standard and 0.01 M Bu₄NBF₄ in Pt and Ag/AgCl as the supporting electrolyte solution, working and reference electrode respectively in water DMSO. Scan rate 20 mV/s was applied throughout the experiment. HOMO values were calculated using potential value of oxidative waves. LUMO values were calculated by addition of HOMO values with the E_{0-0} .

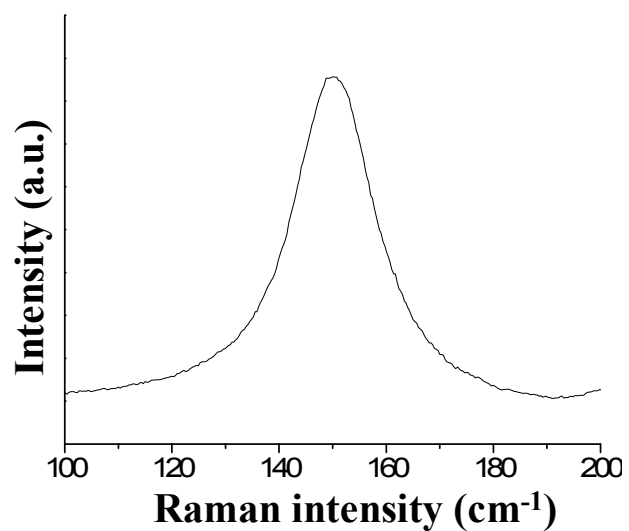


Fig. S8 Magnified Raman shift of NDIPYPZ/sTiO₂-rGO in the range of 100-200 cm⁻¹.

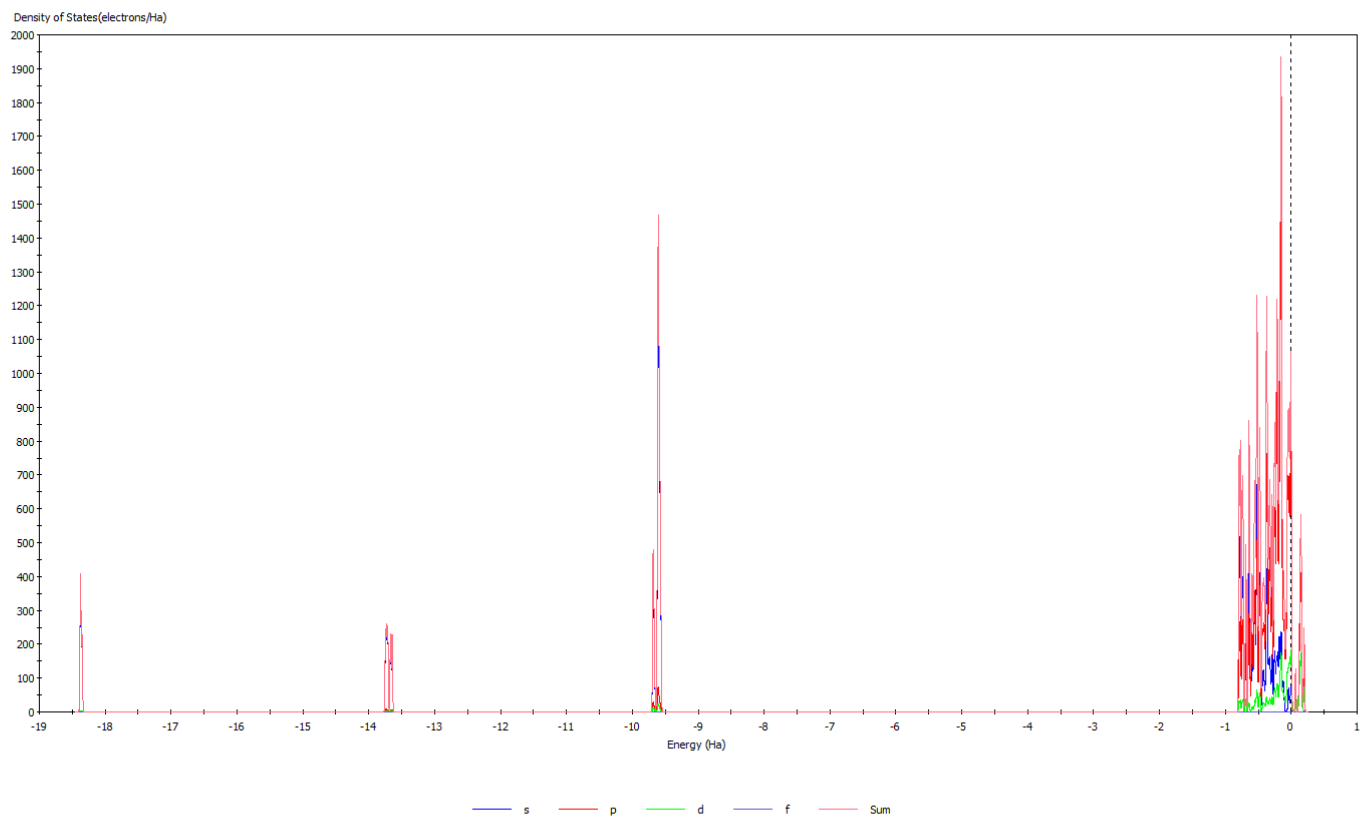


Fig. S9 Partial density of state (PDOS) plot of NBI.

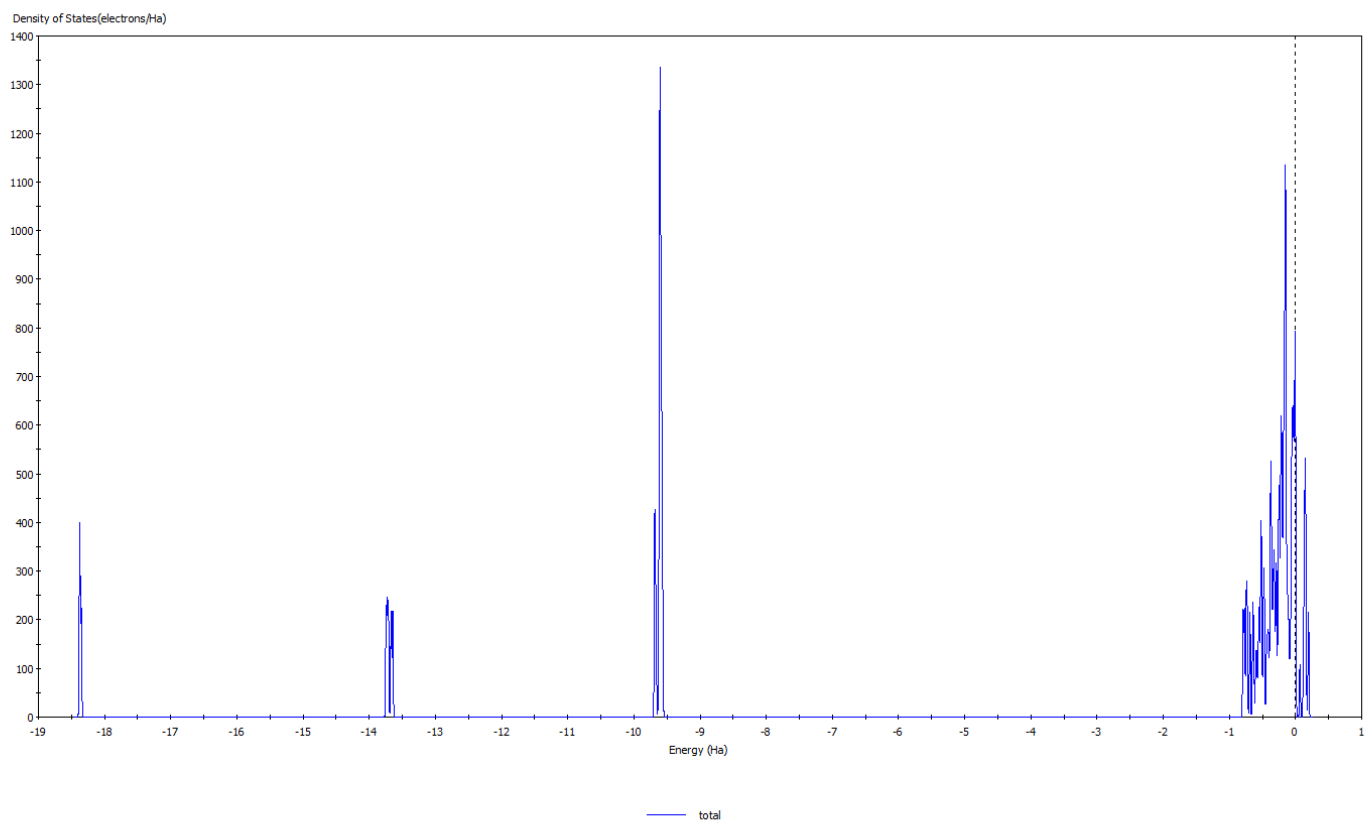


Fig. S10 Total density of state (TDOS) plot of NBI.

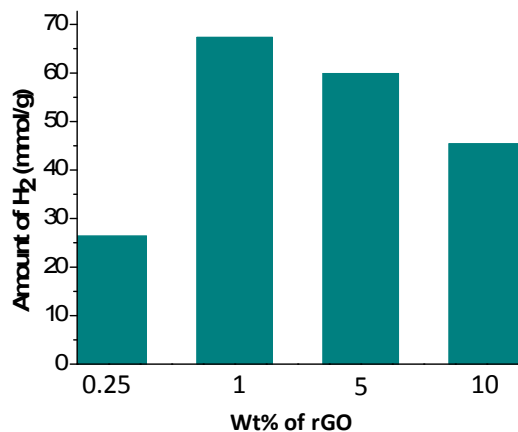


Fig. S11 Effect on hydrogen production for loading of different amount of graphene in NDIPYPZ/sTiO₂-rGO composite.

Table S1. Comparison of hydrogen production activity among different graphene based photocatalysts.

Photocatalyst	Apparent quantum yield (AQY in %)
CdS/ZnO/GO ²	30
Manganese phthalocyanine/graphene ³	0.06
Eosin Y/rGO/Pt ⁴	12.9
CdSe/CdS-Au ⁵	25.4
Graphene-Zn _x Cd _{1-x} S ⁶	1.98
NDIPYPZ/sTiO ₂ -rGO (this report)	28.14

Isotopic experiment

To confirm the source of the hydrogen we have carried out the isotopic experiment. Two different experiments were carried out with $D_2O + \text{dry } CH_3OH$ and $D_2O + CD_3OD$ and the results were incorporated in Table S2 and Fig. S12.

Table S2 Isotopic experiment with different reaction mixture.

Experiment No.	Reaction mixture	Retention time in GC (min)	Area (mVs)
1	1ml D_2O + 300 μl CH_3OH (dry) and 3 mg photocatalyst	1.74	11.39
2	1ml D_2O + 300 μl CD_3OD and 3 mg photocatalyst	1.74	1.5
3	18 ml H_2O + 2 ml CH_3OH and 10 mg of photocatalyst	1.75	64.25
4	Std. H_2 (pure)	1.75	99.29

Note: In the 1st experiment D_2 appeared at the retention time of 1.75 min in the GC, though the evolution of H_2 and HD cannot be ruled out during the photocatalytic process.⁷ But to confirm the generation of D_2 further experiment was carried out with 1ml D_2O in presence of 300 μl CD_3OD where D_2 appeared at the same retention as the previous experiment. Indeed, from the table it is clear that, H_2 and D_2 peak in GC appeared at around same retention time (1.74-1.75 min). This suggests that during the photocatalytic hydrogen generation process, hydrogen was mainly evolved from water, although the contribution of the CH_3OH cannot be ruled out.⁸

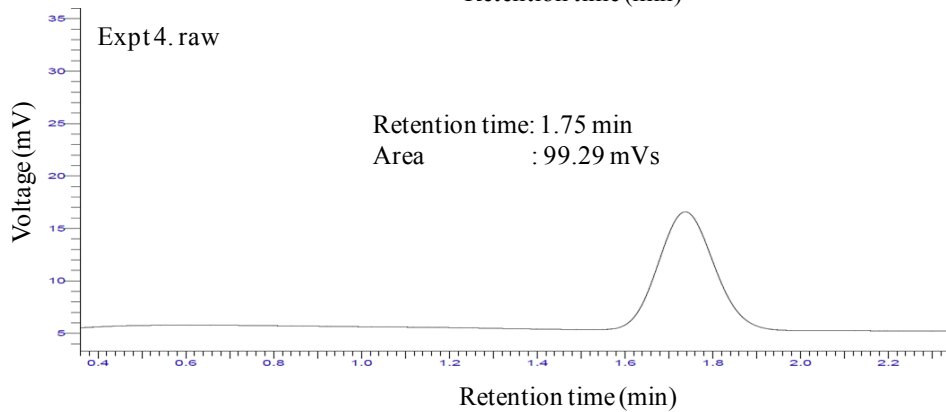
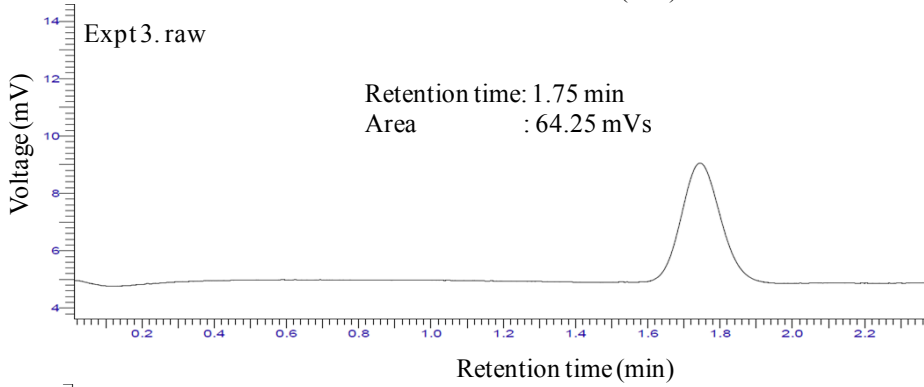
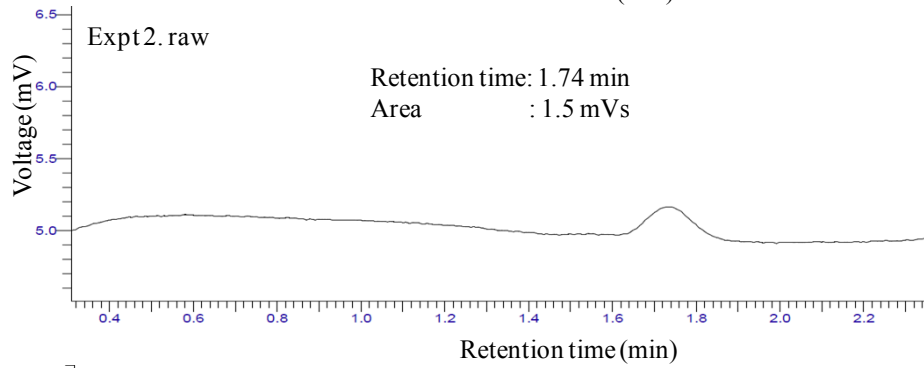
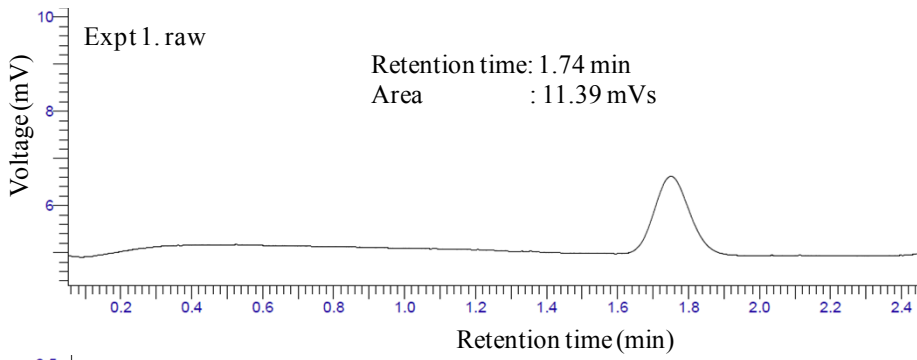


Fig. S12 Action spectra of GC for different photocatalytic experiment.

References

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