#### **Supplementary Information**

## **Experimental section**

## Synthesis of pure PbTiO<sub>3</sub> crystal

Pure phase PbTiO<sub>3</sub> was fabricated through an easy combustion process. All the chemicals used for the research work was of analytical grade. Lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>), titanium dioxide (TiO<sub>2</sub>) and citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) were used as the precursor materials. The citric acid was used as a fuel agent for the reaction system. In a typical synthetic process, all the precursor materials i.e., TiO<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub> and C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> were added to the distilled water preserving a predetermined molar ratio i.e.,1:1:2, respectively and stirred continuously for 3h. The well mixed dispersed solution was gradually evaporated from 80°C to 130°C to achieve a thick viscous gel. The thick viscous gel was then kept at the said temperature to attain a dry gel. The obtained dry gel burnt in the air to form loose powders. The final product was obtained by activating the loose powders in a muffle furnace at 800°C for 4 h.<sup>1</sup>

### Synthesis of B-rGO/PbTiO<sub>3</sub> p-n heterojunction

The B-rGO/PbTiO<sub>3</sub> p-n heterojunction samples were produced by a facile hydrothermal technique. Initially, graphene oxide (GO) was prepared by modified Hummers method.<sup>2,3</sup> In a typical synthetic process, GO (1.5 mg mL-1) was dispersed in 80 mL of deionized water through ultrasonication to obtain a well expoliated graphene oxide. Then after, boric acid (H<sub>3</sub>BO<sub>3</sub>, 9.6 mmol) was introduced into the well expoliated GO solution followed by the addition of single phase PbTiO<sub>3</sub> crystals and stirred continuously at room temperature for 2 h. The mixed suspension solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and the reacted at 180°C for 12 h. After the reaction, the obtained precipitate was washed several times

with excess distilled water and ethanol, and finally dried overnight at 80 °C. Various weight percentages of B-rGO/ PbTiO<sub>3</sub> p-n heterojunction samples were prepared by varying the PbTiO<sub>3</sub> crystal powders i.e., 0.5% (0.5 B-rGO/PT), 1% (1B-rGO/PT), 2% (2B-rGO/PT) and 3% (3B-rGO/PT), respectively. Pure B-rGO nanosheets were also synthesized adopting the same synthetic process in the absence of PbTiO<sub>3</sub>.<sup>4</sup>

#### Characterizations

The phase identification of the prepared samples was examined using Rigaku Ultima IV diffractometer with Cu Ka X-ray radiation ( $\lambda = 1.5$  Å) in the range  $2\theta = 5^{\circ}$ -  $80^{\circ}$ ; scan rate of 5°min<sup>-1</sup>. The surface morphology of the samples was studied in HITACHI S-3400N scanning electron microscopy (SEM) operating at 20kV and Philips TECNAI G2 high resolution transmission electron microscopy (HRTEM) instruments operating at 200 kV. X-Ray photoelectron spectra (XPS) was examined using ESCA+ spectrometer instrument equipped with a monochromatised Al-Ka radiation source (hv = 1486.7ev). The carbon C1s peak at 284.9 eV was taken as reference for binding energy correction. The stretching vibration mode of the materials was studied in JASCO FT/IT-4600 FTIR spectrometer (range of 400-4000 cm<sup>-1</sup>) using KBr pallet as reference material. The Raman spectrum was recorded in a backscattering configuration at room temperature using RENISHAW InVia Raman spectrometer. UV-Vis diffused reflectance spectra analysis was carried out using JASCO 750 UV-visible spectrophotometer (range of 200-800nm) whereas emission spectrum of the samples was recorded by JASCO FP8300 spectrofluorometer at an excitation of 330 nm. TRPL analysis was performed on EDINBURGH PHOTONICS instrument with an excitation wavelength of 280 nm. The photo(electro)chemical (PEC) studies were conducted on IVIUM n STAT electrochemical workstation at room temperature. The working electrode of materials was prepared by

electrophoretic deposition method over fluorine doped tin oxide (FTO) coated surface (1cm x 1cm). An aqueous solution of 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH=6.5) served as an electrolyte in a standard three-electrode cell where FTO-coated materials, commercially available Ag/AgCl electrode and Platinum wire served as working, reference and counter electrodes, respectively. Throughout the PEC studies, a 300W Newport Xe lamp equipped with a UV-light cut off filter ( $\lambda \ge 420$ nm) was used as a visible light irradiation source. Neat FTO doesn't show any photoresponse in the solution. A 0.2V of bias for 270 sec at each 30 sec time interval was applied to evaluate the transient photocurrent (I-t) response. The electrochemical impedance spectroscopy (EIS) measurements were carried out in 10<sup>6</sup> Hz to 0.01 Hz frequency at zero bias potential under open circuit reaction condition. Mott-Schottky plots was analyzed with a potential of 25 mV at 500Hz and 1000 Hz frequency.

# Photocatalytic H<sub>2</sub> evolution

The photocatalytic H<sub>2</sub> evolution was carried out in a sealed quartz batch reactor of capacity 100 mL. The photocatalyst (20 mg) sample was suspended in 20 mL of an aqueous solution containing 10 vol % methanol solution (hole scavenger) and stirred continuously to prevent the photocatalyst to sediment at the bottom of batch reactor. A 125 W medium-pressure Mercury lamp with a UV cutoff filter ( $\lambda \ge 420$ nm) served as a source for visible light. Before the irradiation, nitrogen gas was purged continously into the batch reactor (30 min) to eliminate all the dissolved O<sub>2</sub>. Lastly, the gaseous H<sub>2</sub> evolved was collected by the downward water displacement method and examined by Aligent-78903 gas chromatography instrument using a 5 Å molecular sieve column with a thermal conductivity detector. The wavelength dependent AQY was carried out by applying Xenon lamp (300 W) with different band pass filters ( $\lambda$ =420±5 nm, 450±5 nm).

## Calculation of energy conversion efficiency

Conversion efficiency (%) = (Stored chemical energy/incident light energy)  $\times$  100

The approximate average incident radiation power on the 2B-rGO/PT photocatalyst under light irradiation was calculated to be 120 and stored chemical energy for the same was calculated as

Energy stored = (mol of H<sub>2</sub> produced)  $\times \Delta$  Hc

where  $\Delta$  Hc is the Hydrogen combustion (H<sub>2</sub> +1/2O<sub>2</sub>= H<sub>2</sub>O) produces 285.8kJ/mol

We have calculated the energy stored per unit of time (power) for the rates of H<sub>2</sub> evolution. The highest rate of H<sub>2</sub> evolution was obtained for 2B-rGO/PT photocatalyst, i.e. 293.79  $\mu$ mol/h = 0.081  $\mu$ mol/s under visible-light irradiation using sacrificial reagent (10 vol% MeOH solution).

Power (H<sub>2</sub>) =  $(0.081 \times 10^{-6} \text{ mol H}_2/\text{s}) \times (285.8 \times 10^3 \text{ J/mol H}_2)$ 

 $= 23.14 \times 10^{-3} \text{ J/s} = 0.02314 \text{ W} = 23.14 \text{ mW}$ 

Thus, the conversion efficiency (%) = (Stored chemical energy/incident light energy)  $\times$  100

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=(23.14/120)\times 100
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= 19.28%

#### Calculation of apparent quantum yield of 2B-rGO/PT photocatalyst at $\lambda$ =420nm

Apparent Quantum yield (%) =  $\frac{Number \ of \ reacted \ electrons}{Number \ of \ incident \ photons} \times 100$ 

= 2 X Number of Hydrogen molecules Number of incident photons X100

$$= \frac{2 X NH^2}{N_i} X 100$$

$$\mathbf{N_i} = \frac{I X A X t X \lambda}{h X c}$$

$$= \frac{5.5 X 10^{-3} X 19.625 X 3600 X 420 X 10^{-9}}{6.626 X 10^{-34} X 3 X 10^8}$$

$$= 8.2 X 10^{20}$$

$$\frac{2 X 6.02 X 10^{23} X 22.3 X 10^{-6}}{0.000}$$

Therefore,  $AQY = 8.2 \times 10^{20} \times 100$ 

N is the number of electrons, photons or molecules, I is the light intensity (5.5mW/cm<sup>2</sup>), A is irradiation area with radius 2.5 cm, t = 3600s,  $\lambda$ = 420 nm, h =6.626×10-34 J·s and c= 3.0×10<sup>8</sup> m/s.

The photocatalytic performance of all the synthesized materials using 300W Xe lamp with 420 nm cut-off filter in presence of methanol serving as sacrificial agent. The amount of sacrificial agent was identical for all the photocatalysts. Control experiment was performed in absence of light irradiation or photocatalyst, suggesting hydrogen gas will be generated through photocatalytic reactions. As shown in the fig. S10 (a), the p-n junction materials showed enhanced amount of hydrogen gas in comparison to the bare materials. The highest photocatalytic H<sub>2</sub> production of 279.03 µmol/h was observed for 2B-rGO/PT photocatalyst following the same trend as that observed for photocatalytic H<sub>2</sub> production using a 125 W medium-pressure Mercury lamp with a UV cutoff filter ( $\lambda \ge 420$ nm). In addition, the apparent quantum yield was investigated for the best photocatalyst i.e., 2B-rGO/PT photocatalyst with different monochromatic irradiation ( $\lambda$ =420±5 nm, 450±5 nm and 550±5 nm) as shown in fig. S10 (b), where the apparent quantum yield trend line shows in agreement with UV-Vis diffuse reflectance spectra. The highest apparent quantum efficiency value was estimated to be about 3.27 % at 420 nm, indicating H<sub>2</sub> gas evolution is related to the light induction.<sup>5, 6, 7</sup> Further, the stability and reproducibility of 2B-rGO/PT sample was subjected to four consecutive H<sub>2</sub> evolution photoreaction cycles, fig. S10 (c). The photocatalyst showed no substantial

deactivation for  $H_2$  evolution after multiple repeated cycles, depicting high photoactivity of the material.



Fig. S1 (a) TEM (b) HRTEM (c) SAED pattern of PbTiO<sub>3</sub>



Fig. S2 (a)TEM (b) SAED pattern of B-rGO



Fig. S3 XRD pattern of GO



Fig. S4 FTIR spectra of GO and B-rGO material



Fig. S5 ID/IG ratio of GO, B-rGO, 2B-rGO/PT



Fig. S6 XPS spectra of (a) 2B-rGO/PT in the region of B1s and (b) rGO in the region of C1s



Fig. S7 Plot of  $(\alpha hv)^2$  vs hv of UV-Vis DRS spectrum (a)PbTiO<sub>3</sub> and (b)B-rGO



Fig. S8 M-S plot of (a) rGO in different frequencies (b) comparison of rGO and B-rGO in 500 Hz



Fig. S9 Post characterization (a) XRD (b) FTIR and (c) FESEM image of 2B-rGO/PT heterojunction.



Fig. S10 (a) Photocatalytic H<sub>2</sub> evolution of B-rGO/PbTiO<sub>3</sub> p-n junction, (b) Wavelengthdependent apparent quantum yield (AQY), and (c) repeatability test of 2B-rGO/PT photocatalyst.

Semiconduct	Band gap	Valence band (eV)	Conduction band
or	(eV)		(eV)
B-rGO	2.70	2.00	-0.70
PbTiO <sub>3</sub>	2.88	2.27	-0.61

Table. S1 Calculated values of valence and conduction band edge for B-rGO and PbTiO<sub>3</sub>

Table. S2 Summary of average lifetime of semiconductors

Semiconductor	$\tau_1$ (ns)	β1%	$\tau_2$ (ns)	β2%	$\tau_3(ns)$	β <sub>3</sub> %	$\tau_{av}(ns)$
PbTiO <sub>3</sub>	15.98	13.13	154.50	1.01	2.03	85.85	51.43
2 B-rGO/PT	14.95	12.87	67.74	1.98	3.70	85.14	20.45

Table. S3 R<sub>ct</sub> of the synthesized materials

Materials	Electron-transfer Resistance (R <sub>ct</sub> )
	in Ω
PbTiO <sub>3</sub>	17.26 x 10 <sup>5</sup>
0.5 B-rGO/PT	9.540 x 10 <sup>5</sup>
1 B-rGO/PT	6.152 x 10 <sup>5</sup>
2 B-rGO/PT	2.989 x 10 <sup>5</sup>
3 B-rGO/PT	7.652 x 10 <sup>5</sup>

Table. S4 Comparison of photocatalytic hydrogen evolution activity for 2B-rGO/PT p-n junction with other promising photocatalysts.

Photocatalyst	Light source			Sacrificial agent	H <sub>2</sub> evolution	Reference
					(µmol h <sup>-1</sup> g <sup>-1</sup> )	
1 wt% Cu doped-	125	W	medium	Methanol	900	8

PbTiO <sub>3</sub>	pressure Hg lamp,			
	λ≥420nm			
Pt(P.D.)-	300 W Xe lamp	Methanol	160	9
MnOx(P.D.)/PbTi				
03				
PT/LC(7/3)	150W Xe lamp,	Methanol	8589.25	10
	λ≥400nm			
Pt/PbTiO <sub>3</sub> with	300 W Xe lamp	Triethanolamine	436.5	11
the islands				
O-gC <sub>3</sub> N <sub>4</sub> /2B-rGO	500WXe lamp with an	Triethanolamine	273.1	12
	AM1.5 filter			
2B-rGO/PT	125 W medium	Methanol	14689.5	This work
	pressure Hg lamp,			
	λ≥420nm			
	300 W Xenon lamp,	Methanol	13951.5	
	λ≥420nm			

## References

- [1] R. Yimei, G. Fengcai, W. Junzhen, S. Zhixing and Z. Shulan, *Trans. Tianjin Univ.* 1995, 1, 59–62.
- [2] D.K. Padhi, T.K. Panigrahi, K. Parida, S.K. Singh and P.M. Mishra, ACS Sustain. Chem. Eng. 2017, 5, 10551-10562.
- [3] W.S. Hummers Jr and R.E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339-1339.
- [4] Q. Hao, X. Xia, W. Lei, W. Wang and J. Qiu, *Carbon*, 2015, **81**, 552-563.
- [5] R. Cao, H. Yang, S. Zhang and X. Xu, Appl. Catal., B., 2019, 258, 117997.

- [6] B. Li, Y. Si, B.X. Zhou, Q. Fang, Y.Y. Li, W.Q. Huang, W. Hu, A. Pan, X. Fan and G.F. Huang, ACS Appl. Mater. Interfaces, 2019, 11, 17341-17349.
- [7] H. Gao, R. Cao, S. Zhang, H. Yang and X. Xu, ACS Appl. Mater. Interfaces, 2018. 11, 2050-2059.
- [8] K.H. Reddy and K. Parida, *ChemCatChem*, 2013, 5, 3812-3820.
- [9] R. Li, Y. Zhao and C. Li, Faraday discussions, 2017. 198, 463-472.
- [10] L. Paramanik, K.H. Reddy, S. Sultana and K. Parida, *Inorg. Chem.* 2018, 57, 15133-15148.
- [11]G. Liu, L. Ma, L.C. Yin, G. Wan, H. Zhu, C. Zhen, Y. Yang, Y. Liang, J. Tan and H.M. Cheng, *Joule*, 2018, 2, 1095-1107.
- [12] L.K. Putri, B.J. Ng, W.J. Ong, H.W. Lee, W.S. Chang, S.P. Chai, J. Mater. Chem. A, 2018, 6, 3181-3194.