

Supporting Information

Defect engineering in conjugated polyimide for promoting visible-light-driven photocatalytic benzylamine oxidation

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Materials. Melamine (MA), Pyromellitic anhydride (PD), NaHCO₃, Isopropanol (IPA), Triethanolamine (TEOA) β -Carotene, Methanol, Acetonitrile, Superoxide dismutase (SOD), Hydrochloric acid (HCl) were purchased from Aladdin Chemical Co., Ltd., China. The purity of all reagents is analytical (AR) and not further purified.

Preparation of PI. 0.84 g (6.7 mmol) of MA and 2.18 g (10 mmol) of PD were ground in an agate mortar until homogeneous. The mixture was transferred to a covered corundum crucible (semi-closed system) and heated to 325 °C at a heating rate of 7 °C min⁻¹ for 4 h. The resulting solid was ground well and washed with water at 50 °C and alcohol to obtain a yellow powder sample and labeled as PI.

Characterizations. The scanning electron microscope (SEM) image was obtained on a JEOL JSM 4800F SEM. Transmission electron microscopy (TEM) images and HRTEM images were carried out on a JEM-2100F microscope at an acceleration voltage of 200 kV. The X-ray diffraction (XRD) patterns were gained on a Bruker AXS D8 Focus with filtered Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet iS10 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) was tested using an ESCALABMKII spectrometer with an Al-K α achromatic X-ray source. N₂ adsorption-desorption isotherms and pore-

size distributions were obtained at 77 K using a Quanta chrome Auto sorb iQ apparatus. Prior to the experiments, the samples were degassed under vacuum at 120 °C for 12 h. The UV-vis diffuse reflectance spectra (DRS) measurements were gathered on a UV-2600 UV-vis spectrophotometer (Shimadzu), and BaSO₄ was used for a reference. Photoluminescence (PL) spectra were measured on a VARIAN Cary Eclipse spectrophotometer with the excitation wavelength of 380 nm. The electron paramagnetic resonance (EPR) measurements were carried out on a JEOL JES-FA200 spectrometer. Element analysis is tested on EMGA-930. Thermogravimetric/differential thermal (TG/DTA) analysis in air with a heating rate of 7 °C min⁻¹.

Electrochemical Analysis. Electrochemical measurements were conducted with a CHI660E Electrochemical Workstation in a standard three electrode cell using a Pt plate, Ag/AgCl electrode and sample deposited fluoride-tin oxide (FTO) as counter electrode, reference electrode and the working electrode, respectively. The electrolyte solution is 0.2 M Na₂SO₄ aqueous solution. Working electrode manufacturing method is as follows: The 20 mg catalyst is dispersed in 2 ml of ethanol, and then a bulk solution is formed by ultrasound. Transferring suspensions onto a 1×5 cm² FTO conductive glass using a spin-coating method. The exposure area of the catalyst is 3 cm². Finally, working electrode is obtained by drying at room temperature. For photocurrent measurement (*i-t* curves), a 300 W (CELHXF300, AULIGHT) Xe lamp was used as the light source and using a CHI700E electrochemistry station for testing in 0.2 M Na₂SO₄ under visible-light illumination at -0.4 V. The working electrode is irradiated

from the back (FTO substrate) to reduce the effect of the experiments. Electrochemical impedance spectra (EIS) was tested using a CHI700E electrochemistry station in 0.2 M Na₂SO₄ under visible-light illumination with the frequency ranging from 0.01 Hz to 10 kHz at -0.2 V. The EIS data were recorded using a normal three-electrode system, in which samples onto a 1×3 cm² FTO glass with an active area of ca. 2.0 cm² were prepared as the working electrode, Pt wire as a counter electrode, and Ag/AgCl as a reference electrode.

Photocatalysis for selective aerobic oxidation of benzylamine. The photocatalytic reaction was carried out on WATTCAS Parallel Light Reactor (WP-TEC-1020HPL) with 10 W COB LED. 0.2 mmol benzylamine and 5 mL acetonitrile were added into 20 mL quartz tube, 5 mg of catalyst was added for ultrasonic uniform dispersion. The quartz tube is placed under the LED light source of 420-425 nm and reacts for a period of time. After the illumination, the reaction solution was centrifuged and the products in the supernatant were detected by GC-Agilent 7820 chromatography. The chromatographic column was 19091J-413 with a diameter of 30 m × 0.320 mm. The nitrogen flow rate was 6 mL/min and the split ratio was 10:1. We set the temperature of the column box at 80 °C, heat it up to 280 °C at a rate of 66 °C/min, and start to run after keeping it for a period of time.

Photocatalytic hydrogen production. The photocatalytic activities of the as-prepared samples were investigated by the water splitting hydrogen production under visible light irradiation. The photocatalytic water decomposition reaction was carried out in a quartz reaction vessel connected to a closed gas circulation and evacuation system. 10

mg of as-prepared sample was suspended in 60 mL of aqueous solution containing triethanolamine as the sacrificial electron donor. 3 wt % Pt was loaded onto the surface of the catalyst by an in situ photo deposition method using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as precursor. The suspension was thoroughly degassed and irradiated with a 300 W Xe lamp equipped with a 420 nm cut-off filter. The temperature of the reactant solution was maintained at 283 K by a flow of cooling water during the reaction. The evolved gas was analyzed every 0.5 h by gas chromatography equipped with a thermal conductive detector. For the stability test, the system was evacuated every 3 h and repeated for 4 times. The apparent quantum yield (AQY) for H_2 evolution was carried out in a quartz reaction vessel connected to a closed gas circulation and evacuation system. 10 mg of as-prepared sample was suspended in 60 mL of aqueous solution containing triethanolamine as the sacrificial electron donor. 3 wt% Pt was loaded onto the surface of the catalyst by an in situ photo deposition method using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as precursor. The suspension was thoroughly degassed and irradiated using 300 W Xe lamp equipped with different band-pass filter (400 ± 20 nm, 420 ± 20 nm, 450 ± 20 nm, respectively). The spot diameter is 1 cm^2 . The distance between the light and the reaction liquid surface is about 12 cm. The average intensity of irradiation was measured by Beijing Normal University UV-420 optical power meter. The AQY was calculated based on the following equation:

$$\text{AQY} = \frac{N_e}{N_p} \times 100\% = \frac{2 \times M \times NA \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

where N_e is the amount of reaction electrons, N_p is the incident photons, M is the

amount of H_2 molecule, N is Avogadro constant, h is the Planck constant, c is the speed of light, S is the irradiation area, P is the intensity of the irradiation, t is the photoreaction time, and λ is the wavelength of the monochromatic light.

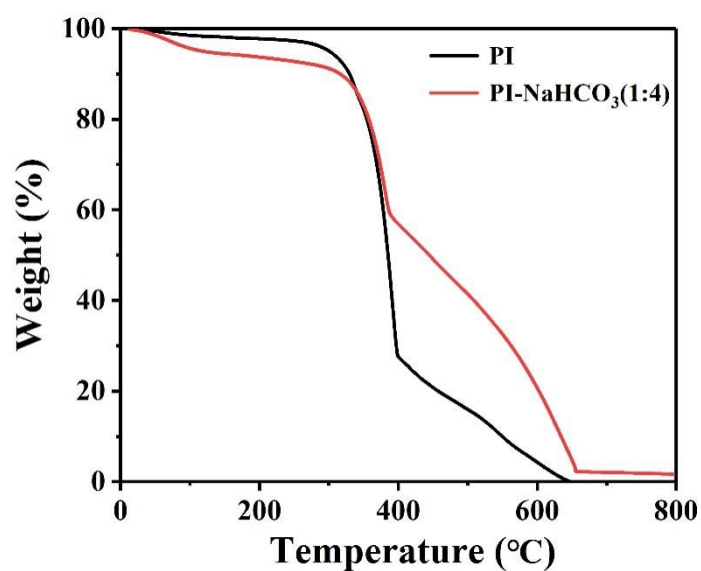


Fig. S1 TGA curve of the PI and PI-NaHCO₃ (1:4).

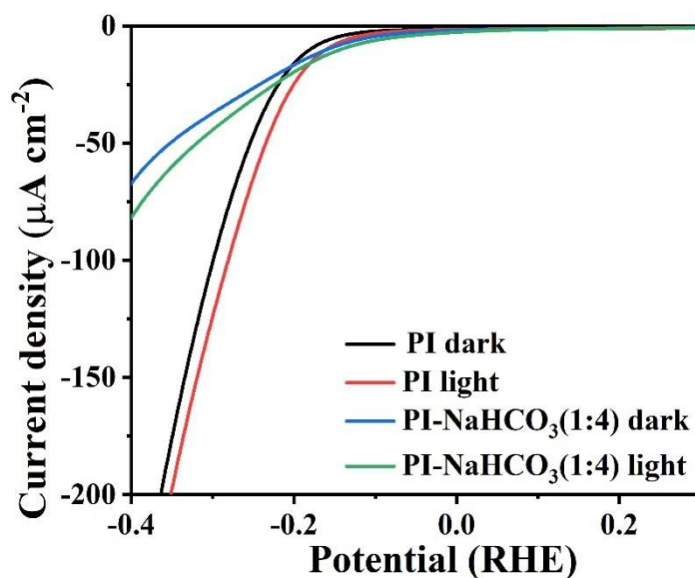


Fig. S2 LSV curves of PI and PI-NaHCO₃ (1:4) under dark and light.

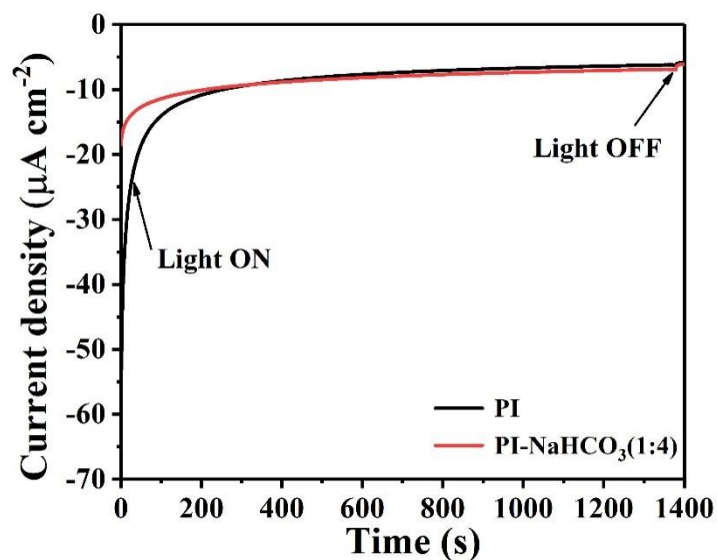


Fig. S3 I-t stability curve of PI and PI-NaHCO₃ (1:4) under visible-light irradiation.

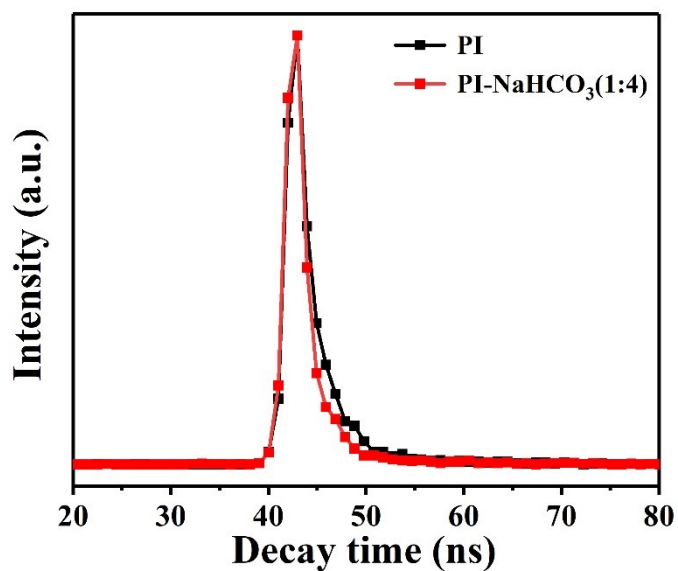


Fig. S4 Time-resolved fluorescence kinetics monitored at the corresponding emission peaks of PI and PI-NaHCO₃ (1:4).

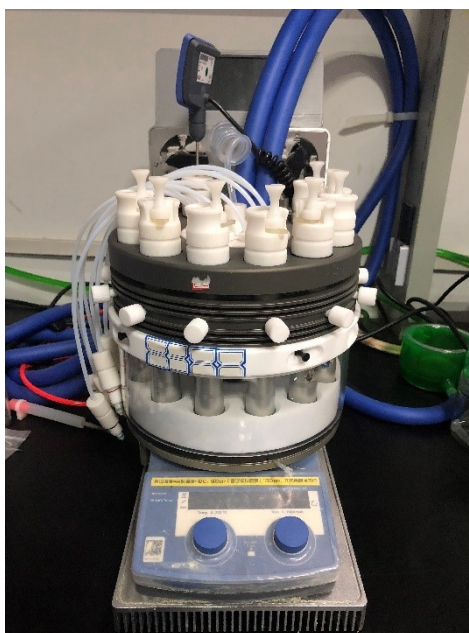


Fig. S5 Image of reactor for photocatalytic selective oxidation of benzylamine.

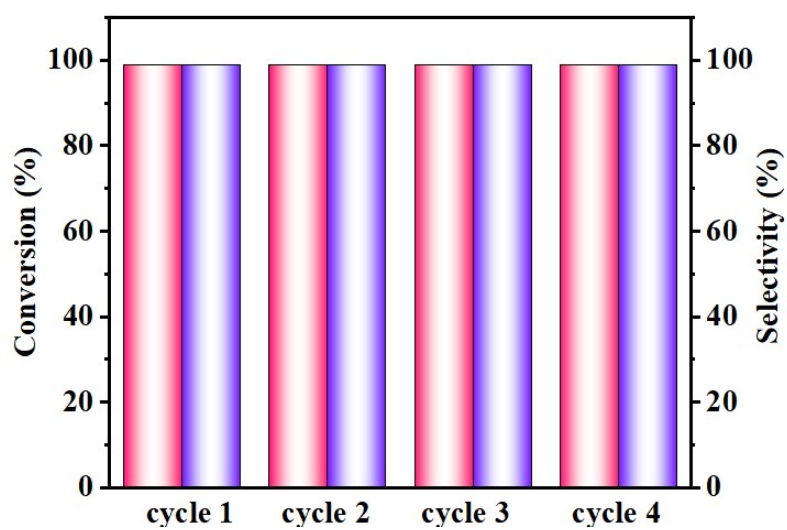


Fig. S6 The recycling test of PI-NaHCO₃ (1:4) photocatalyst for the LED at 420-425 nm selective aerobic oxidation of benzylamine.

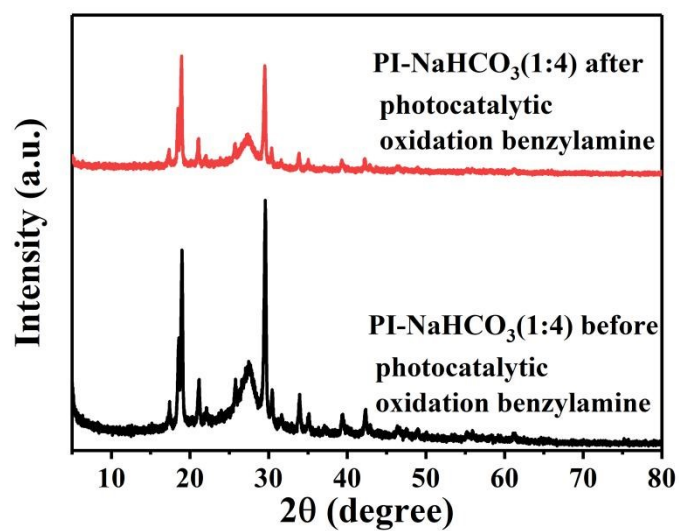


Fig. S7 The XRD after photocatalytic oxidation of benzylamine by PI-NaHCO₃ (1:4).

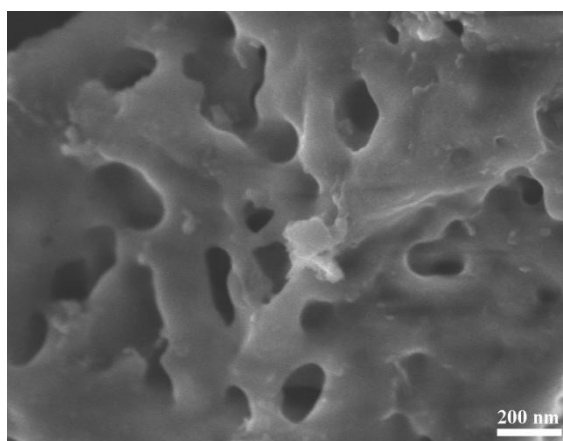


Fig. S8 The SEM after photocatalytic oxidation of benzylamine by PI-NaHCO₃ (1:4).

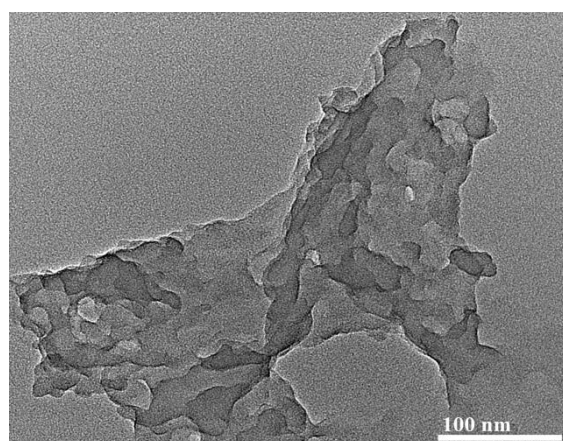


Fig. S9 The TEM after photocatalytic oxidation of benzylamine by PI-NaHCO₃ (1:4).

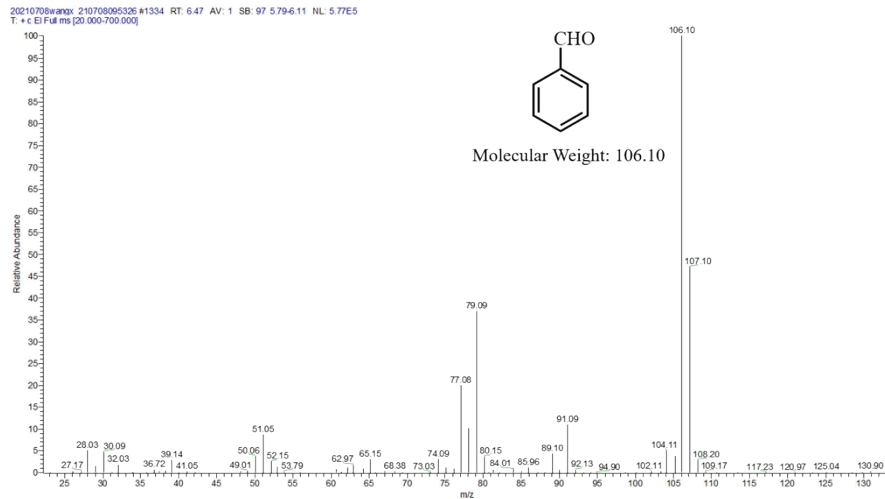


Fig. S10 GC-MS trace of benzaldehyde.

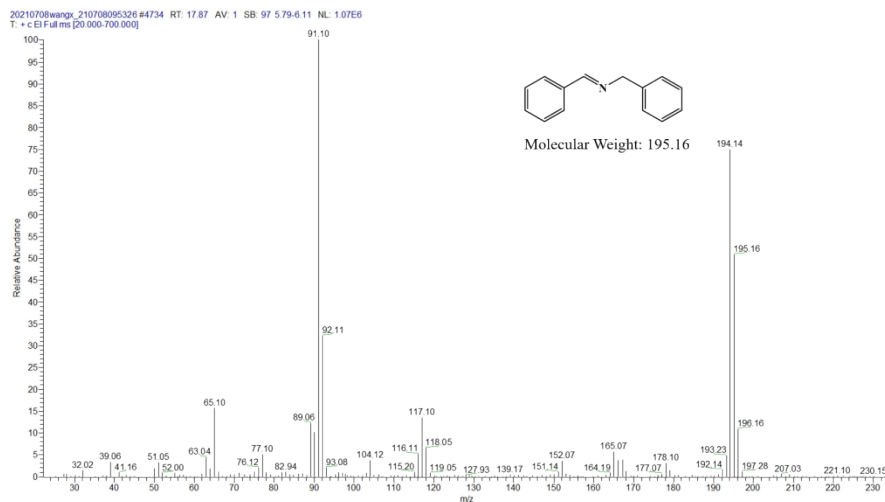


Fig. S11 GC-MS trace of N-benzyl-1-phenylmethanimine.

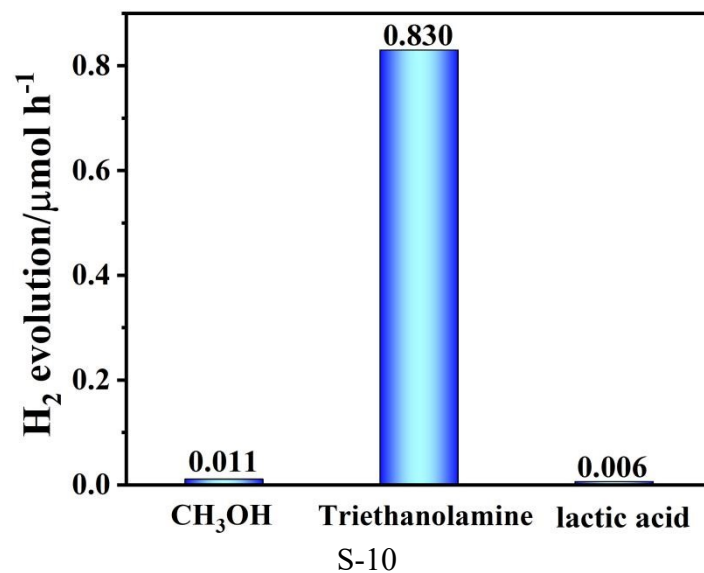


Fig. S12 Photocatalytic H₂ evolution with PI-NaHCO₃ (1:4) at different sacrificial agents.

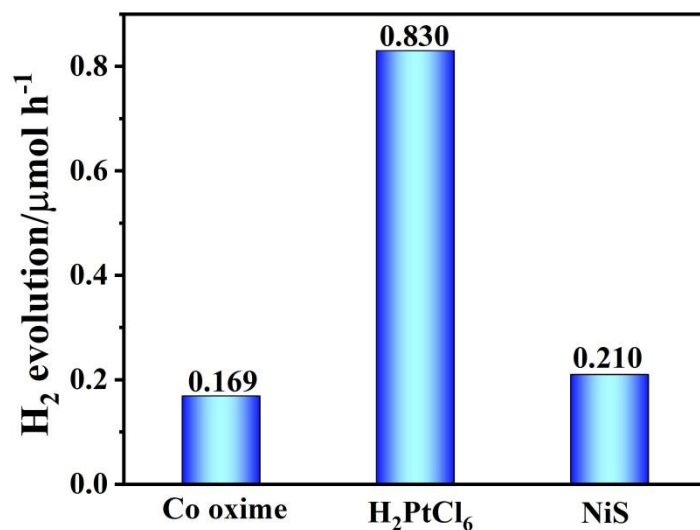


Fig. S13 Photocatalytic H₂ evolution with PI-NaHCO₃ (1:4) at different cocatalysts.

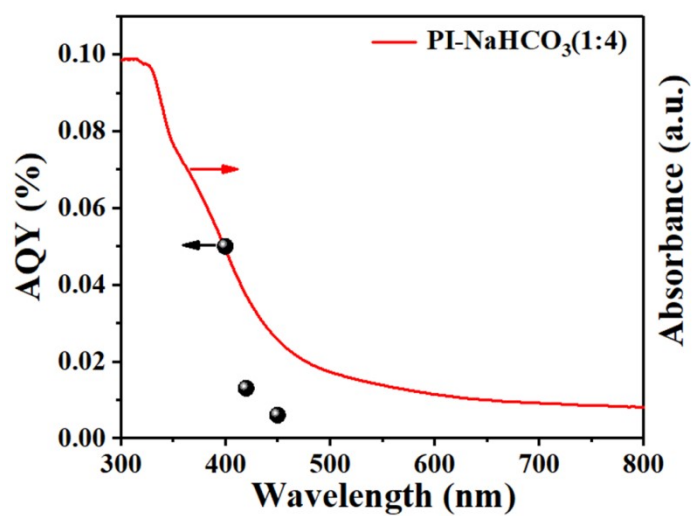


Fig. S14 The wavelength dependence of apparent quantum yield (AQY) with PI-NaHCO₃ (1:4) at different irradiation wavelengths.

Table S1. EDX analysis results of PI and PI-NaHCO₃ (1:4).

Sample	C/at%	N/at%	O/at%
PI	37.27	42.58	20.15
PI-NaHCO ₃ (1:4)	41.02	47.00	11.98

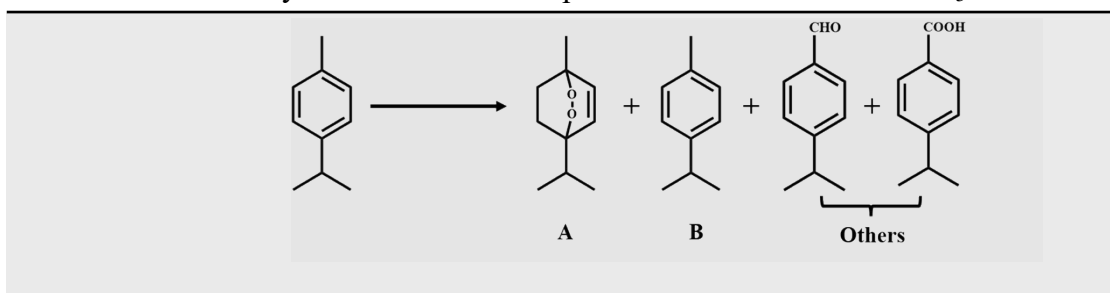
Table S2. Elemental analysis results of PI and PI-NaHCO₃ (1:4).

Sample	C/wt%	N/wt%	O/wt%	H/wt%
PI	56.366	15.001	25.624	3.009
PI-NaHCO ₃ (1:4)	59.279	15.361	21.668	3.692

Table S3. The Fluorescence decay lifetimes and their percentages of photoinduced carriers in the PI and PI-NaHCO₃ (1:4).

$$(y=A_1*\exp(-x/\tau_1)+A_2*\exp(-x/\tau_2))$$

Sample	τ_1 (ns)	τ_2 (ns)	A ₁	A ₂	τ_{avg} (ns)
PI	1.3846	4.2673	6.408	0.144	1.5716
PI-NaHCO ₃ (1:4)	1.1640	/	7.264	/	1.1640

Table S4. Photocatalytic oxidation of α -terpinene over PI and PI-NaHCO₃.

Entry	Catalyst	λ (nm)	atmosph ere	Time/ h	Conv. ^[a] / %	Sel. ^[b] /%		
						A	B	C
						ascari dole	p- cymene	others
1	/	420	Air	5	5.38	trace	5.38	trace
2	PI-NaHCO ₃ (1:4)	/	Air	5	trace	-	-	-
3	PI-NaHCO ₃ (1:4)	420	Ar	5	3.44	trace	3.44	trace
4	PI	420	Air	5	90.73	14.36	71.05	5.32
5	PI-NaHCO ₃ (1:1)	420	Air	5	92.95	27.32	63.43	2.20
6	PI-NaHCO ₃ (1:4)	420	Air	5	100	17.19	79.74	3.07
7	PI-NaHCO ₃ (1:8)	420	Air	5	93.79	13.71	75.12	4.96

Experimental conditions: 5 mL of acetonitrile, 0.1 mmol of α -terpinene, PI-NaHCO₃ (1:4) (5.0 mg) and irradiated with LED at 420-425 nm. [a] Conversion; [b] Selectivity.