

Experimental Details

Materials

Cesium carbonate (Cs_2CO_3), lead bromide (PbBr_2), oleic acid (OA), oleylamine (OAm), octadecene (ODE), methyl acetate (MeOAc), Merck orange PPV copolymer, toluene, and titanium butoxide (TBOT) were purchased from Sigma-Aldrich (U.S.A).

Material characterizations

Powder X-ray diffraction (XRD) patterns were analyzed using a Bruker D8 Advance with target Cu $\text{K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). High-resolution transmission electron microscopy (HR-TEM) images were obtained using a JEOL NEO ARM with 100 kV and a dual SDD EDS system. X-ray photoelectron spectroscopy (XPS) data were analyzed using a Thermo Fisher Scientific theta probe vane system. FT-IR spectra were recorded by a Nicolet 6700 Spectrometer from pelletized KBr powder.

UV-Vis spectroscopy analysis was performed using JASCO V-730 with absorption spectra. Photoluminescence (PL) spectra time correlated single photon counting (TCSPC) were measured using a PicoQuant FluoTime 300 EasyTau with a 405-nm pulsed laser diode.

Synthesis of CsPbBr_3 NCs

CsPbBr_3 NCs (PNCs) were synthesized using hot injection. First, 0.47 g (1.05 mol) of Cs_2CO_3 , 1.5 ml of OA and 20 ml ODE were mixed in a three-neck flask (100 ml). While stirring, the mixture was vacuumed at 100 °C for 1 h then heated to 140 °C under N_2 gas before injection until Cs_2CO_3 had fully reacted with OA. Then 0.407 g (1.05 mol) of PbBr_2 was mixed with 25 ml of ODE in another flask (100 ml) and vacuumed at 120 °C for 1 h. During the drying process, 1.5 ml of OA and OAm were heated at 120 °C and injected into the PbBr_2 solution to form Pb-oleate. The temperature of the mixture was increased to 170 °C and 2 ml of Cs-oleate was quickly injected and quenched by immersing the flask in an ice-water bath. After synthesis, PNCs twice the amount of MeOAc was added into PNCs dispersion and centrifuged at 7500 rpm for 5 min twice to remove excess ligands. After washing, precipitates were re-dispersed in toluene for further use.

Synthesis of $\text{CsPbBr}_3/\text{TiO}_x$ composites

The amount of CsPbBr_3 in toluene was adjusted into 1 mg ml^{-1} by evaporating all solvent and weighing. The 20 μl of TBOT was pre-mixed in 1 ml of toluene and added dropwise to 10 ml of PNCs dispersion while stirring. After injection, the mixture was stirred for 3 h at 40% relative humidity. After reaction, the solution was centrifuged at 5000 rpm for 5 min, then precipitates were dried for 24 h under vacuum.

Synthesis of amorphous TiO_2 nanoparticles

Amorphous TiO_2 nanoparticles (control TiO_x) were synthesized by above mentioned composite synthesis without CsPbBr_3 PNCs in toluene via hydrolysis reaction.

Photocatalytic activity test

Merck orange PPV copolymer is a light-emitting polymer that is widely used in light-emitting diodes (LEDs). To evaluate photocatalytic activity in toluene as harsh condition, a material that dissolves in non-polar solvent and that has stable structure was chosen. Then 10 mg of $\text{CsPbBr}_3/\text{TiO}_x$ heterostructures was dispersed in 100 ml PPV copolymer solution ($1.0 \times 10^{-5} \text{ mg ml}^{-1}$) and stirred in darkness for 30 min to adjust the adsorption equilibrium. After stabilization, the solution was irradiated with visible light of AM 1.5g spectra condition with 100 mW cm^{-2} using white to green LED (Fiber Optic Korea CO.,

LTD). A sample of the solution was taken after every hour of irradiation, then centrifuged to remove powder. Photocatalytic efficiency was analyzed by comparing the absorption

ns of the solutions. CO₂ reduction experiment was conducted with dried sample powder in a sealed dry flask. For CO₂ conversion activity, 20 mg of powder was dried in a three-neck flask and purged with CO₂ gas at 1 atm (99.995%, Air Korea Co., LTD) for 10 min. A purged flask was sealed with rubber sleeve septa and placed above the LED. Every hour, a 0.5-ml sample of reacted gases was drawn then analyzed using gas chromatography (ChroZen GC Co., LTD), a thermal conductivity detector (TCD) and a flame ionization detector (FIB). All the photocatalytic reactions were performed under sunlight, white LED and green LEDs with steady light intensity (Fig. S11 and Table S3).

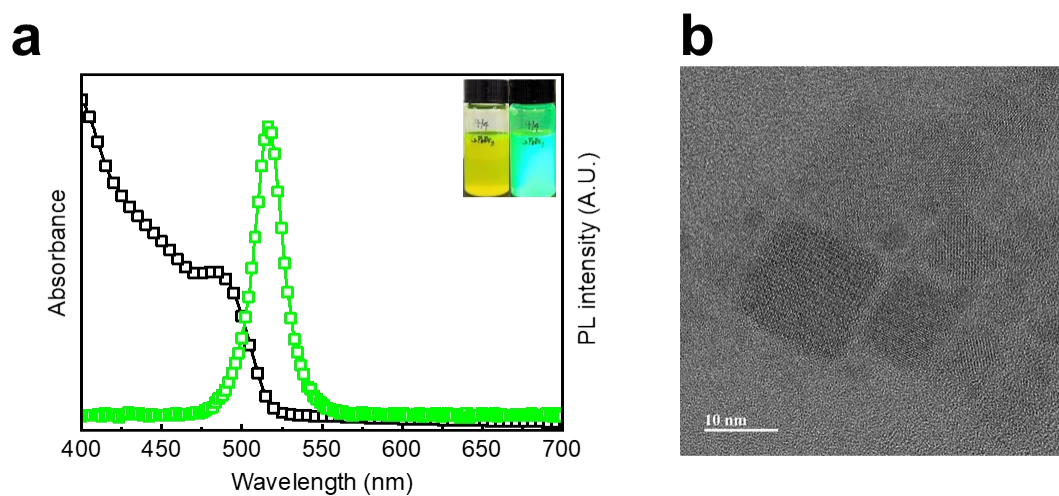


Fig. S1 (a) UV-vis absorption and PL spectra (Inset: photographs of solution under room light (left) and UV light with a wavelength of 365 nm (right)) and (b) a high-resolution TEM image of synthesized CsPbBr₃ PNCs.

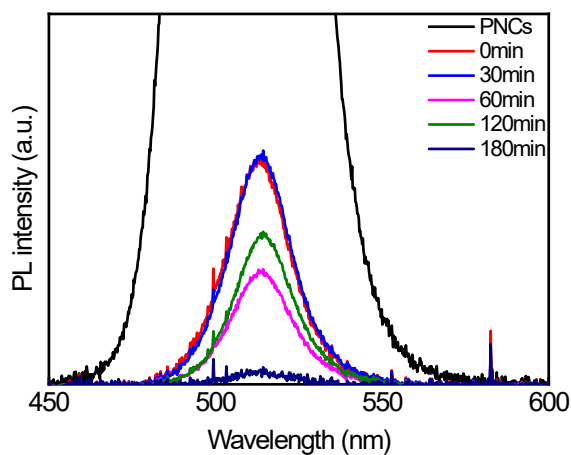


Fig. S2 PL intensity of CsPbBr₃/TiO_x heterostructures with different hydrolysis duration.

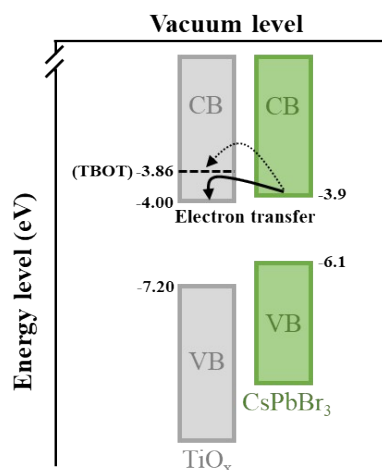


Fig. S3 Scheme of energy level and electron transfer on CsPbBr₃ PNCs, TiO_x and TBOT

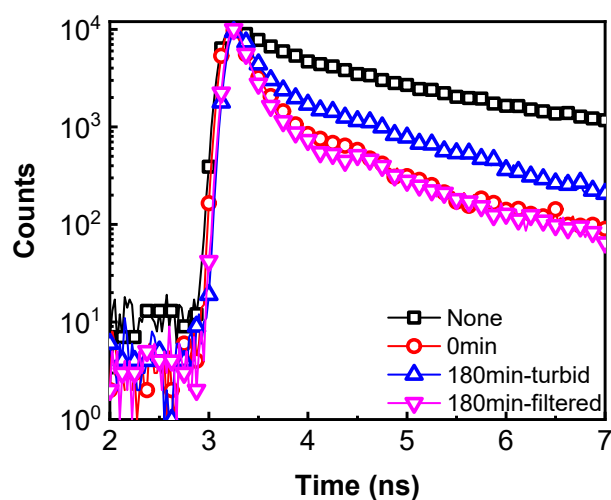


Fig. S4 Time-resolved PL spectra of CsPbBr₃ PNCs, hydrolysis of PNCs/TBOT 0min, 180min-turbid and 180min-filtered samples

We think about possible mechanisms that induce such gradual increase of PL lifetime in composites with hydrolysis time. First, we considered energy level of TBOT and TiO_x, which higher (deeper) work function could extract electrons more efficiently from CsPbBr₃ PNCs (conduction band minimum (CBM) ~ -3.9 eV).²⁸ Using scanning Kelvin probe (SKP5050, KP technology inc.), we measured work function of TBOT and TiO_x and it was -3.86 and -4.01 eV, respectively. These indicate that TiO_x can extract electrons from CsPbBr₃ PNCs than can TBOT (Fig. S3). Therefore, electron transfer rate is not a reason of longer PL lifetime in CsPbBr₃/TiO_x composites than in CsPbBr₃/TBOT.

Second, we considered that PNCs aggregate during the hydrolysis of TBOT and result in increase of PL lifetime^{29,30} because the color of PNC solution gradually changes from bright green to turbid yellow with hydrolysis (inset of Fig. 1b) due to aggregation of nanoparticles and we measured the PL lifetime of the turbid solution without any filtration.

To investigate the effects of aggregation of nanoparticles on PL lifetime, we performed the experiment again and compared the PL lifetime of a CsPbBr₃/TBOT solution without hydrolysis (marked "0 min" in Fig. S4), a turbid solution after 180 min of hydrolysis (marked "180 min-turbid" in Fig. S4), a supernatant solution of "180 min-turbid" solution after centrifugation (marked "180 min-filtered" in Fig. S4). PL lifetime decreased directly after addition of TBOT ("0 min" sample)

and increased with hydrolysis of TBOT (“180 min-turbid” sample) as shown in initial manuscript (Fig. S4). “180 min-filtered” sample showed decreased PL lifetime compared to the “180 min-turbid” sample therefore, we attribute the increase of PL lifetime upon hydrolysis of TBOT to the artifact that nanoparticles aggregate upon hydrolysis and result in long PL lifetime (Fig. S4).^{29, 30} The aggregated nanoparticles in solution after hydrolysis of TBOT can be confirmed by SEM image (Fig. S5) and the opaque solution color (inset of Fig.1b).

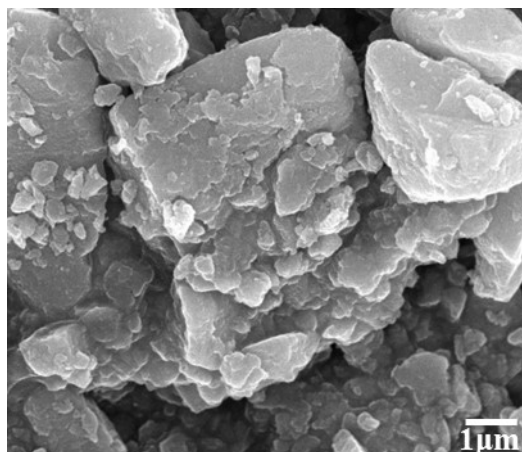


Fig S5. SEM image of a 180 min-turbid sample

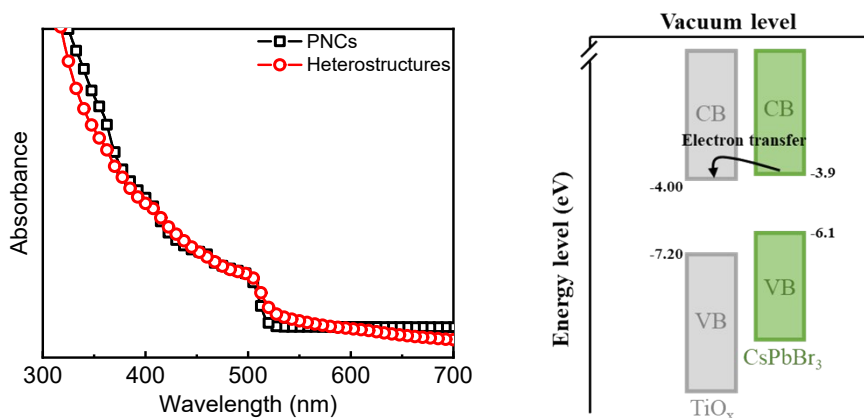


Fig. S6 (a) Absorption spectra of CsPbBr₃ PNCs and heterostructures and (b) electron transfer mechanism between the interface of CsPbBr₃/TiO_x composites.

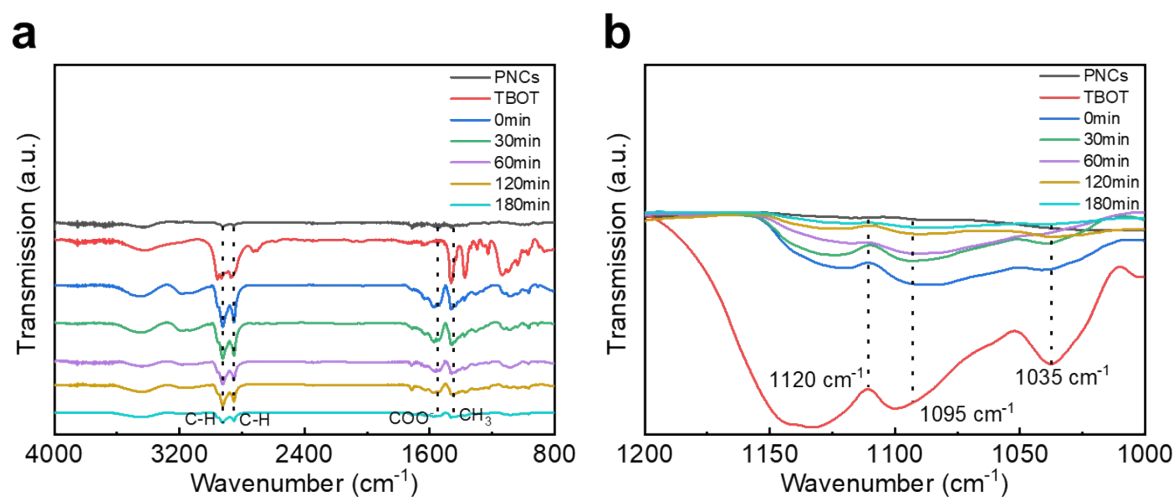


Fig. S7 (a) FTIR spectra and (b) magnified FTIR spectra of $\text{CsPbBr}_3/\text{TiO}_x$ heterostructures with different hydrolysis duration.

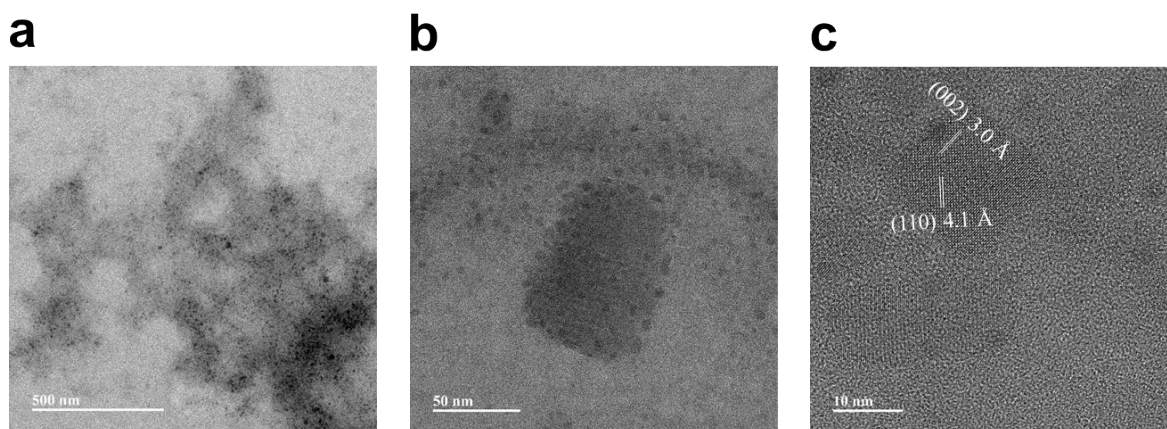


Fig. S8 TEM images of $\text{CsPbBr}_3/\text{TiO}_x$ heterostructures with a (a) low resolution, (b) high-resolution and (c) lattice constant.

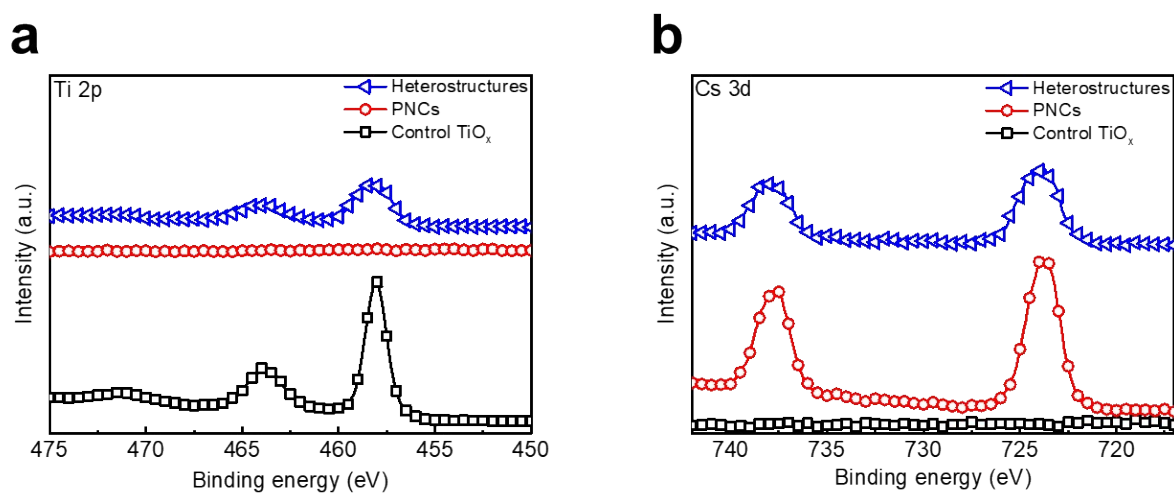


Fig. S9 XPS spectrum corresponding to (a) Ti 2p and (b) Cs 3d of heterostructures, PNCs and control TiO_x .



Fig. S10 Measured light intensity using calibrated reference cell depending on time (a) sunlight, (b) white LED and (c) green LED.

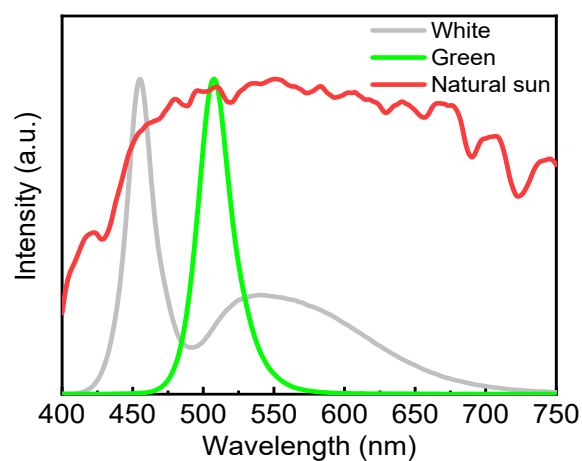


Fig. S11 Light spectra of white LED, green LED and natural sun, which were used for CO₂-reduction experiments and organic-degradation experiments.

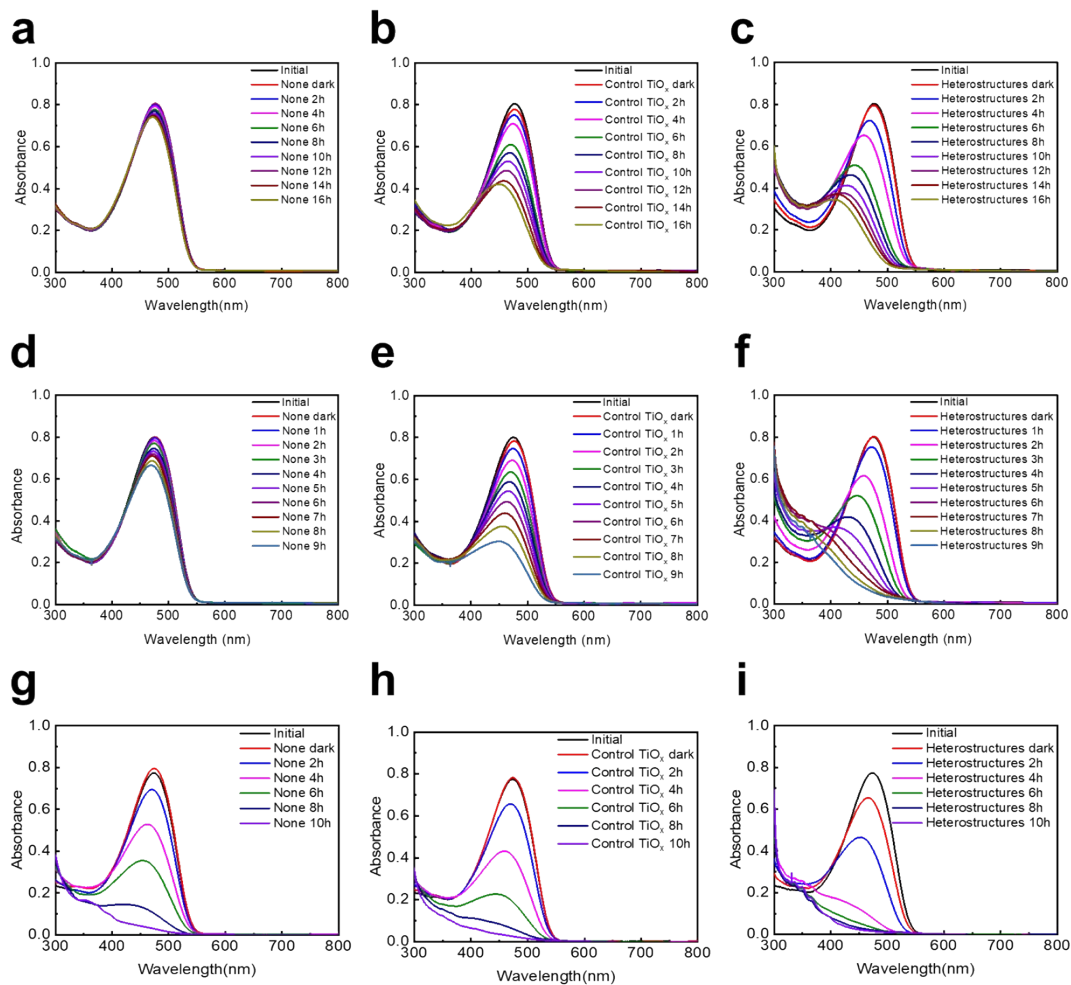


Fig. S12 UV-vis spectra of orange PPV copolymer during photocatalytic reaction with bare PPV-copolymer, control TiO_2 and heterostructures under (a-c) visible light irradiation, (d-f) green light irradiation and (g)~(i) outdoor natural sunlight.

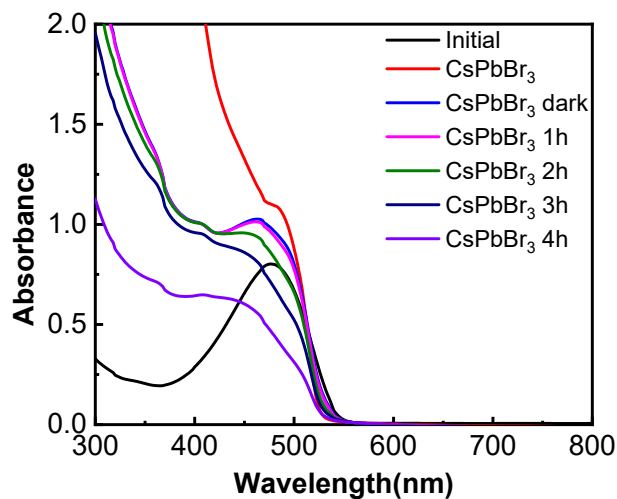


Fig. S13 UV-vis spectra of orange PPV copolymer during photocatalytic reaction with bare PPV-copolymer and CsPbBr_3 PNCs in visible region.

Initial absorbance of copolymer, CsPbBr_3 and mixture with no light irradiation to ensure absorption-desorption equilibrium

were analyzed using UV-vis spectroscopy. According to results, as soon as the CsPbBr₃ was injected into copolymer dispersion, mixture absorbance increased because CsPbBr₃ can be easily dispersed in toluene and overlapped with the copolymer peak. After irradiating visible region white LED for 1-3 hr, degradation efficiency showed 1.3, 8.3 and 20.3%, which is much lower than the heterostructures.

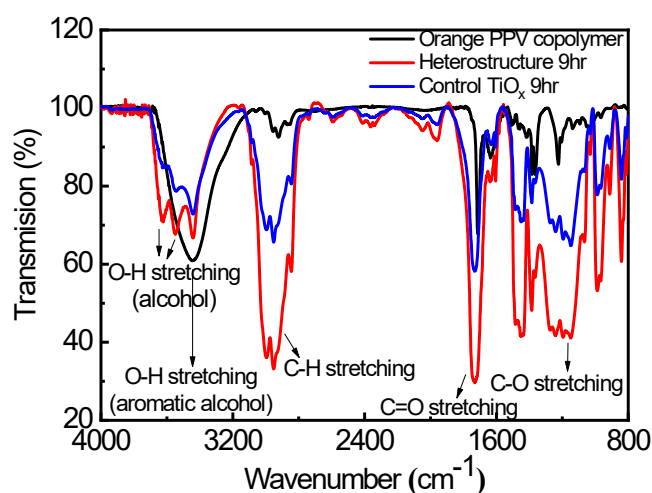


Fig. S14 FTIR analysis of orange PPV copolymer before degradation (black line), after degradation with CsPbBr₃/TiO_x heterostructures for 9 h (red line) and after degradation with TiO_x for 9 h (blue line).

Bare PPV copolymer (black curve) and decomposed polymer from control TiO_x (blue curve) and CsPbBr₃/TiO_x heterostructures (red curve) were dried and pelletized to compare their structure deformation by using FT-IR analysis. Decomposed copolymers showed peaks shifted to larger wavenumbers compared with bare polymer; this change means that long chains in structure decomposed to shorter molecules. Furthermore, polymers showed increased C-H stretching peaks of alkene/alkane/aliphatic ether, C-C stretching peaks of aromatic, C-O stretching peaks of aliphatic ether/primary alcohol after photocatalytic decomposition. Moreover, O-H stretching peaks of an aromatic alcohol at 3600 ~ 3200 cm⁻¹ decreased while sharp peaks of alcohol appeared after degradation owing to reduced polymer concentration and concomitant decrease in the number of hydrogen bonds between R-OH. These results indicate that long chains of copolymer were decomposed to shorter chains by the photocatalytic reactions.

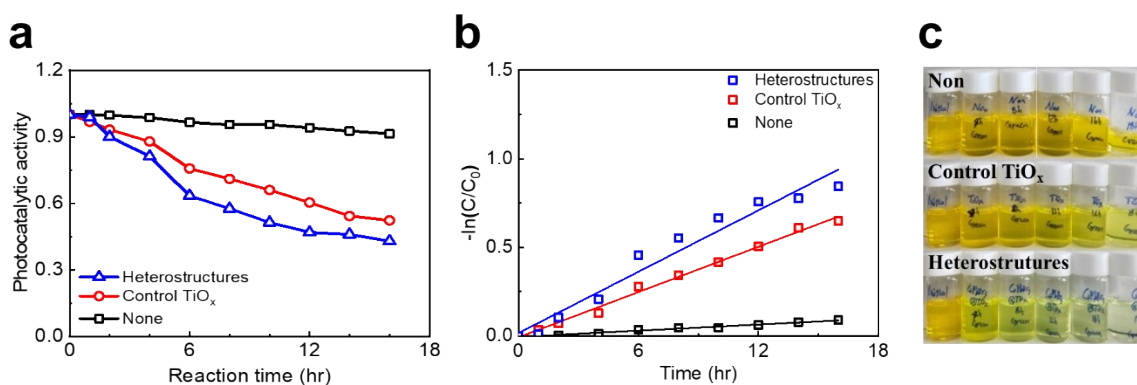


Fig. S15 (a) Photocatalytic activity, b) kinetic curves and c) photographs of PPV copolymer with control TiO_x and heterostructures and without any catalytic materials.

Table S1. Average lifetime τ_{ave} of heterostructures solutions during hydrolysis.

No.	Duration (min)	Average life-time (ns)
1	As-synthesized	26.51
2	0	1.80
3	30	4.88
4	60	8.69
5	120	9.50
6	180	10.33

Table S2. Summary of the photocatalytic CO₂ conversion efficiency results.

No.	Sample	CO ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	R _{electron} consumption ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^{a)}	Light source
1	Bare CO ₂	0.02	0.04	Visible
2	Control TiO _x	0.09	0.18	Visible
3	PNCs	7.10	14.2	Visible
4	Heterostructures	12.77	25.54	Visible
5	Bare CO ₂	0.03	0.06	Sunlight
6	Control TiO _x	3.86	7.72	Sunlight
7	PNCs	7.44	14.88	Sunlight
8	Heterostructures	30.43	60.86	Sunlight

^{a)} R_{electron} consumption = 2*(CO production rate)

Table S3. Summary of sunlight intensity measurement.

No.	Sunlight (mW/cm ²)	White LED (mW/cm ²)	Green LED (mW/cm ²)
1h	27.87	100.17	7.67
2h	27.63	99.96	7.47
3h	28.64	100.00	7.48
4h	27.97	100.00	7.43

References

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