

Supplementary Information

CO₂, water, and sunlight to hydrocarbon fuels: A sustained sunlight to fuel (Joule-to-Joule) photoconversion efficiency of 1%

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Methods

Blue Titania (BT) nanoparticle synthesis. Blue titania (BT) nanoparticles were synthesized according to our previously reported method¹. In brief, 200 mg P25 nanoparticles were mixed with 30 mg sodium borohydride (NaBH_4 , 98%) purchased from Alfa Aesar using a mortar and pestle. The mixture was then placed in a quartz tube furnace and heated at 350 °C for 0.5 h. The resulting sample was copiously washed with deionized (DI) water and ethanol, a cycle repeated five times. Finally, the sample was dried at 90 °C overnight.

Synthesis of $\text{Cu}_x\text{-Pt}_{0.35\%}\text{-BT}$. Blue titania nanoparticles were sensitized with a fixed amount (0.35 wt.%) of Pt nanoparticles according to our previous report¹. 100 mg of $\text{Pt}_{0.35\%}\text{-BT}$ was dispersed in a solution of 20 ml DI water and 5 ml methanol. Variable concentrations of $\text{CuNO}_3 \cdot 6\text{H}_2\text{O}$ were added to the above mixture and stirred under dark for 1 h in a closed system. The suspension was then illuminated under AM1.5 for 2 h. Finally, the samples were washed with DI water and dried in a vacuum oven at 90 °C for 12 h. The resulting samples were identified as $\text{Cu}_x\text{-Pt}_{0.35\%}\text{-BT}$, where $x = 0.50, 0.75, 1.00, \text{ and } 1.25$ corresponding to theoretically calculated wt.% Cu.

Material characterization. X-ray powder diffraction (XRD) spectroscopy was recorded on a Panalytical, Empyrean X-ray diffractometer using $\text{Cu } k\lambda$ radiation ($\lambda = 1.54 \text{ \AA}$) operating at 40 kV and 30 mA. The lattice structure was observed by a field emission tunnelling electron microscopy (FE-TEM) taken from Hitachi HF-3300 operating at 300 kV. The elemental composition of $\text{Cu}_{1.00\%}\text{-Pt}_{0.35\%}\text{-BT}$ was measured using the energy dispersive spectroscopy (EDS) attachment of the HF-3300 FE-TEM. UV-Visible diffuse reflectance spectroscopy (UV-vis DRS) were measured upon a

Cary series UV-visible near infrared spectrophotometer with a diffuse reflectance accessory. Photoluminescence (PL) spectroscopy was carried out on Cary Eclipse fluorescence spectrophotometer ($\lambda_{\text{excitation}} = 320 \text{ nm}$) with a diffuse reflectance accessory. X-ray photoelectron spectroscopy (XPS) was conducted using Thermo VG, K-alpha using Al K α line as the X-ray source. Electron paramagnetic resonance (EPR) spectra were recorded using a Jeol-FA100 spectrometer at 100 K. Time-resolved PL measurements was performed using a home-built optical microscope system at room-temperature. The sample was excited by a pico-second pulsed diode laser (PicoQuant, LDH-P-FA-355) with a 355 nm wavelength (FWHM = 56 ps) and repetition rate of 40 MHz. The excitation source was focused from 40 \times (NA = 0.6) objective (Nikon). Fourier-transform infrared (FTIR) analysis was performed using a Thermo Scientific Nicolet Continuum spectrometer. Powder samples were prepared in KBr, and pellets were pressed from the powder mixture.

Photocatalytic CO₂ reduction.

We have utilized a continuous flow-through system for CO₂ and water reduction under 1 sun condition. In short, in this case, the photocatalytic powder is dispersed upon a nanoporous disk, composed of spun glass through which reactant flows while under AM1.5 illumination. Product analysis was conducted every 0.5 h by an online gas chromatography (GC) unit (Shimadzu, GC-2014) having helium carrier gas. The GC was equipped with a flame ionization detector (FID, Restek-Rt-Q-bond column, ID = 0.53 mm and length = 30 m). Photocatalyst stability was evaluated by repeated testing of the same sample for CO₂ photoreduction; after each 12 h

test cycle the photocatalyst was vacuum annealed at 100 °C for 2h, a process previously used to regenerate the photocatalyst^{1,2}.

Hydrogen (H₂) detection was performed using a gas chromatograph with Ar as carrier gas (Agilent, 7890B) using Molecular sieve (Msieve) 5A column (G3591-7003, 2 m x 1/8 inch, 2 mm SS packed type). Carbon monoxide (CO) was determined using gas chromatography (GC) unit (Shimadzu, GC-2014) with Rt-Msieve 5A column (30 m, ID = 0.32 mm, 30 μm). Isotopic ¹³CO₂ and control experiments were performed to confirm the carbon source. ¹³CO₂ (¹³C 99%), diluted in pure He gas (99.999%) to give a final ¹³CO₂ concentration of 500 ppm, was purchased from Sigma Aldrich. The ¹³CH₄ produced from moist ¹³CO₂ gas was analysed using a gas chromatography-mass spectrometer (GC-MS) manufactured by Shimadzu, GC-MS-QP2010 ULTRA (Restek Rt Q-bond column, ID= 0.32 mm and length = 30 m). Moist CO₂ was introduced into the photocatalyst (40 mg) loaded photoreactor, and the gaseous products analysed after 3 h of AM1.5 illumination. Two control tests were performed: (i) He/H₂O_(g) mixture, and (ii) a blank photoreactor test (no photocatalyst) under AM1.5 illumination. H₂¹⁸O (97 atom % ¹⁸O) was purchased from Sigma-Aldrich. Isotopic oxygen evolution test was conducted on gas chromatography-mass spectrometer (GC-MS) manufactured by Shimadzu, GC-MS-QP2010 ULTRA (Restek Rt-Msieve 5A column, fused silica PLOT, ID = 0.53 mm and length = 30 m).

(1) Photoconversion efficiency calculation for 6 h

Methane: $(3 \text{ mmol g}^{-1}) * 40 \text{ mg sample} = 120 \times 10^{-6} \text{ mole} * 810 \text{ kJ mol}^{-1} = 97.2 \text{ J}$

Ethane: $(0.150 \text{ mmol g}^{-1}) * 40 \text{ mg sample} = 6 \times 10^{-6} \text{ mole} * 1560 \text{ kJ mol}^{-1} = 9.4 \text{ J}$

Energy content of fuel produced by CO₂ photoreduction during 6 h period: 106.6 J

AM1.5 energy input for 6 h = $(4.88 \text{ cm}^2)(100 \text{ mJ s}^{-1} \text{ cm}^{-2})(3600 \text{ s h}^{-1})(6 \text{ h}) = 10,540.8 \text{ J}$

AM1.5, 100 mW cm⁻² incident upon 4.88 cm² surface area.

Solar energy in to fuel energy out (Joules to Joules) = (106.2/10,540) x 100 = **1.0 %**

(2) AQY calculation for 12 h

Yield of CH₄ produced in 12 h = 0.283 mmol g⁻¹ h⁻¹, hence the number of reacted electrons = 1.4 x 10²¹. Substituting this value and that of manuscript E.7 into equation A.1, the AQY for CH₄ is AQY = 45%. The yield of C₂H₆ produced in 8 h = 0.020 mmol g⁻¹ h⁻¹, the corresponding number of reacted electrons = 1.7 x 10²⁰. Substituting this value and that of E.7 into equation A.1 we find the AQY for C₂H₆ is AQY = 5%. The total AQY over 12 h = 50%.

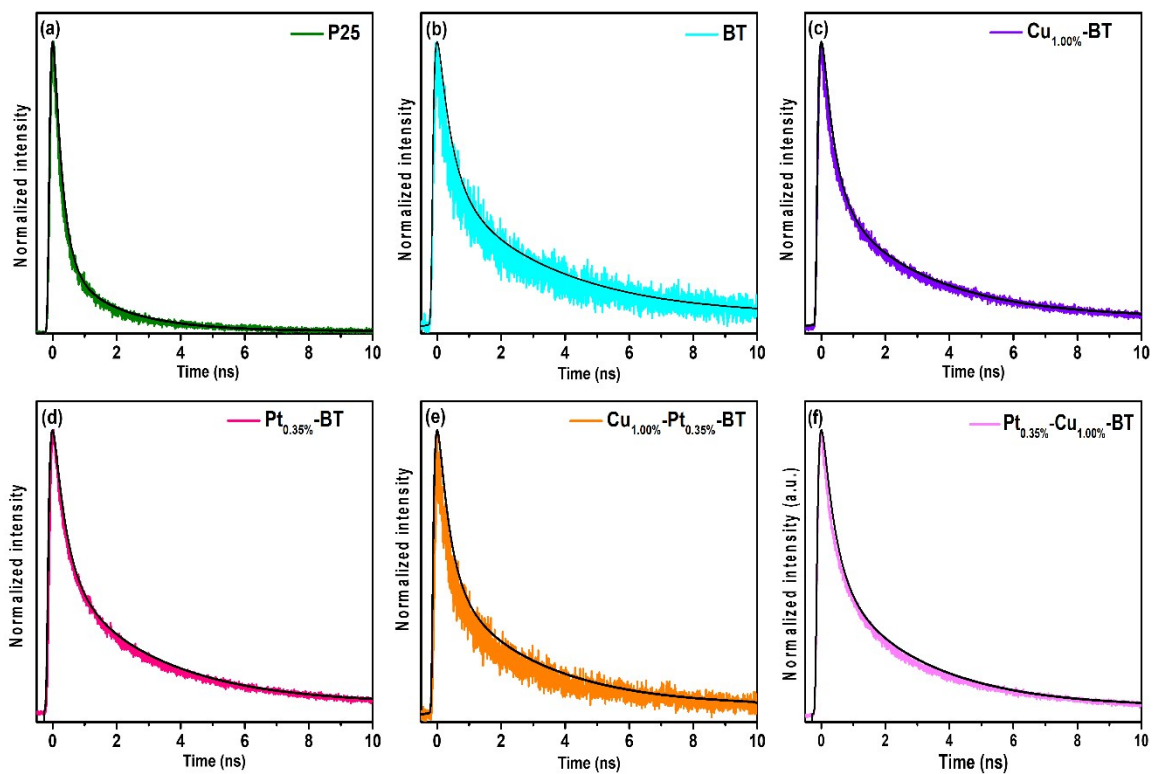


Fig. S1. Time resolved photoluminescence spectroscopy results of (a) P25, (b) BT, (c) $\text{Cu}_{1.00\%}\text{-BT}$, (d) $\text{Pt}_{0.35\%}\text{-BT}$, and (e) $\text{Cu}_{1.00\%}\text{-Pt}_{0.35\%}\text{-BT}$ (f) $\text{Pt}_{0.35\%}\text{-Cu}_{1.00\%}\text{-BT}$ samples.

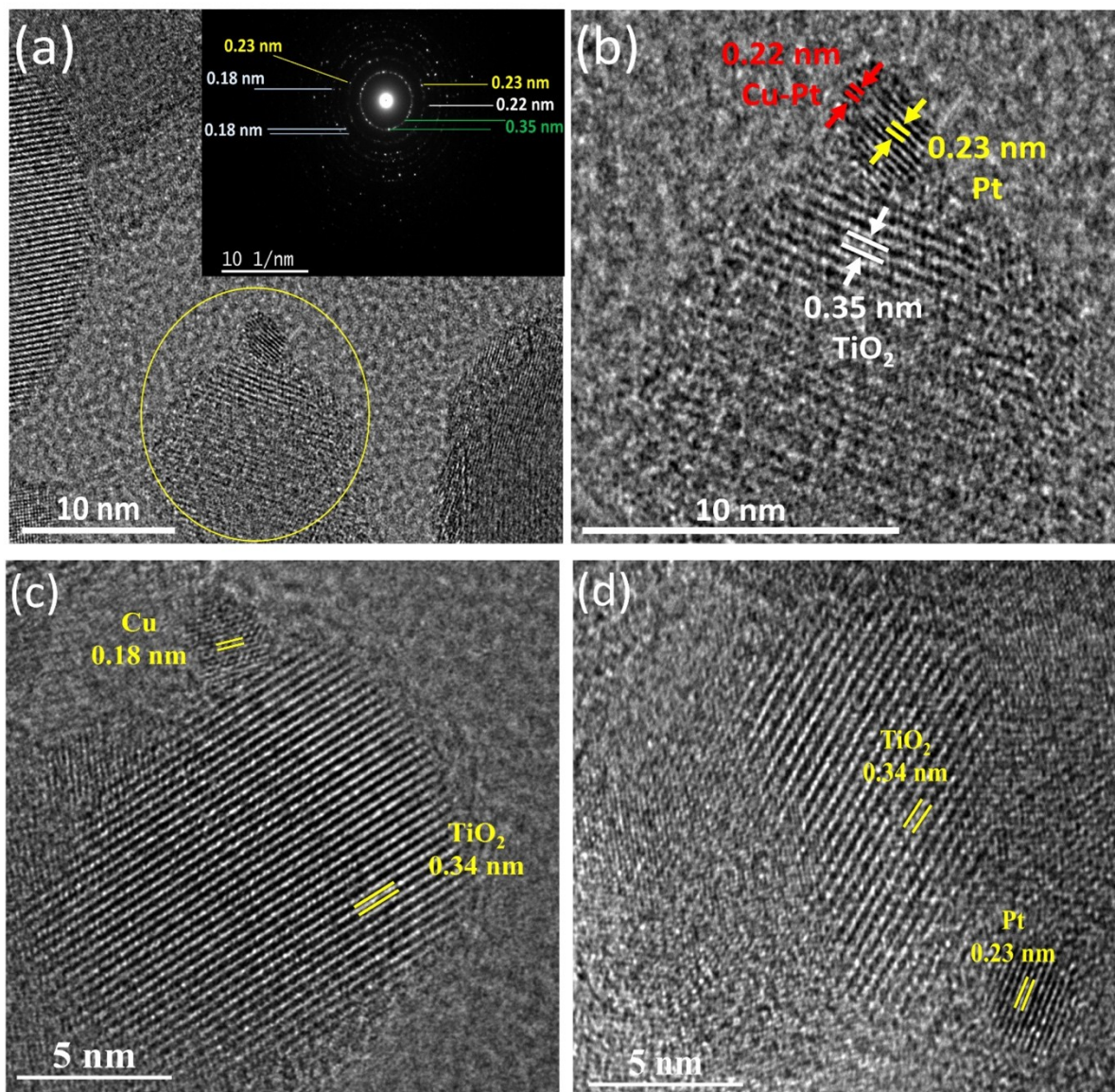


Fig. S2. HR-TEM images of $\text{Cu}_{1.00\%}\text{-Pt}_{0.35\%}\text{-BT}$ sample.

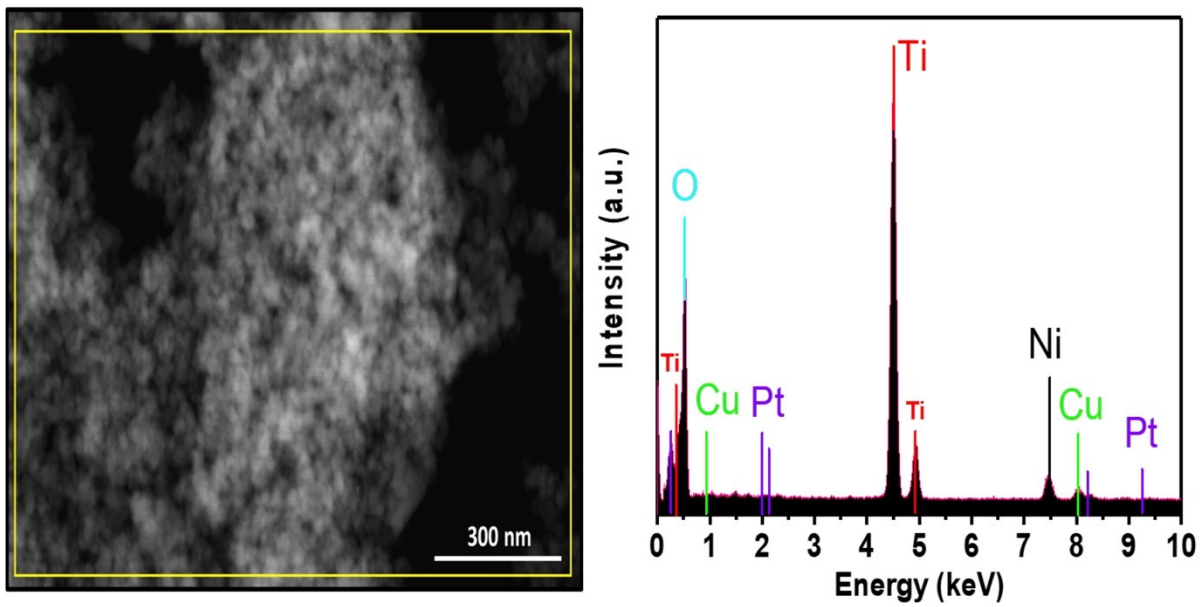


Fig. S3. EDS image of Cu_{1.00%}-Pt_{0.35%}-BT sample.

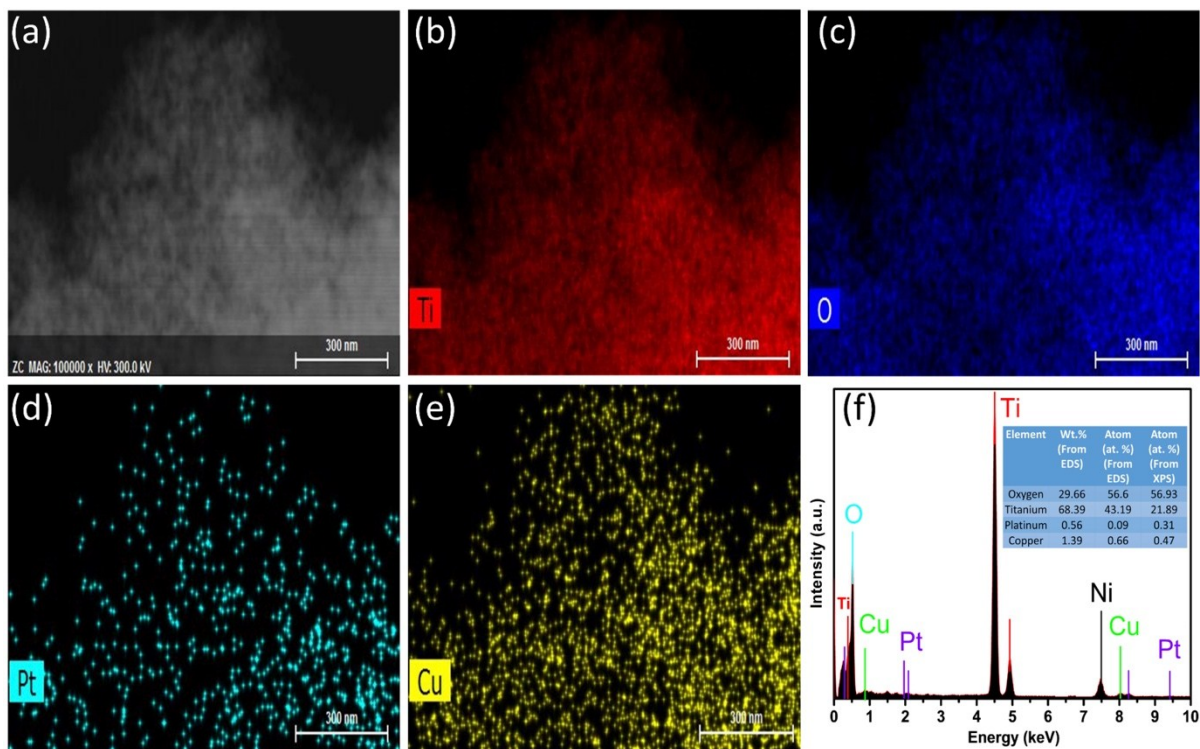


Fig. S4. (a) TEM Elemental mapping showing the presence of (b) Ti, (c) O, (d) Pt, (e) Cu, and (f) EDS, for $\text{Cu}_{1.00\%}\text{-Pt}_{0.35\%}\text{-BT}$ sample.

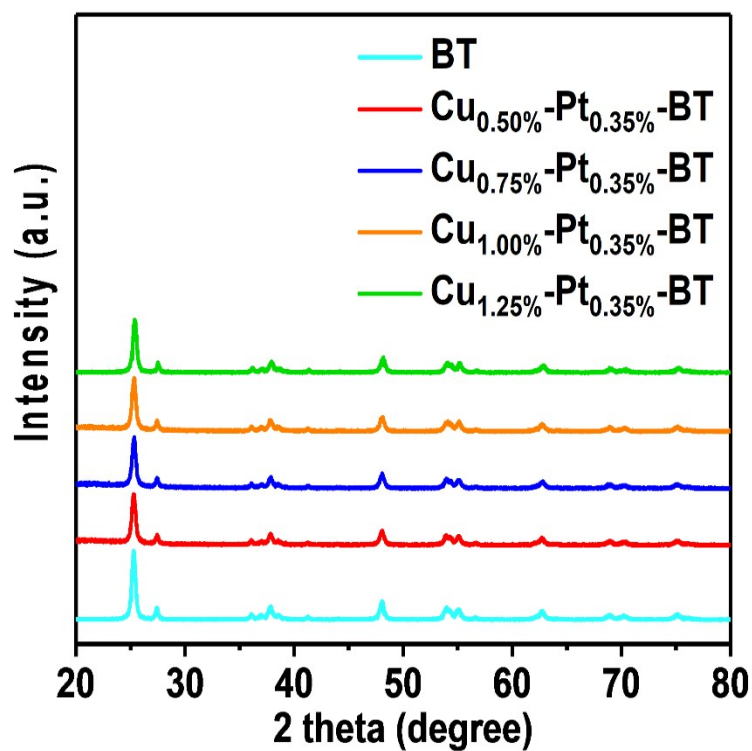


Fig. S5 XRD patterns of Cu-Pt deposited blue titania nanoparticles.

Identical XRD patterns were obtained for all the samples prepared, which demonstrates that both Cu and Pt nanoparticles deposition did not affect the original crystalline phase of composition of blue titania nanoparticles. The results imply that no large Cu or Pt related crystallites were formed.

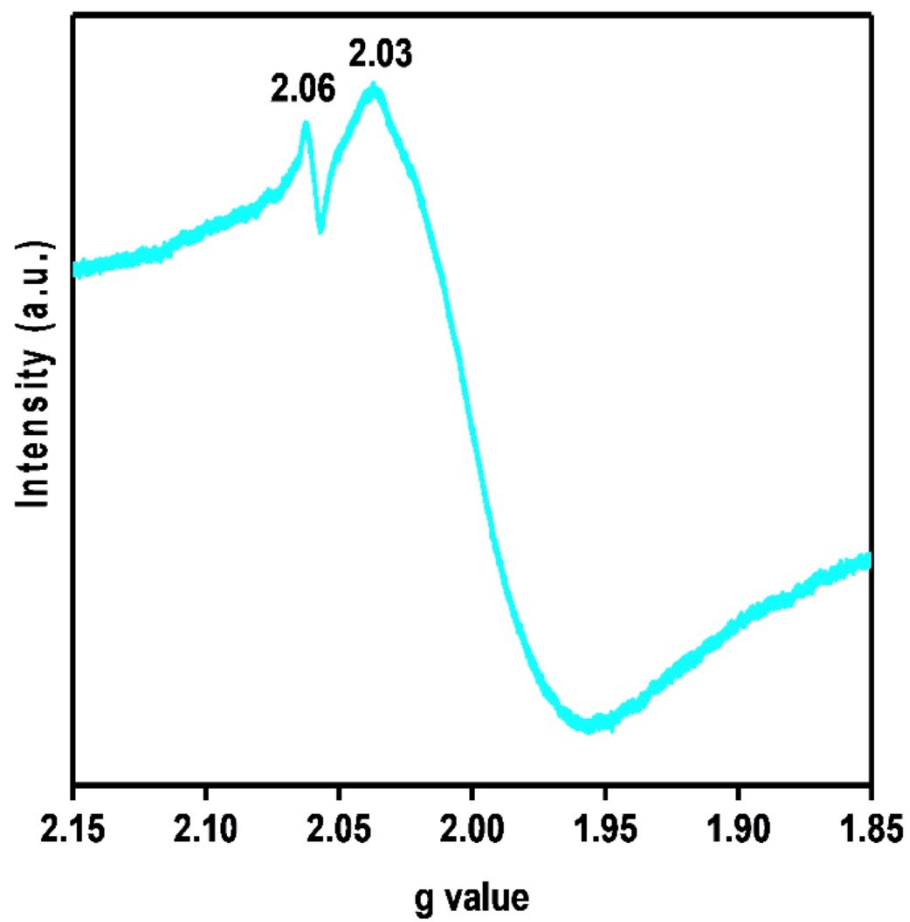


Fig. S6 Electron paramagnetic resonance (EPR) spectroscopy result of blue titania.

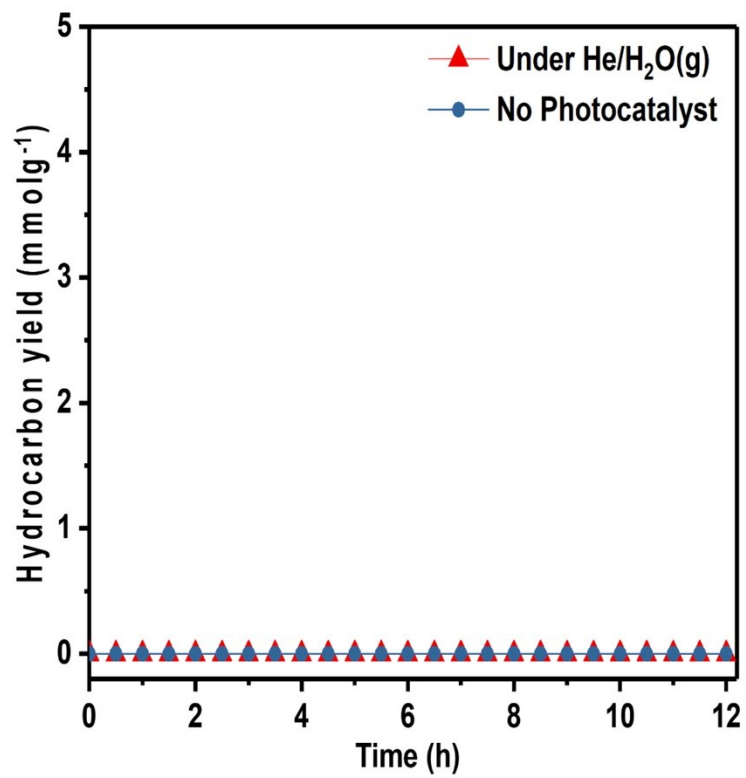


Fig. S7 Control test results of Cu_{1.00%}-Pt_{0.35%}-BT sample.

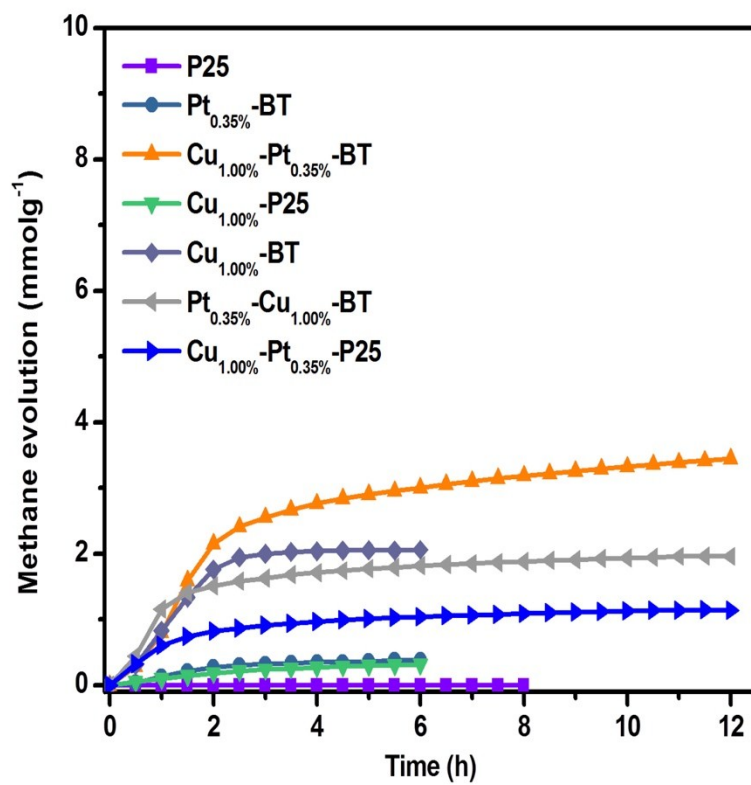


Fig. S8 Control samples test results with respect to Cu_{1.00%}-Pt_{0.35%}-BT sample (Methane evolution).

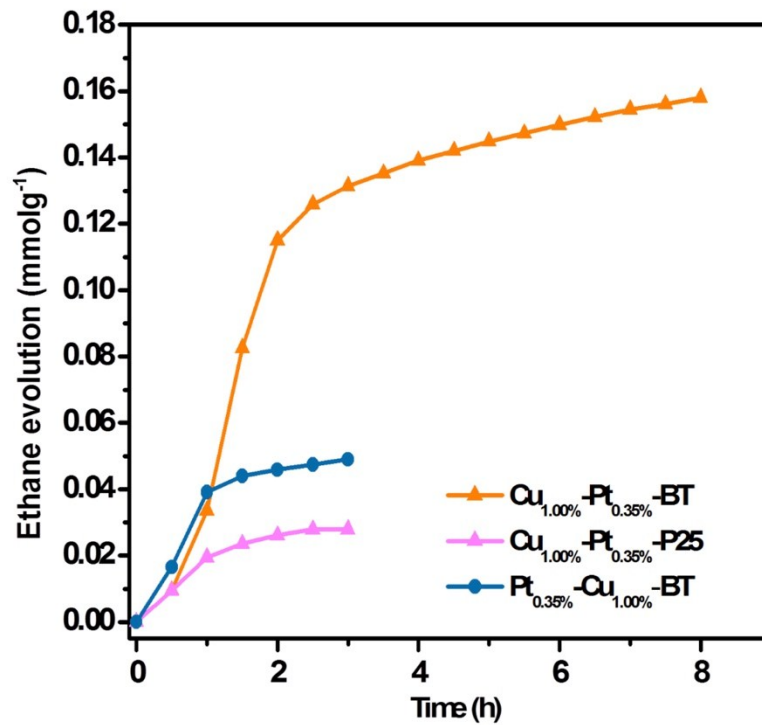


Fig.S9 Control samples test results with respect to Cu_{1.00%}-Pt_{0.35%}-BT sample (Ethane evolution).

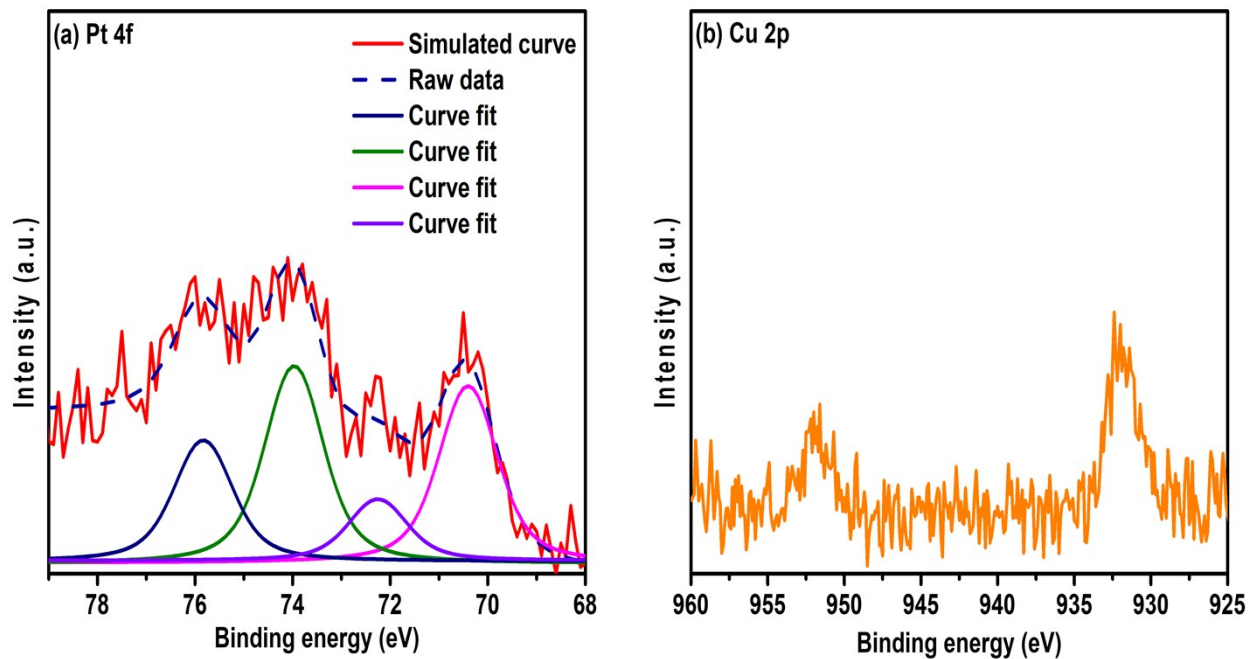


Fig. S10 XPS results for $\text{Cu}_{1.00}\text{-Pt}_{0.35}\text{-BT}$ sample after 12 h photocatalytic CO_2 reduction test (a) Pt 4f, and (b) Cu 2p.

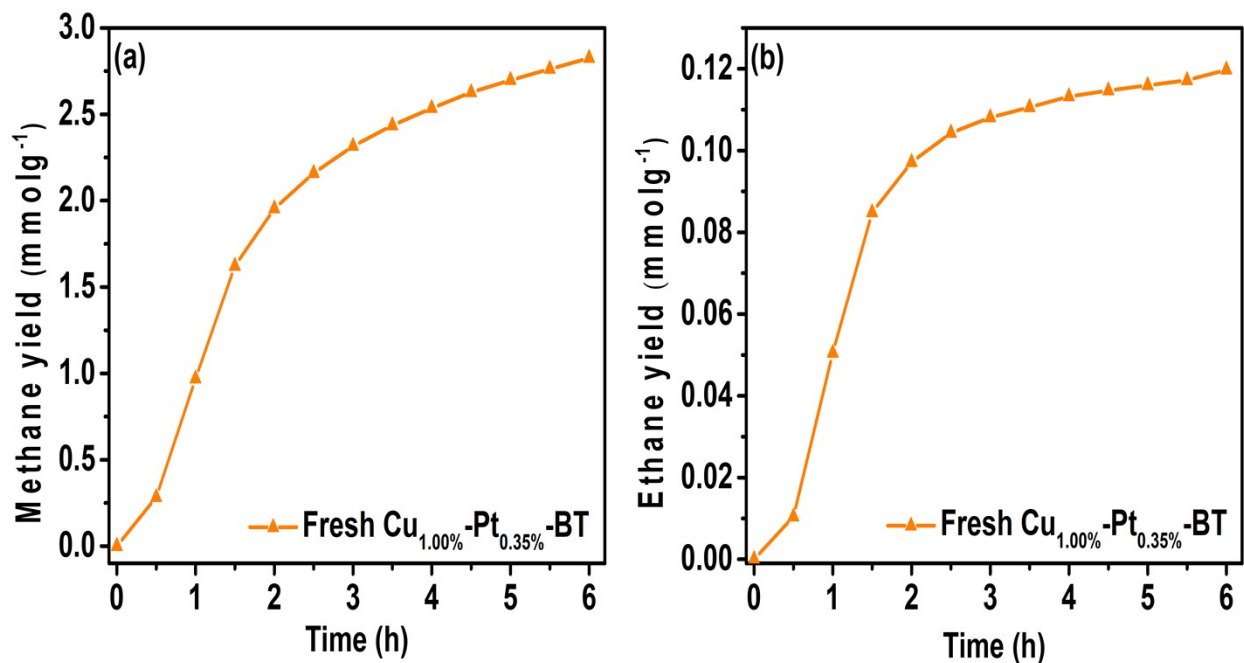


Fig. S11. Fuel output obtained by synthesizing a fresh $\text{Cu}_{1.00\%}\text{-Pt}_{0.35\%}\text{-BT}$ photocatalyst sample, i.e. 'from scratch,' and testing it in different GC unit: (a) Methane yield, and (b) Ethane yield.

Table S1. Comparison of previous works pertained with CO₂ photoreduction into hydrocarbon products.

Photocatalyst	Photocatalytic CO ₂ reduction test condition	Hydrocarbon yield
G-TiO ₂ ³	0.1 g of sample dispersed on glass reactor with an area of 4.2 cm ² . A 300 W Xe arc lamp used as light source.	CH ₄ = 10.1 μmolg ⁻¹ h ⁻¹ C ₂ H ₆ = 16.8 μmolg ⁻¹ h ⁻¹
Nf/Pd-TiO ₂ ⁴	Experiments were carried out in the presence of sodium carbonate, and CO ₂ was purged for 30 min prior to irradiation. Initially the pH of the suspension was adjusted to different values (pH 1, 3, and 11). A 300 W Xe arc lamp (Oriel) was used as a light source.	CH ₄ ≈ 1.4 μmolg ⁻¹ h ⁻¹ C ₂ H ₆ ≈ 0.7 μmolg ⁻¹ h ⁻¹
Au@TiO ₂ yolk-shell hollow sphere ⁵	0.1 g of sample dispersed on glass reactor with an area of 4.2 cm ² . The volume of reaction system used was about 230 ml. A 300 W Xe arc lamp used as light source.	CH ₄ = 2.52 μmolg ⁻¹ h ⁻¹ C ₂ H ₆ = 1.67 μmolg ⁻¹ h ⁻¹
Reduced Titania nanoparticles ⁶	100 mg photocatalyst illuminated using 300 W Xe lamp (AM 1.5G)	CO = 1818 ppmg ⁻¹ CH ₄ = 477 ppmg ⁻¹
Cu(I)/TiO _{2-x} nanoparticles ⁷	50 mg photocatalyst preheated using 250 W infrared lamp followed by illumination using 150 W solar simulator (Oriel)	CO = 4.3 μmolg ⁻¹ h ⁻¹
Ti ³⁺ -self doped TiO ₂ brookite nanosheets ⁸	Mixture of CO ₂ (99.99%) and water vapour. Visible light irradiation using 300 W Xe lamp (≥420 nm)	CO = 23.5 μmolg ⁻¹ h ⁻¹ CH ₄ = 11 μmolg ⁻¹ h ⁻¹
0.35 weight percent-Pt-Blue Titania ¹	40 mg photocatalyst loaded onto photoreactor followed by illumination with 100 W solar simulator (Oriel, LCS-100 with AM 1.5G filter)	CH ₄ = 80.35 μmolg ⁻¹ h ⁻¹
Reduced {001}-TiO _{2-x} ⁹	0.03 g catalysts dispersed on petri dish. The volume of reactor used was 300 ml and tests were done using 300 W Xe lamp (AM 1.5G)	CO ≈ 0.8 μmolg ⁻¹ CH ₄ ≈ 0.9 μmolg ⁻¹
TiO ₂ -Pd/C composite ¹⁰	125 mg catalyst was taken in 125 ml NaOH solution with CO ₂ inflation. Tests were carried out in 225 ml cylindrical glass reactor with a built in light source of 32 W Hg lamp.	CH ₄ = 5.70 ± 0.11 × 10 ⁻⁶ mol

1 weight percent -Pt Graphene-Blue Titania nanoparticles ²	40 mg photocatalyst loaded onto photoreactor followed by illumination with 100 W solar simulator (Oriel, LCS-100 with AM 1.5G filter)	CH ₄ = 37 μmolg ⁻¹ h ⁻¹ C ₂ H ₆ = 11 μmolg ⁻¹ h ⁻¹
Self-doped TiO ₂ ¹¹	Self-assembled reactor (380 ml). Illumination with two 300 W Xe lamp.	CO = 0.075 μmol per m ² CH ₄ = 0.015 μmol per m ²
Au-Pd alloying at TiO ₂ {101} facet ¹²	10 mg photocatalyst was coated on quartz plate. Illumination using 300 W Xe lamp.	CH ₄ = 2.72 μmolg ⁻¹ h ⁻¹
Porous hyperlinked polymer-TiO ₂ -graphene composite ¹³	20 mg photocatalyst was placed on a circular glass dish. The CO ₂ was generated by the reaction of sodium hydrogen carbonate with diluted sulphuric acid after removing the air. A 300 W Xe lamp was used as the light source.	CH ₄ = 27.62 μmolg ⁻¹ h ⁻¹
Pt-Ultrathin TiO ₂ nanosheets ¹⁴	10 mg sample spread in chamber with 0.08 MPa CO ₂ . Water vapour added through bubbling (50 ml chamber volume). A 300 W Xe lamp was used as the light source.	CH ₄ = 66.4 μmolg ⁻¹ h ⁻¹
Pt-Carbon doped titania ¹⁵	0.1 g photocatalyst filled in reactor (volume 357 ml) with 100 ml NaOH. A 8 W Hg UV lamp was used as light source.	CO ≈ 0.25 μmolg ⁻¹ h ⁻¹ CH ₄ = 2.5 μmolg ⁻¹ h ⁻¹
Nanorattle Au@PtAg-ZIF-8 ¹⁶	30 mg photocatalyst sprinkled on bottom of Pyrex cell reactor (600 ml). Water was sprayed around the catalyst. Illumination with 500 W Xe lamp at UV-vis (λ = 200–1000 nm).	CO = 14.5 μmolg ⁻¹ h ⁻¹ CH ₄ = 1.2 μmolg ⁻¹ h ⁻¹
<i>Current work</i>	<i>40 mg photocatalyst loaded onto photoreactor followed by illumination with 100 W solar simulator (Oriel, LCS-100 with AM 1.5G filter)</i>	<i>CH₄ = 500 μmolg⁻¹h⁻¹ C₂H₆ = 25 μmolg⁻¹h⁻¹</i>

Table S2. Information obtained from TRPL decay curves according to bi-exponential decay.

Sample	τ_s (ns)	τ_f (ns)	τ_{average} (ns)	τ_{CT} (ns)	$\eta(\%)$
BT	3.36	0.43	2.90	--	--
Pt _{0.35%} -BT	2.99	0.40	2.53	19.82	12.76
Cu _{1%} -BT	2.99	0.37	2.56	21.83	11.72
Pt _{0.35%} -Cu _{1%} -BT	2.85	0.41	2.41	14.26	16.90
Cu _{1%} -Pt _{0.35%} -BT	2.78	0.32	2.39 (Minimum)	13.59 (Minimum)	17.58 (Maximum)

$$\text{Charge transfer lifetime}^{17} (\tau_{\text{CT}}) = (\tau_{\text{semi}} \times \tau_{\text{hybrid}}) / \tau_{\text{semi}} - \tau_{\text{hybrid}}$$

$$\text{Photoinduced Charge transfer efficiency}^{17} (\eta\%) = \tau_{\text{hybrid}} / \tau_{\text{CT}}$$

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