

Supporting Information

Visible Light CO₂ Reduction to CH₄ Using Hierarchical Yolk@shell TiO_{2-x}H_x Modified with Plasmonic Au-Pd Nanoparticles

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Experimental section

Materials and apparatus

All the chemical reagents used in our experiments were purchased from Sigma-Aldrich and Merck and were used as received without further purification. Water was purified with a Milli-Q system (≥ 18 MU.cm).

UV–vis DRS of samples was obtained using AvaSpec-2048 TEC spectrometer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer (X'pert Company) with monochromatized Cu K α radiation ($\lambda = 1.5406$ Å). XPS measurements were performed using a VG scientific photoelectron spectrometer ESCALAB-210 using Al K α radiation (1486.6 eV) from an X-ray source operating at 15 kV and 20 mA. Microscopic morphology of products was visualized by SEM (Tescan, Mira3). Transmission electron microscopy (TEM) pictures were obtained on TEM-Tecnai G2 and Philips CM30 with accelerating voltage of 150 kV. High resolution transmission electron microscopy (HRTEM) was obtained on JEOL JEM 2010 - TEM under 220 kV. Textural properties of the samples were determined by N₂ and CO₂ physisorption using a Micromeritics TriStar II Plus. Photoluminescence of samples were measured by PL (Agilent Cary 5000). Gas chromatography (GC) analysis was performed using a Bruker SCION 456-GC instrument with a flame-ionization detector (FID) and thermal conductivity detector (TCD) by BR-1701, SCION-PLOT Q and SCION-Molsieve 5A GC-columns. Photochemical reactions were carried out in a cylindrical glass reactor with a 300 W Xenon lamp (Lelesil innovative system, India), equipped with magnetic stirrer and chiller to control the temperature (15 °C) during the experiments.

Methods

Preparation of Au-Pd core/shell nanoparticles: The Au-Pd core/shell nanoparticles were prepared according to the literature with some modifications [1]. Briefly, 0.1 mmol of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was added to 10 mL of oleylamine in a three-necked flask fitted with a condenser and a stir bar. The solution was heated to 150 °C and kept at this temperature for 1 h for the reduction of Au^{3+} by oleylamine, which also serves as the capping agent. Subsequently, 0.015 mmol of $\text{Pd}(\text{OAc})_2$ was swiftly added to the Au seed solution under vigorous stirring at 150 °C, and the mixture was continuously heated at 150 °C for 2 h for the formation of Au-Pd core/shell nanoparticles. After reaction, the prepared nanoparticles were precipitated by adding 5 mL methanol, recovered by centrifugation and washing several times with methanol, and then re-dispersed in 10 mL of toluene for further use.

preparation of hierarchical urchin like yolk@shell $\text{TiO}_{2-x}\text{H}_x$ decorated by Au-Pd nanoparticles (HUY@S-TOH/AuPd): The urchin like yolk@shell $\text{TiO}_{2-x}\text{H}_x$ decorated by Au-Pd were prepared according to the our recently report [2]. In detail, 1.2 ml titanium(III) chloride was added to 30 ml absolute ethanol and stirred at 40 °C for 5 min. 4.8 ml glacial acetic acid was then added dropwise to the above solution. After 10 min, 1.2 g urea and 1.2 g poly ethylene glycol (Mw 20000) were added and allowed to react for 30 min under stirring. Finally, the transparent solution was transferred into a 50 ml Teflon-lined autoclave and the solution was kept at 150 °C for 12 h in an oven. After the synthesis, the precipitation was separated by centrifugation, washed with ethanol in turn for 3 times and dried at 60 °C for 12 h to gain Y@S-TO. The obtained Y@S-TO microspheres (0.5 g) were mixed into a solution containing H_2O (6 mL), EtOH (6 mL) and NaOH (0.48 g) and sonicated for 10 min after vigorously stirring (20 min). Then the suspension was added into a Teflon-lined stainless-steel autoclave (18 mL in capacity). The autoclave was heated at 150 °C for 3h, and then allowed to cool to room temperature

naturally and the product was isolated by centrifugation. After that, the precipitate was immersed in a dilute HCl (100 mL, 0.1 M) for 5 min and then washed with deionized water until pH value was close to 7, and then dried at 80 °C for 12 h to obtain hierarchical urchin like yolk@shell TiO₂ (HUY@S-TO). The resulting HUY@S-TO microspheres were calcined at 500 °C (heating rate: 3 °C/min) for 3 h under H₂/Ar (1:1) atmosphere (flow rate: 200 psi). At the end of the heating period, the sample was cooled to room temperature naturally under H₂/Ar atmosphere, named HUY@S-TOH. The HUY@S-TOH microspheres (0.25 g) were dispersed in THF (20 mL) and sonicated for 30 min. The obtained suspension was transferred to a flask and as-prepared Au-Pd solution was added under vigorous stirring. After 5h stirring, the precipitate was separated by centrifugation, washed with ethanol in turn for 3 times and dried under vacuum at 50 °C for 12 h. For comparison, the process was repeated with P25 and Y@S-TO (instead of HUY@S-TOH) to produce P25/AuPd and Y@S-TO/AuPd, respectively.

preparation of HUY@S-TOH/Au and HUY@S-TOH/Au: The urchin like yolk@shell TiO_{2-x}H_x decorated by monometallic Au or Pd nanoparticles were prepared according to the method described in our recently report [2].

Photocatalytic experiments: The photoreduction of CO₂ was carried out in a 500 mL cylindrical glass reactor with a 300 W Xenon lamp (Lelesil innovative system), equipped with magnetic stirrer and chiller to control the temperature (15 °C) during the experiments (Figure S8). Prior to reaction 400 mL of milli-Q water was put into the photoreactor and pure CO₂ (99.9%) was bubbled through the solution in the reactor for at least 30 min to ensure that all dissolved oxygen was eliminated. Then, catalyst powder was added into above solution, and the magnetic stirrer and irradiation lamp were turned on to start the photoreaction. The reaction was investigated in two liquid phase and gas phase modes [3, 4]. In the gas phase examination, the system was

sealed after catalyst loading and samples were continuously taken from the gaseous part in the upper part of the photoreactor and analysed using GC-FID and GC-TCD. For the liquid phase investigation, the CO₂ was continuously bubbled throughout the process. The liquid samples were continually taken from the reaction cell at given intervals (1 h) for quantitative analysis and stored in the 1 ml vials. The injections were done from the gaseous part in the upper part of the vial based on the external standard using a gas chromatograph.

For investigation of the reaction using the visible region (Figure S10), a glass reactor was exposed to a 300 W Xe lamp (LOT-Oriel GmbH & Co) equipped with an ultraviolet cutoff filter (GG-400) to provide visible light (>400nm). The reaction conditions were preserved similar to the one previously explained for cylindrical glass reactor.

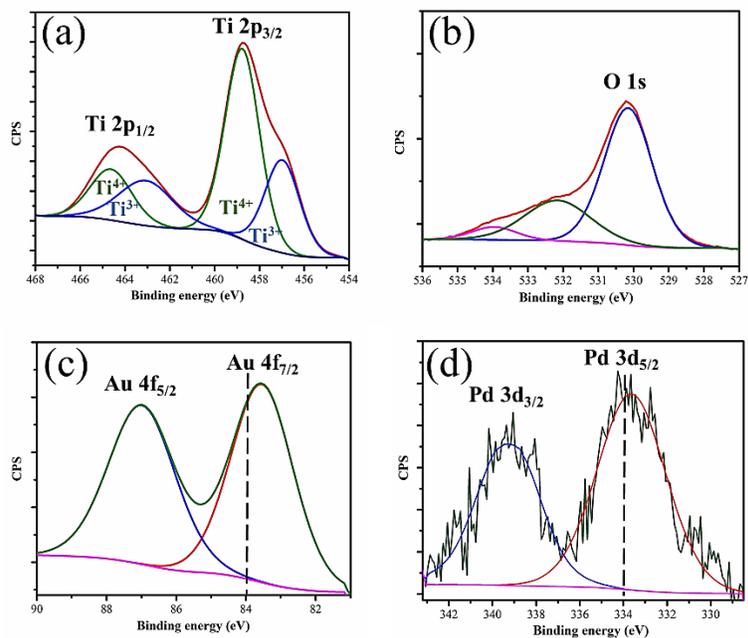


Figure S1. XPS Ti 2p (a), O 1s (b), Au 4f (c) and Pd 3d (d) spectra of HUY@S-TOH/AuPd architecture.

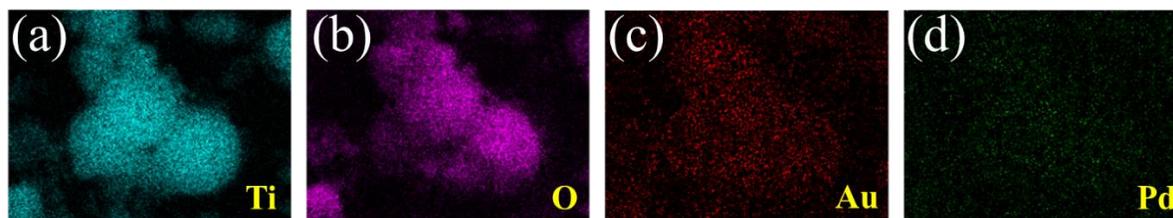


Figure S2. EDS mapping images of Ti (a), O (b), Au (c) and Pd (d) in the HUY@S-TOH/AuPd architecture.

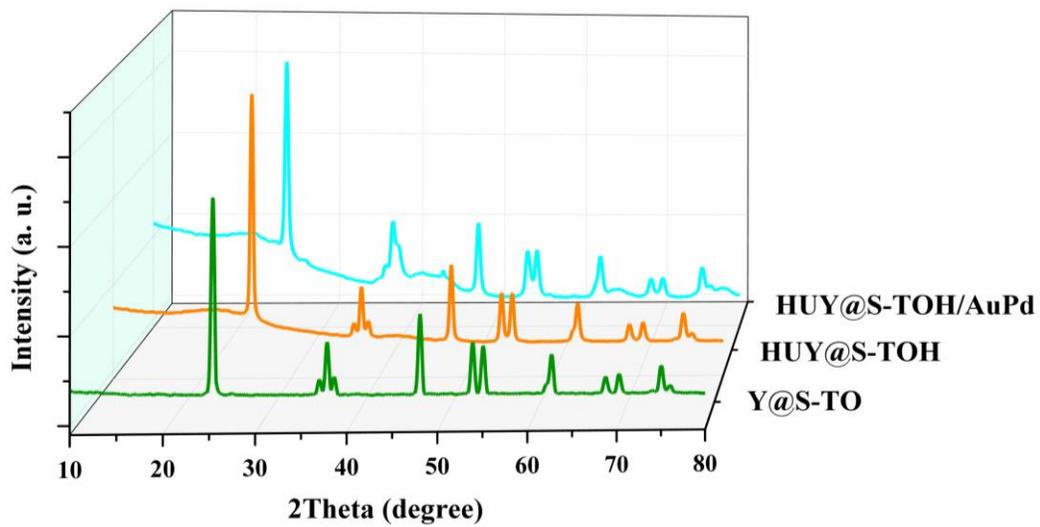


Figure S3. XRD patterns of Y@S-TO, HUY@S-TOH and HUY@S-TOH/AuPd architectures.

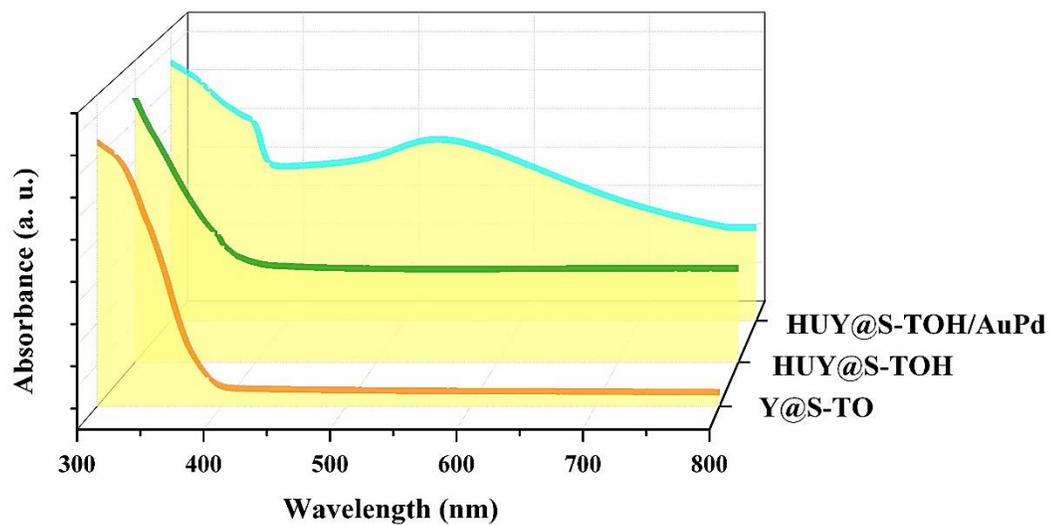


Figure S4. DRS analysis of Y@S-TO, HUY@S-TOH and HUY@S-TOH/AuPd architectures.

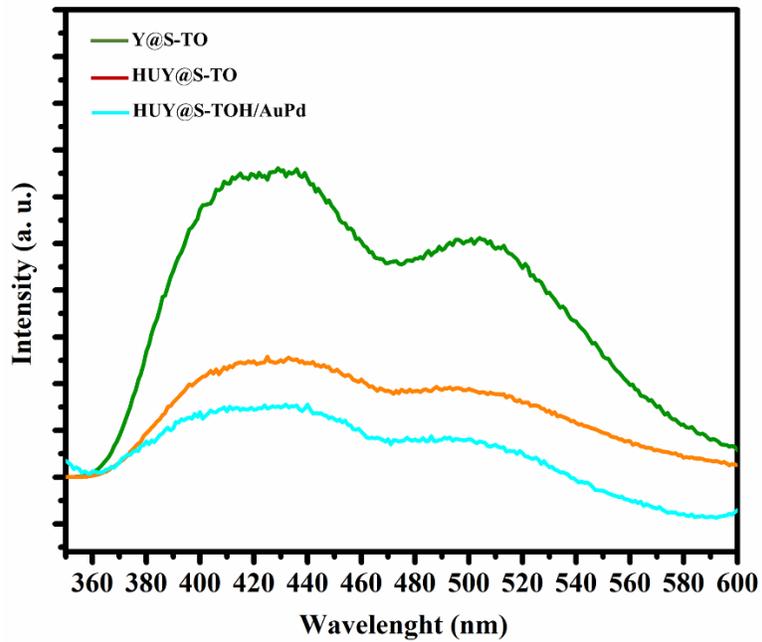


Figure S5. PL spectra of Y@S-TO, HUY@S-TOH and HUY@S-TOH/AuPd architectures.

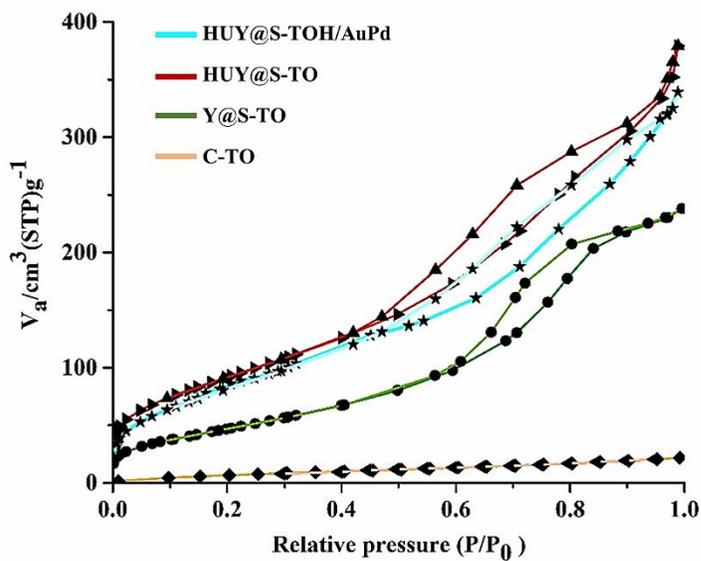


Figure S6. N₂ adsorption and desorption of C-TO, Y@S-TO, HUY@S-TO and HUY@S-TOH/AuPd structures.

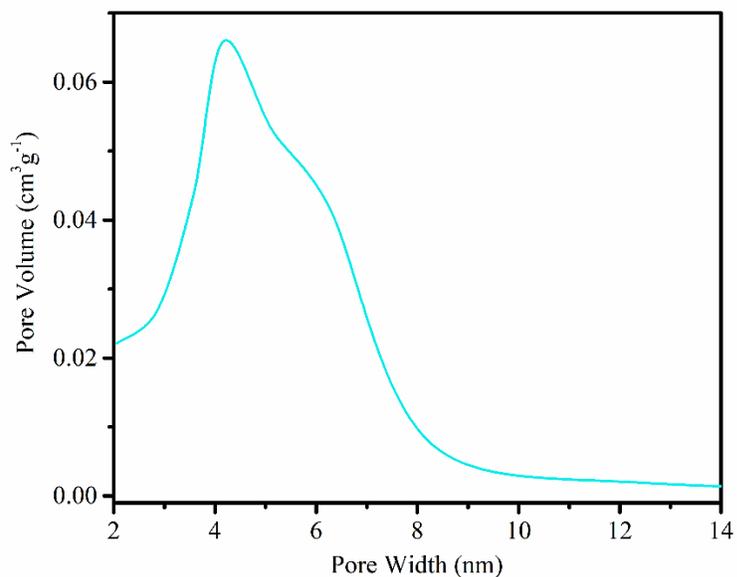


Figure S7. Pore volume distribution of HUY@S-TOH/AuPd architecture.

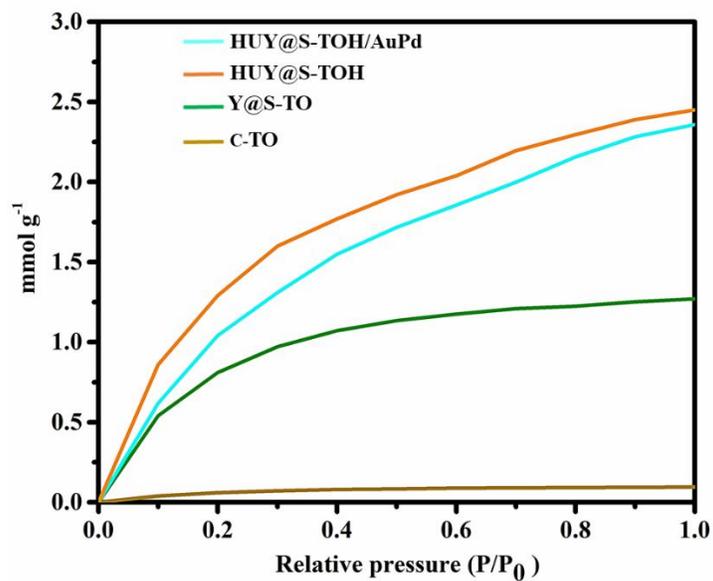


Figure S8. CO₂ adsorption of C-TO, Y@S-TO, HUY@S-TO and HUY@S-TOH/AuPd structures.

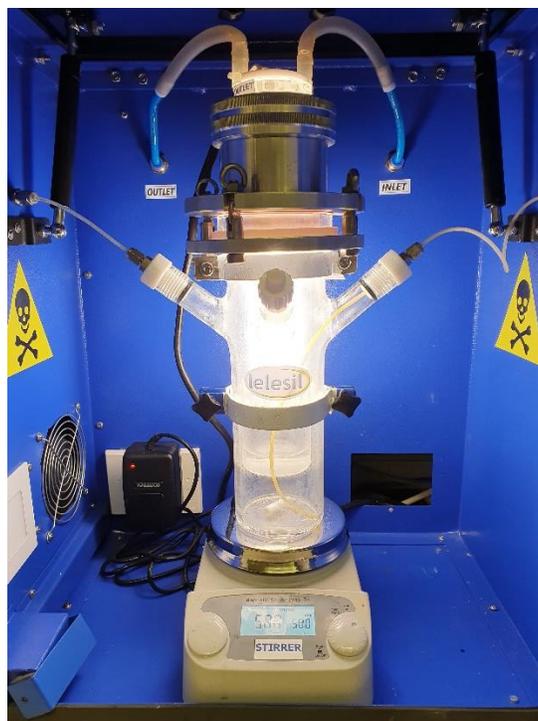


Figure S9. Picture of used photo-reactor for photoreduction of CO₂.

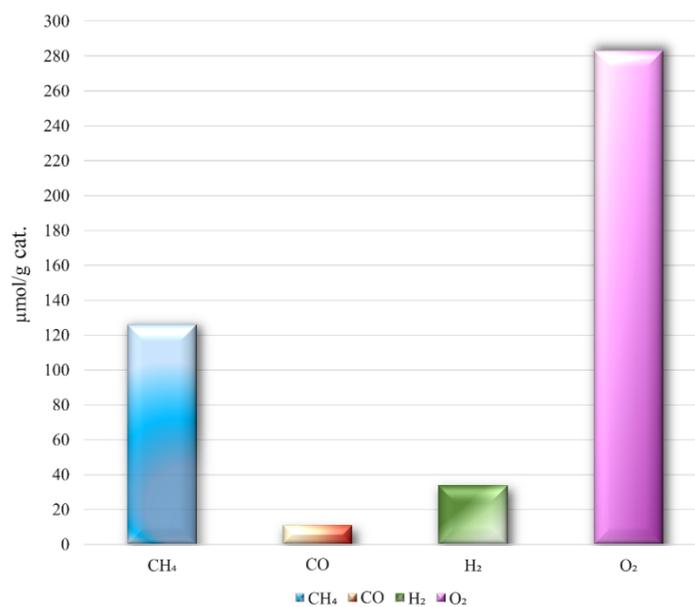


Figure S10. CO₂ reduction and water oxidation products in presence of HUY@S-TOH/AuPd photocatalyst.

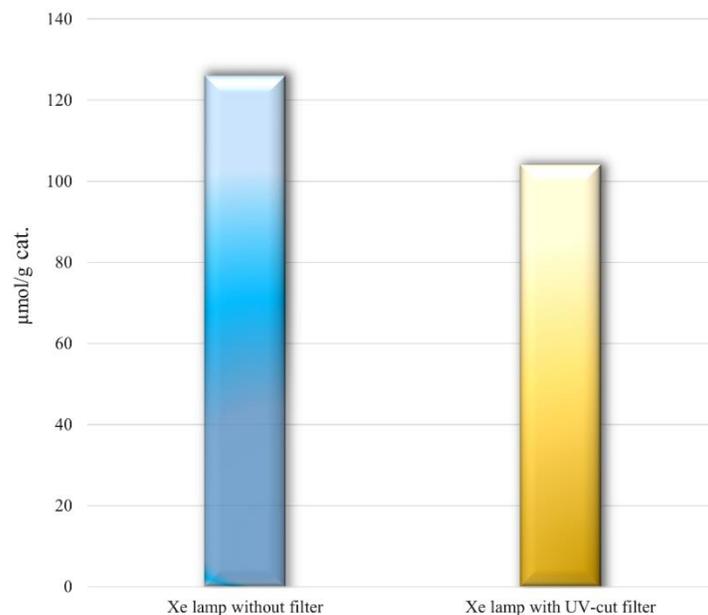


Figure S11. CH₄ production in presence of HUY@S-TOH/AuPd photocatalyst using Xe lamp with/without UV-cut filter.

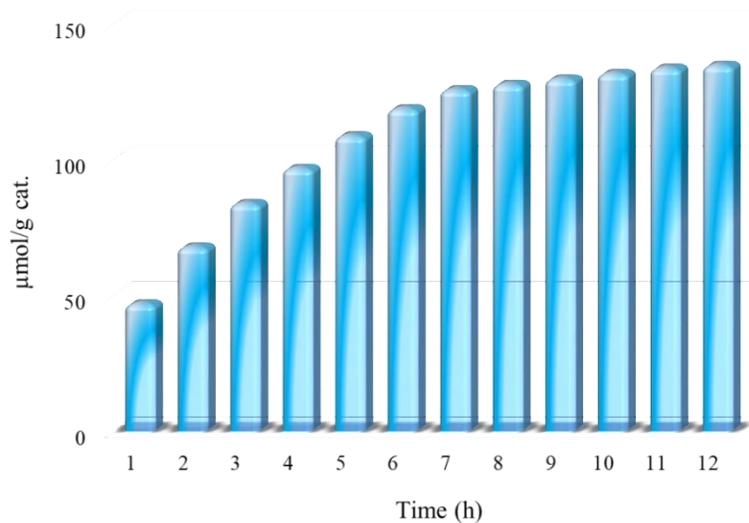


Figure S12. Time-dependent CH₄ production during CO₂ photo reduction experiment of using HUY@S-TOH/AuPd photocatalyst.

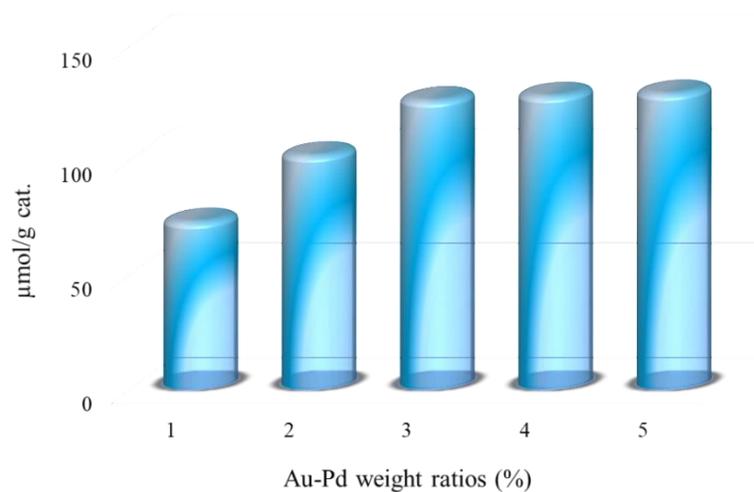


Figure S13. Effect of Au-Pd weight percentage on the HUY@S-TOH/AuPd photocatalytic CH₄ production.

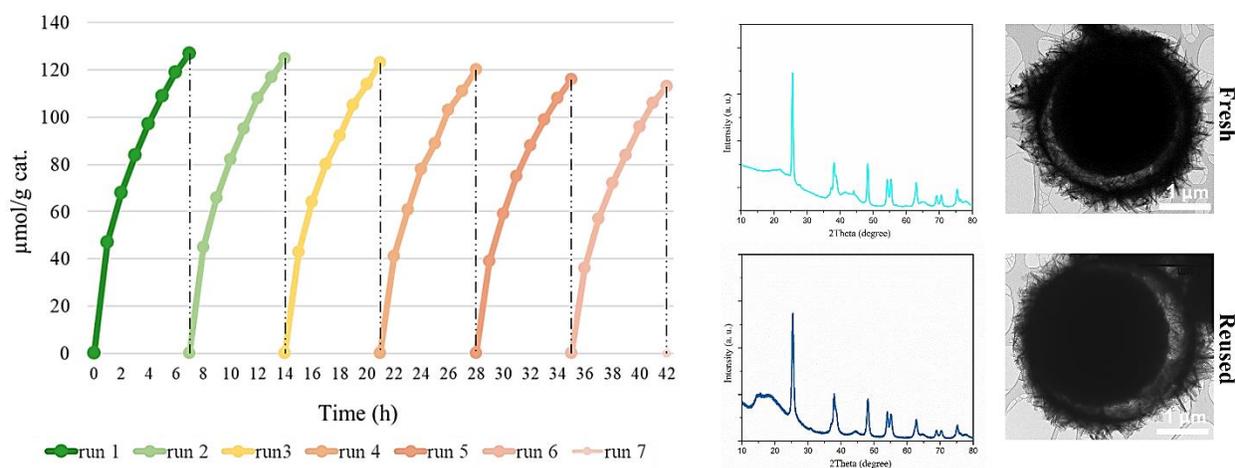


Figure S14. Reusability study of HUY@S-TOH/AuPd architecture in the photocatalytic CO₂ conversion to CH₄. Left: catalytic test, middle XRD (fresh – reused), right TEM (fresh – reused)

Table S1. Comparison of the specific surface area and photocatalytic activity of HUY@S-TOH/AuPd structures prepared in presence of different alcohols.

	HUY@S-TOH/AuPd (MeOH/H₂O)	HUY@S-TOH/AuPd (EtOH/H₂O)	HUY@S-TOH/AuPd (1-PrOH/H₂O)	HUY@S-TOH/AuPd (2-PrOH/H₂O)	HUY@S-TOH/AuPd (t-BuOH/H₂O)
Surface area (m²·g⁻¹)	289	306	301	264	189
CH₄ (μmol·g⁻¹)	117	126	119	114	106

Table S2. Comparing the efficiency of different photocatalyst in CO₂ conversion to CH₄

Entry	Photocatalyst	Light source	Reusability (run)	CH₄ yield (μmol/g_{cat}·h)	Ref.
1	Cu/Pt@TiO ₂	Xe lamp (200 W)	---	33	[5]
2	Au/Cu-TiO ₂	Xe lamp (1000 W)	---	44	[6]
3	Ultrathin W ₁₈ O ₄₉ Nanowires	Xe lamp (300 W)	---	16.2 (666 ppm/g _{cat} ·h)	[7]
5	Cu ₂ S/ CuS Nanorod	solar simulator (AM 1.5G)	---	39.42	[8]
6	Pt/RuO ₂ /Zn ₂ GeO ₄ Nanoribbons	Xe lamp (300 W)	---	25	[9]
7	3D-SiC@2D-MoS ₂ Heterostructure	Xe lamp (300 W)	5	14.4 (323 μL/g _{cat} ·h)	[10]
8	HUY@S-TOH/AuPd	Xe lamp (300 W)	6	47	This work

References

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