

Supporting Information

Double-cocatalysts promote charge separation efficiency in CO₂ photoreduction: spatial location matters

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1. Experimental Section

1.1. General information

All chemicals, including potassium persulfate (KPS, AR), sodium dodecyl sulfate (SDS, AR), styrene (AR), sodium hydroxide (NaOH, AR), Pluronic triblock copolymer P123 (EO₂₀PO₇₀EO₂₀, $M_{av} = 5800$, Aldrich), Titanium isopropoxide (TTIP, AR), titanium tetrachloride (TiCl₄, AR), tetraethyl orthosilicate (TEOS, AR), ethanol (EtOH, AR), methanol (MeOH, AR), cobalt acetate tetrahydrate (Co(AC)₂·4H₂O, AR), ammonium hydroxide (NH₃·H₂O, AR), chloroplatinic acid heahydrate (H₂PtCl₆·6H₂O, Pt>37.5%), ethylene glycol (EG, AR) and ultrapure water were used as received without any purification.

1.2. Synthesis of Pt/HTSO and Pt/HCTSO

Generally, the poly-styrene spheres as macropore templates were synthesized first, 0.225 g SDS, 0.3 g KPS, 62.5 mL EtOH and 147.5 mL H₂O was mixing together in a three necks flask, and stirring for 30 min. After that, the sealed flask was charged with N₂ to 1 bar and then heated to 343 K, then 18 mL fresh washed styrene inject to

the flask. The reaction was kept at 343 K for 19 h to finish the polymerization. The obtained poly-styrene emulsion was dried in an oven for 2 days to get the poly-styrene opal.

The hierarchical ordered $\text{TiO}_2\text{-SiO}_2$ composites (HTSO) was synthesized following EISA (evaporation induced self-assemble) method with two templates. Generally, The Ti-Si sol precursor was synthesized by mixing 1.0 g P123, 15 mL EtOH, 0.45 mL TEOS, 0.26 mL TiCl_4 and 1.66 mL TTIP together. The obtained sol was stirring at 25 °C for 2 h; after that, the dried poly-styrene opal pieces were immersed in the Ti-Si sol precursor in a petri dish and evaporated at 40 °C for 3 days and 70 °C for 3 days, the relative humidity in the oven was setting at 50-60%. The sample was collected from the petri dish carefully and calcinated at 500 °C for 4 h with the heating rate of 1 °C/min. After that the as made sample was collected and denotes as HTSO. For the preparation of HCTSO, different amount of $\text{Co}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$ (10 mg, 20 mg, 40 mg, 80 mg) was added to the Ti-Si sol before the impregnation with PS opal.

The Pt/HTSO and Pt/HCTSO was synthesized by mixing 0.2 g HTSO or HCTSO in MeOH and sonicated for 15 min, after that, $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ EG solution (5 mg/mL) with different volume (0.84 mL, 2.1 mL and 4.2 mL corresponds to 0.8 wt%, 2 wt% and 4 wt% loading amount respectively) was added to the mixture dropwise. After 30 min stirring, then mixture was refluxed at 353 K for 3 h. The final product was obtained by centrifuge the mixture, washed with H_2O for many times and dried in vacuum overnight.

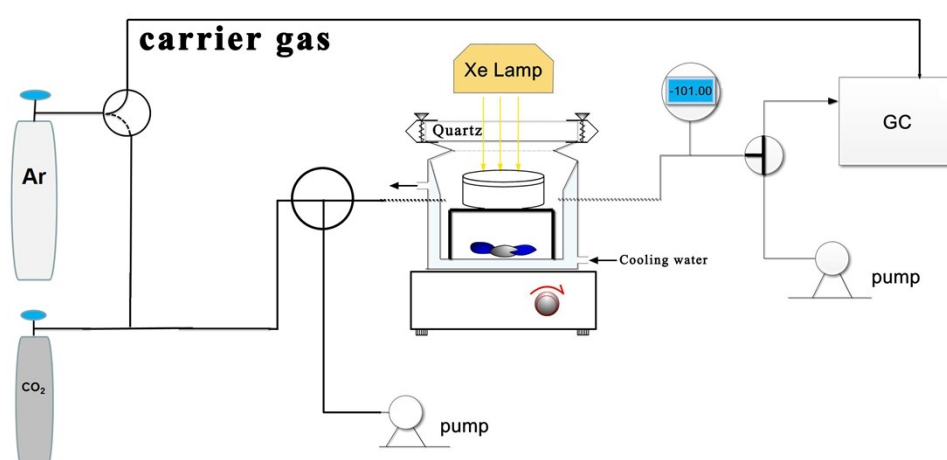
1.3. Synthesis of Pt-CoO_x/HTSO

The CoO_x/HTSO was synthesized by mixing HTSO with 15 mL EtOH, after 20 min stirring, 1 mL Co(AC)₂·4H₂O EtOH solution (0.01 M) was added to the mixture and stirred for another 30 min, after that, 0.5 mL NH₃·H₂O added and stirred for another 30 min, then the suspension was transferred into 20 mL autoclave sealed and maintained at 424 K for 3 h. The final product was obtained by centrifuge the mixture, washed with H₂O for many times and dried in vacuum overnight. The Pt-CoO_x/HTSO was synthesized by the same route with Pt/HTSO.

1.4. Photocatalytic tests

Typically, for each test, the fresh powdered catalyst was dispersed into water and sonicated for 5 min, the mixture emulsion then transferred into a petri dish with a diameter of 6 cm. After evaporation in an oven, the thin layered catalyst was deposited on the petri dish. The petri dish was then placed on a glass holder in the homemade setup (300 mL total volume glass reactor covered with round shaped quartz plate). Under the petri dish there is a fan shaped Teflon covered stir to make the gas phase well-distributed. Afterwards, the photoreactor was vacuumed at 101.5 ± 0.5 KPa (relative pressure) for 0.5 h, and CO₂ (99.995%) was introduced into the photoreactor subsequently. After that, 1 mL ultrapure H₂O was injected into the reactor and dispersed homogeneously in the reactor. A 300 W Xe lamp was used as the light source and coupled with an AM 1.5 filter. During the irradiation, the temperature in the reactor will rise to 40 °C and the pressure value will be confined to 10 KPa. Certain amount of gases mixture will be taken every 1 hour and analyzed by the GC (gas chromatograph, Shimadzu 2014). CH₄, CO and CH₃OH can be

detected by the flame ionization detector (FID) with Ar as the carrier gas and 5 A molecular sieve columns was used to separate the CO and CH₄. A methanation reactor was equipped in the GC to convert the CO into CH₄ for detection. O₂, N₂, H₂, and CO₂ can be detected by the thermal conductivity detector (TCD) in the same time (Fig. S1). Data reproducibility was checked by performing the same reaction in duplicate and draws the same results with low dispersion (< 5 %).



Scheme S1. Set up diagram for CO₂ photoreduction.

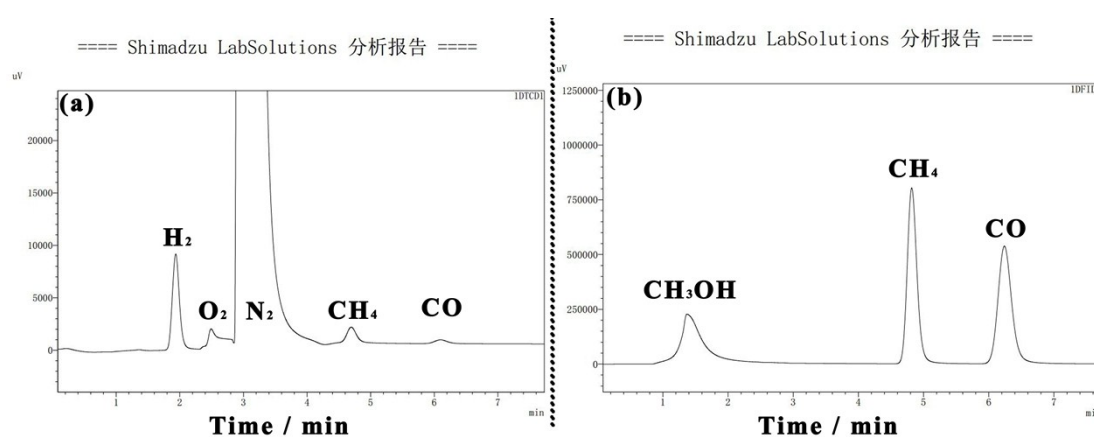


Fig. S1 The result of standard gases analysis by GC.

1.5. Photocatalyst characterization

The powder X-ray diffraction (XRD) including wide angle XRD and small angle

XRD tests of all samples were characterized, data was collected in the range 10-80° (2 θ) using a Rigaku D/MAX 2550 diffract meter (Cu K radiation, $\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 40 mA. The morphologies were characterized by transmission electron microscopy (JEM-2100, JEOL), elemental mapping of Pt/HCTSO and Pt-CoO_x/HTSO was performed by energy dispersive X-ray spectroscopy (EDX). BET surface area measurements were carried out by N₂ adsorption at 77 K using an ASAP2020 instrument. The instrument employed for XPS studies was a Perkin-Elmer PHI 5000C ESCA system with Al K α radiation operated at 250 W. The shift of the binding energy due to relative surface charging was corrected using the C1s level at 284.6 eV as an internal standard. The photoluminescence (PL) emission spectra of the solid catalysts were measured using luminescence spectrometry (Cary Eclipse) at room temperature under the excitation wavelength at 315 nm. The electrochemical measurements were carried out on an electrochemical analyzer (CHI 660 D electrochemical station, CHI Instruments Inc.) at room temperature. The standard three-electrode system consisting of a working electrode (as-prepared samples as the working electrodes with an active area of ca. 0.65 cm²), a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The transient photocurrent responses of different samples were carried out in 0.5 M Na₂SO₄ aqueous solution under 300W Xe lamp irradiation with an AM 1.5 filter.

Table S1 Physical properties of Pt/HCTSO with different Pt and CoO_x contents

Samples	Mean pore size (nm)	S_{BET} (m²/g)
HTSO	3.3	210.8
0.8% Pt/HCTSO (0.8%)	4.3	189.2
2% Pt/HCTSO (1.6%)	5.6	189.5

Table S2. Pt/HTSO with different Pt loading amount for photoreduction of CO₂ and water vapor^a

Photocatalyst	Formation rate (μmol/g.h)			Selectivity for CH ₄ (%) ^b
	H ₂	CH ₄	CO	
0.8% Pt/HTSO	65.3	4.8	1.3	22.3%
2% Pt/HTSO	43.6	6.6	2.4	36.5%
4% Pt/HTSO	N.D ^c	0.99	N.D ^c	-

^aReaction conditions: catalyst, 30mg deposited homogeneously on a petri dish with the diameter of 6cm; pressure in the reactor, 4-10kPa; H₂O, 1mL; irradiation time, 4h. ^bSelectivity: = $[8n(\text{CH}_4)] / [2n(\text{CO}) + 8n(\text{CH}_4) + 2n(\text{H}_2)] * 100\%$. ^cN.D.: not detectable.

Table S3. Pt/HCTSO with different Pt and CoO_x contents for photoreduction of CO₂ and water vapor^a

Photocatalyst	Formation rate (μmol/g·h)			Selectivity for CH ₄ (%) ^b
	H ₂	CH ₄	CO	
0.8% Pt/HCTSO	65.3	4.8	1.3	22.3
0.8% Pt/HCTSO (0.4%)	31.0	3.3	0.2	30.0
0.8% Pt/HCTSO (0.8%)	14.1	9.3	0.3	72.1
0.8% Pt/HCTSO (1.6%)	7.2	5.5	0.07	75.1
0.8% Pt/HCTSO (3.2%)	N.D. ^c	1.2	0.1	98.2
2% Pt/HCTSO (1.6%)	1.5	6.7	0.03	94.7

^aReaction conditions: catalyst, 30mg deposited homogeneously on a petri dish with the diameter of 6cm; pressure in the reactor, 4-10kPa; H₂O, 1mL; irradiation time, 4h. ^bSelectivity: = $[8n(\text{CH}_4)] / [2n(\text{CO}) + 8n(\text{CH}_4) + 2n(\text{H}_2)] * 100\%$. ^cN.D.: not detectable.

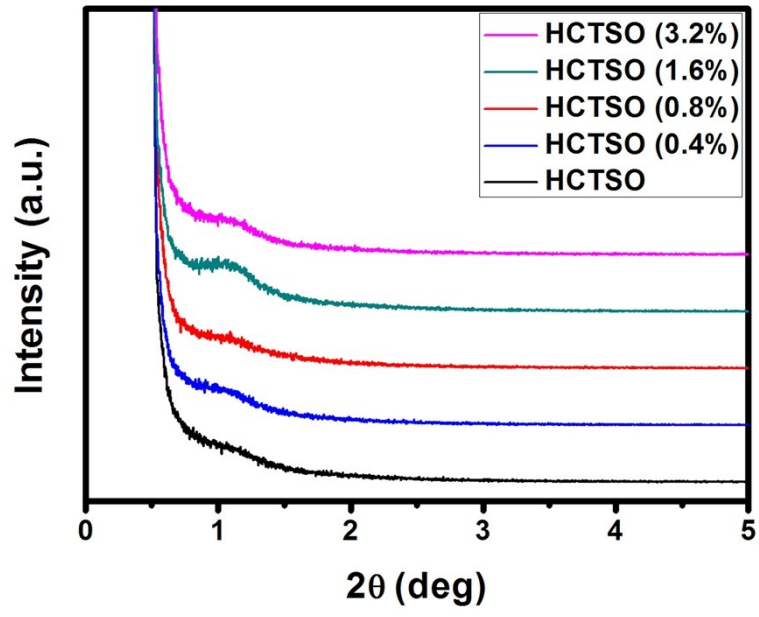


Fig. S2 Small angle XRD patterns of HCTSO with different CoO_x content.

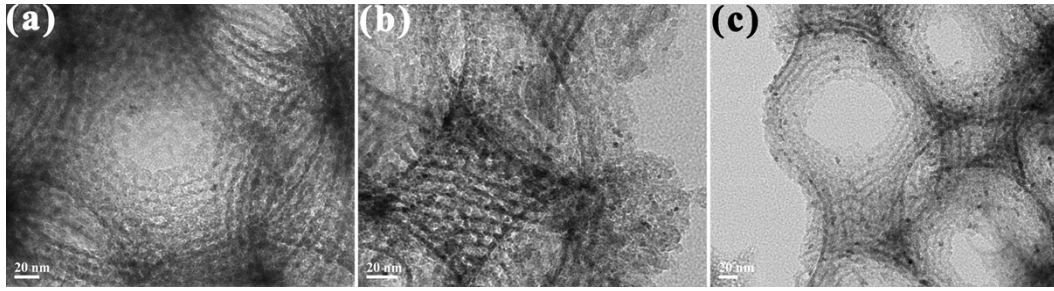


Fig. S3 TEM images of (a) 0.8% Pt/HTSO, (b) 2% Pt/HTSO and (c) 4% Pt/HTSO.

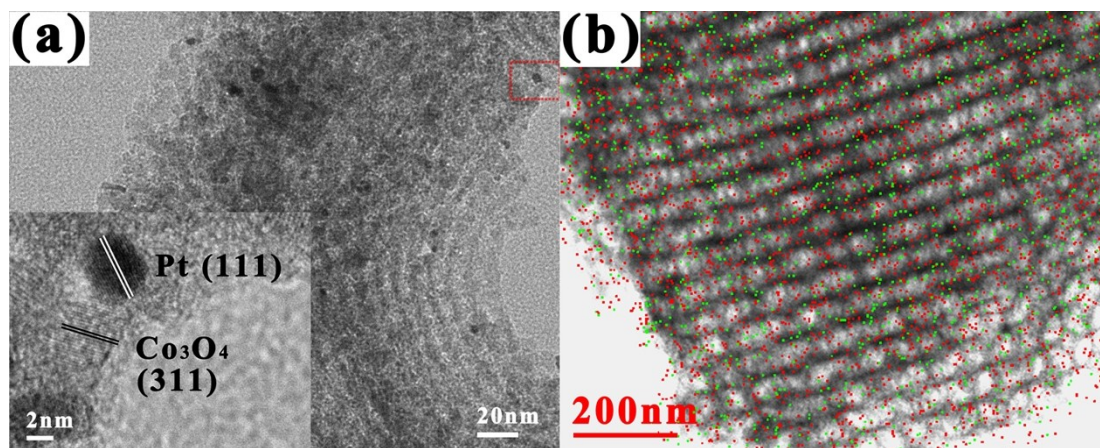


Fig. S4 TEM images of (a) 2% Pt-CoO_x/HTSO where the red square indicates the location of the HR-TEM image. EDS-Mapping images of (b) 2% Pt-CoO_x/HTSO.

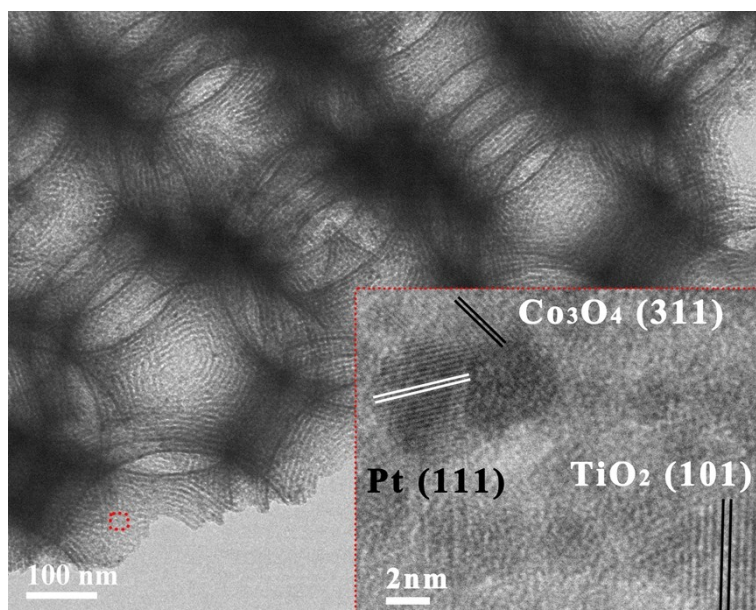


Fig. S5 TEM and HR-TEM (inset) image of 0.8% Pt/HCTSO (3.2%).

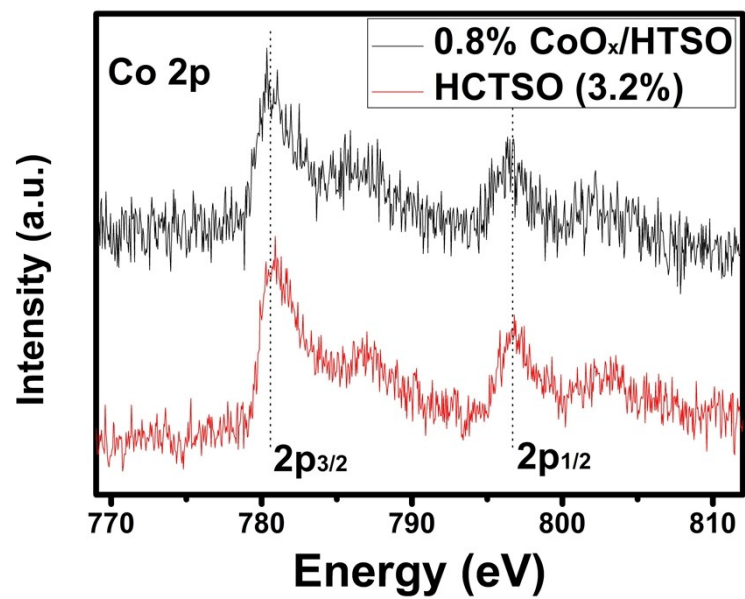


Fig. S6 Co 2p XPS spectra of 0.8% CoO_x/HTSO and HCTSO (3.2%).

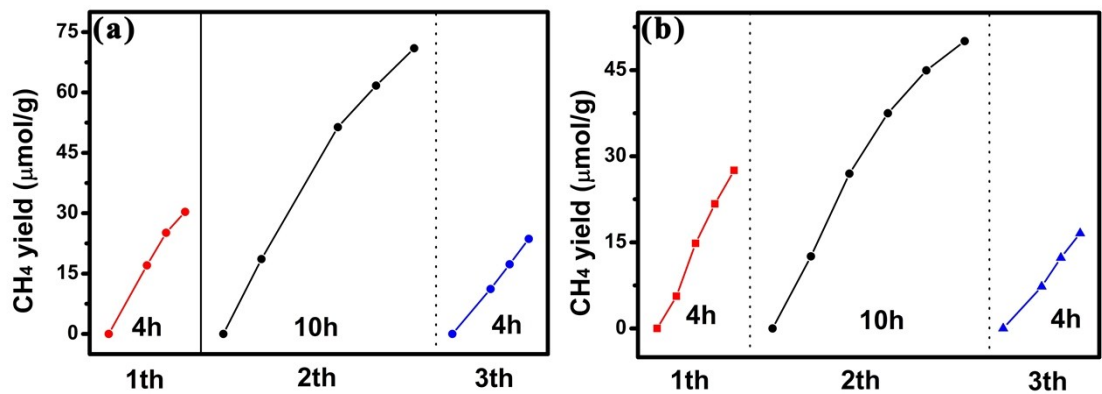


Fig. S7 Cyclic experiments of CO₂ photoreduction evaluation over (a) 0.8% Pt/HCTSO (0.8%) and (b) 2% Pt/HCTSO (1.6%).