Electronic Supplementary Information

$3DOM-LaSrCoFeO_{6-\delta}$ as a highly active catalyst for thermal and photothermal reduction of CO₂ with H₂O to CH₄

S1

Experimental details

Materials

Methyl methacrylate (MMA), Potassium persulfate ($K_2(SO4)_2$, KPS), La(NO_3)₃.6H₂O, Sr(NO_3)₂, Co(NO_3)₂.6H₂O, Fe(NO_3)₃.9H₂O, CH₃OH (\ge 99.5%), citric acid C₆H₈O₇ (\ge 99.7%), C₂H₅OH (\ge 99.5%), CH₃COOH (\ge 99.5%), NH₄OH (25%) and ethylene glycol C₂H₆O₂ (\ge 99.0%) were purchased from Sinopharm Chemical Reagent Company Ltd. Deionized water was used in all experiments. All reagents were of analytical grade and were used without further purification.

Synthesis of monodisperse PMMA microspheres

Monodisperse poly(methyl methacrylate) (PMMA) spheres (diameter 720 nm) were synthesized by literature techniques and packed into colloidal crystals.¹ Potassium peroxosulfate (0.0375 g) water (50 g) and methanol (100 g) were stirred at 120 rpm, heated at 70 °C, and degassed with flowing argon in a separable three-neck 250 mL round-bottom flask. After equilibrating to 70 °C, methyl methacrylate (MMA) (5 g) was poured into the flask, and the resulting suspension was stirred at 70 °C for 5 h. The PMMA colloidal crystal template was prepared by centrifugation (2800 rpm) of the colloidal suspension in a 50 mL centrifugation tube for 2 h. The obtained template was dried under vacuum at 35 °C for 24 h for preparation of 3DOM-LSCF.

Preparation of 3DOM-LSCF

A total metal ions concentration 2M of $(La(NO_3)_3.6H_2O, Sr(NO_3)_2, Co(NO_3)_2.6H_2O, Fe(NO_3)_3.9H_2O$ with mole ratio (La : Sr : Co : Fe = 1 : 1 : 1 : 1) and equal mole of citric acid $C_6H_8O_7$ hydrates mixture were dissolved with 5 mL of ethylene glycol (EG) by stirring in a 100 mL beaker at 50 °C for 1 h and adjusting the pH to 6.0 using a concentrated NH₄OH solution. Methanol 5 mL was added and stirred at 50 °C for 1 h. Then, the PMMA colloidal crystals template were soaked in the solution for 3 h. Excess solution was removed from the impregnated PMMA colloidal crystals by vacuum filtration. The obtained sample was allowed to dry in air at room temperature overnight. A 1.0 g amount of the sample was mixed with 2.5 g of quartz sand (10-15 mesh) and calcined in a tubular furnace (inner diameter ca. 12 mm) in an air flow of 60 mL min⁻¹. The temperature was raised at a rate of 1 °C min⁻¹ to 550 °C (or 650, 750, 850, 950 °C) and held for 4 h.

For comparison purposes, the bulk LSCF catalyst was also prepared with the same method without PMMA template.

Characterization

All the samples were characterized by an X-ray Diffractomer (Holland PANalytical X'pert Pro MRD) with Ni-filtered CuK α radiation (λ = 0.154056 nm; 40 kV, 40 mA) in the range of 20-80° (2 θ) at a scanning rate of 10° min⁻¹. Rietveld structure refinement was performed with the program X'Pert High Score Plus (version 3.0.5) using a pseudo-Voigt profile function and polynomial background model. The morphology of each sample was characterized by a scanning electron microscopy (Phenom-World's Phenom Pro Desktop SEM, Netherlands). An energy dispersive X-ray spectrometer (EDS) detector attached to the SEM (S-3400N, Hitachi) was used to measure the element composition and distribution with the X-Flash Detector 4010 (Burker, ALX). Transmission

electron microscopy (TEM) images were obtained by a FEI Tecnai G2 F20 with a beam energy of 300 keV. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200W monochromated AI K α radiation (hv = 1,486.6 eV). The 500 μ m X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. XPS data were analysed using Thermo Scientific Avantage Data System software (version 5.957), and a SMART background was subtracted before peak deconvolution and integration. The specific surface area of each sample was measured by the BET technology using nitrogen adsorption and desorption isotherms at 77 K on a Micrometrics ASAP 2020 HD88 system. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method in the P/P₀ range 0.05-1. The pore-size distribution was calculated on the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) model. The Mott-Schottky curves were measured using a three-electrode system on the CS350 Electrochemical Workstations (Wuhan Corrtest Instruments Corp., Ltd) in a 1M LiClO₄/Propylene carbonate (PC) electrolyte. UV-vis diffuse reflectance spectra of the samples were measured in the range of 200-800 nm using a UV-vis spectrophotometer (Hitachi U-3900, Japan) with BaSO₄ as the reflectance standard. The band gap energy (E_e) of the material was calculated from the absorption data by using $E_g = 1240/\lambda_g$ (eV) where Eg is the band-gap energy and λ_g (nm) is the wavelength corresponding to the intersection point of the vertical and horizontal parts of the spectrum.^{2, 3}

Photocatalytic activity measurements

The thermal and photothermal reduction of CO₂ with H₂O to CH₄ has been carried out in a gas-closed circulation system described in Figure S1 and the volume of reactor was about 150 mL. In the typical experiments, 0.1 g of the tested catalyst was put in a quartz reactor. The reaction setup was vacuum-treated several times, and the high purity CO_2 (\geq 99.999%) was flown through the whole system for 5 mins to ensure complete removal of air from the system and the maximum adsorption of CO₂ molecules on active sites of catalysts. A positive pressure of CO₂ was maintained at 25 kPa inside the system. The water was injected into reaction system when the temperature reached 110 °C and the thermal catalytic activity evaluation was performed at different temperatures 150, 250, 350 °C without light. The photothermal catalytic activity evaluation was performed at 350 °C with visible light. The temperature maintained through the heating jacket in out of the reactor and the temperature control device. A 300 W high-pressure Xe lamp (Beijing CEAULight, China, CEL-HXF300, spectral output 320-2500 nm, overall radiant output 50 W, UV output 2.6 W, IR output (>770 nm) 28.8W, Visible output (390-770 nm) 5000 Lumens) with a UV-light filter ($\lambda \ge 420$ nm) was used as the light source and the distance from a point source of light to the surface of catalysts was kept 10 cm. The total light intensity ranging from 420 nm to 780 nm on the surface of quartz window was detected to be 145 mW/cm² by an irradiation meter (Beijing CEAULight, China, CEL-NP2000) at the central point. Taking samples per hour and quantitative analysis was performed on a GS-Tek (Echromtek A90) equipment with a capillary column (GsBP-PLOT Q, 30mx0.53mmx30µm, TCD and FID), using Pure N₂ (99.999%) as carrier gas. The quantification of CH₄ yield product was based on the external standard and the use of calibration curve.



Figure S1. Reactor used for thermal and photothermal catalytic reduction of CO₂ in the presence of H₂O to CH₄.



S2 Original GC data

Figure S2. The original GC data of photothermal catalytic reduction of CO_2 with H_2O vapor to CH_4 over 3DOM-LSCF catalyst for 8 h.

S3

Table 4 The yield, TON and Solar-to-Methane (STM) energy conversion efficiency of thermal and photothermalreduction of CO_2 with H_2O vapor to CH_4 over 3DOM-LSCF catalyst.

		3DOM-LSCF										
Time (h)		Yield	^[a] (%)		TON ^[b]				STM ^[c] efficiency (%)	Selectivity		
	150 °C	250 °C	350 °C	350 °C + Vis- light	150 °C	250 °C	350 °C	350 °C + Vis- light	350 °C + Vis-light	(%)		
1	0.016	0.171	0.956	5.620	0.0032	0.034	0.192	1.130	0.721	100		
2	0.027	0.301	1.140	6.663	0.0053	0.060	0.229	1.340	0.854	100		
3	0.033	0.448	1.369	7.543	0.0067	0.090	0.275	1.517	0.967	100		
4	0.037	0.497	1.660	8.120	0.0074	0.100	0.334	1.632	1.041	100		
5	0.040	0.543	1.819	8.520	0.0080	0.109	0.366	1.713	1.093	100		
6	0.044	0.588	1.896	9.069	0.0088	0.118	0.381	1.823	1.163	100		
7	0.046	0.643	2.023	9.312	0.0093	0.129	0.407	1.872	1.194	100		
8	0.048	0.672	2.083	9.613	0.0097	0.135	0.419	1.933	1.233	100		

Table 5 The yield, TON and Solar-to-Methane (STM) energy conversion efficiency of thermal and photothermalreduction of CO_2 with H_2O vapor to CH_4 over LSCF catalyst.

		LSCF										
Time (h)		Yield	^[a] (%)		TON ^[b]				STM ^[c] efficiency (%)	Selectivity		
	150 °C	250 °C	350 °C	350 °C + Vis- light	150 °C	250 °C	350 °C	350 °C + Vis- light	350 °C + Vis-light	(%)		
1	0.011	0.132	0.626	3.491	0.0023	0.027	0.126	0.702	0.448	100		
2	0.016	0.218	0.690	4.344	0.0032	0.044	0.139	0.873	0.557	100		
3	0.019	0.279	0.808	4.904	0.0037	0.056	0.163	0.986	0.629	100		
4	0.022	0.311	0.922	5.224	0.0044	0.063	0.185	1.050	0.670	100		
5	0.026	0.336	0.994	5.589	0.0053	0.068	0.200	1.124	0.717	100		
6	0.028	0.376	1.075	5.858	0.0057	0.076	0.216	1.178	0.751	100		
7	0.031	0.411	1.103	5.984	0.0062	0.083	0.222	1.203	0.767	100		
8	0.033	0.430	1.135	6.054	0.0065	0.086	0.228	1.217	0.776	100		

^[a] Moles of product (CH_4) per 100 moles of CO_2 .

^[b] Turn over number = number of moles of product per moles of catalyst precursor.

^[c] Calculated follow our previous study.⁴

Table 6 Summary of the various photocatalytic systems employed for CO_2 reduction.

Catalyst	Co- catalyst	Conditions	Light-source and Temp.	Major product	R _{max}	Ref.
LaSrCoFeO _{6-ð} Nanoparticles (LSCF)	-	CO_2 and H_2O vapor	300 W high-pressure Xe lamp, UV cutoff filter (λ≥420 nm, 145 mW/cm ²), 350 °C	CH4	351.32 ^[a]	This study
LaSrCoFeO _{6-ð} 3DOM structured (3DOM-LSCF)	-	CO_2 and H_2O vapor	300 W high-pressure Xe lamp, UV cutoff filter (λ≥420 nm, 145 mW/cm ²), 350 °C	CH4	557.88	This study
m-WO _{3-x} Mesoporous	-	CO_2 and H_2O vapor	300 W high-pressure Xe lamp, UV cutoff filter (λ≥420 nm, 145	CH4	25.77	4

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Cu/SrTiO₃ Nanocubes	-	CO₂ and H₂O vapor	300 W high-pressure Xe lamp, (320-780 nm, 630	CH4	1.80	5
Mo/WO₃ Mesoporous	-	CO_2 and H_2O vapor	mW/cm ²), 250 °C 300 W high-pressure Xe lamp, UV-light filter (λ≥420 nm, 320 mW/cm ²), 250 °C	CH₄	5.96	6
ZnO@Cu-Zn-Al LDH Core-shell structured	-	CO_2 and H_2O vapor	300 W high-pressure Xe lamp, (320-780 nm, 580 mW/cm ²), 200 °C	CH₄	57.10	7
TiO ₂ /Zeolite Micropores	-	CO_2 and H_2O vapor	75 W high-pressure Hg lamp (λ≥280 nm), 55 °C	CH_4	13.30	8
WO₃ Nanosheets	-	CO_2 and H_2O vapor	300 W Xe arc lamp, UV cutoff filter ($\lambda \ge 420$ nm)	CH_4	16.10	9
CaTiO ₃ Nanoparticles	-	CO_2 and H_2O vapor	UV-lamp (365 nm, 6 W/cm²), 30 °C	CH_4	17	10
Zn/Ti LDH	-	CO_2 and H_2O vapor	Hg lamps (185 nm, 4 W and 254 nm, 8 W), 60-65 °C	CH_4	3.77 ^[b]	11
NaNbO ₃ Nanocubes	1 wt % Pt	CO_2 and H_2O vapor	300 W Xe lamp	CH_4	5.25	12
HNb ₃ O ₈ Nanobelts	-	CO ₂ and H ₂ O vapor	350 W Xe-lamp	CH_4	3.58	13
CdS-WO ₃ Heterostructure Hollow spheres	-	CO_2 and H_2O vapor	300 W Xe arc lamp, UV cutoff filter (λ≥420 nm)	CH_4	1.02	14
RGO-CdS Nanorods	-	CO_2 and H_2O vapor	300 W Xe arc lamp, UV cutoff filter ($\lambda \ge 420$ nm, 150 mW/cm ²)	CH₄	2.51	15
CuO-TiO ₂ Hollow microspheres	-	CO_2 and H_2O vapor	Hg UV lamp (40 W; 254 nm, 20 mW/cm ²)	CH_4	2.07	16
NaTaO₃ Nanoparticles	0.5 wt % Ru	CO_2 and H_2O vapor	300 W UV-enhanced Xe lamp (λ>200 nm) without filter	CH_4	51.80	17
Co-doped TiO ₂ (Co-OMT-4)	-	CO_2 and H_2O vapor	300 W Xe lamp, UV cutoff filter (λ≥420 nm)	CH_4	0.09	18
Cu ₂ O/TiO ₂ Nanojunction Porous-structured	Pt	CO_2 and H_2O vapor	300 W Xe lamp	CH_4	55.70 ^[c]	19
NaTaO ₃ Nanoparticles	1 wt % Au	CO_2 and H_2O vapor	200 W Hg-Xe arc lamp	CH_4	36	20
SrTiO ₃ Leaf architectured	1 wt % Au	CO_2 and H_2O vapor	300 W Xe lamp	CH_4	275	21
CuO-TiO _{2-x} N _x Hollow nanocubes	-	CO_2 and H_2O vapor	300 W Xe lamp with anAM1.5filtermW/cm2)	CH ₄	41.30 ^[d]	22
ZnGa ₂ O ₄	1 wt %	CO ₂ and	300 W Xenon arc lamp	CH_4	50.40 ^[e]	23
TiO ₂ /SrTiO ₃ Heterojunction Nanotubes, and		H_2O vapor CO_2 and H_2O vapor	300 W Hg lamp, 10.4 mW/cm ²	CH₄	20.83 ^[f]	24
SnNb ₂ O ₆ 2D Nanosheets	-	CO_2 and H_2O vapor	300 W Xe lamp, UV cutoff filter (λ≥420 nm), 25 °C	CH ₄	110.90 ^[g]	25
La-modified TiO ₂	-	CO_2 and	300 W Xe arc lamp	CH_4	3.46 ^[h]	26

Nanoparticles		H ₂ O vapor				
SrNb ₂ O ₆		CO_2 and	100 W Xe lamp (λ = 300-	СЦ	0.22	27
Nanoplates	-	H_2O vapor	780 nm).	CH ₄	0.55	27

 R_{max} Maximum formation rate reported for the major product (s), in [a] μ mol g⁻¹, [b] μ mol h⁻¹ g⁻¹, [c] nmol h⁻¹g⁻¹ [d] ppm g⁻¹ h⁻¹, [e] ppm h⁻¹, [f] ppm h⁻¹ cm⁻², [g] μ L h⁻¹ g⁻¹, [h] μ mol

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