Supporting Information

Photothermal catalytic activity of combustion synthesized $LaCo_xFe_{1-x}O_3$ (0 ≤ x ≤1) perovskite for CO_2 reduction with H_2O to CH_4 and CH_3OH

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S1. Experimental information

Preparation of catalysts

$La(NO_3)_3·6H_2O$, $Fe(NO_3)_3·9H_2O$, $Co(NO_3)_3·6H_2O$, and citric acid were procured from Shanghai Titan chemicals Co., Ltd. These chemicals as raw material were directly used to compound series $LaCo_xFe_{1-x}O_3$ mixed-oxide perovskites, which was without any further purification treatment.

In a typical experiment, the catalyst in accordance with the formula $LaCo_xFe_{1-x}O_3$ (x=0, 0.2, 0.4, 0.6, 0.8 and 1) were synthesized via a modified sol-gel combustion route. The metal nitrates of $La(NO_3)_3·6H_2O$, $Fe(NO_3)_3·9H_2O$ and $Co(NO_3)_3·6H_2O$ were mixed together in an aqueous solution and until the formation of a clear solution, then citric acid was added into the mixed solution under constant stirring, the molar ratio between the total amount of nitrates and the acid was1:1.2. The resulting solution were then heated at 80℃ until a sol formation, then the sol completely dried overnight at 120℃ in a oven. After that, these materials were calcined in air at 500, 600, 700, 800, 900℃ for 2h, heating rate of 5℃·min^{-1}, to obtain perovskite type nanoparticles.

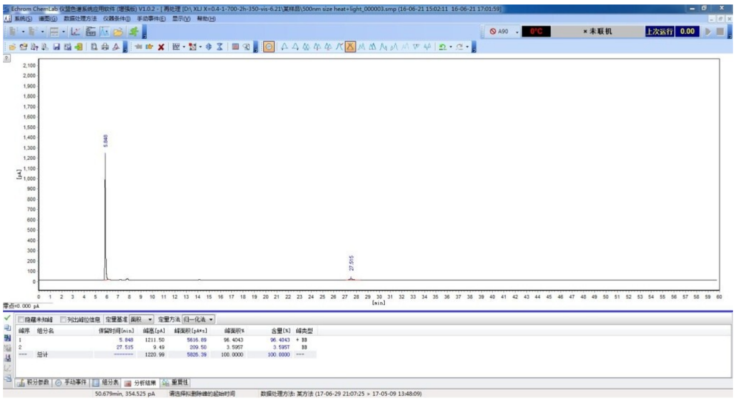
Characterization

The synthesized samples were characterized using X-ray diffraction (PAN alytical X'pert), their crystalline phases were determined by Cu Ka radiation (λ = 0.154nm) at 40 kV and 40 mA. The XRD patterns were record in the range between 10° and 80° at the scan rate of 10° min^{-1}. The morphologies and sizes of the products were determined by Scanning Electron Microscopy (SEM, JSM-7000F). TEM images of samples were obtained using a FEI TECNAI G2F20 transmission electron microscopy with a beam energy at 300 kV voltage. BET specific surface areas of the samples were performed by using a Micrometics USA ASAP2020 instrument with adsorption-desorption of N_2 at 77K, samples were degassed 2h at 150℃. The UV-Vis diffuse reflectance spectrum of all the samples were obtained by using a UV-Vis spectrophotometer (SHIMADZU UV-3600, Japan) with $BaSO_4$ as the reflectance standard. The element composition and distribution was measure by using an energy dispersive X-ray spectromemeter (EDS) detector attached to the SEM (S-3400N, Hitachi) with a Bruker-AXS 133 eV XFlash 4010 Detector. X-ray photoelectron spectroscopy (XPS) was characterized by an ESCALAB 250 instrument with Al Kα (hν=1486.6eV) source at a residual gas pressure of below 10^{-10} Pa. Mott-Schottky curves were measured using a three-electrode system on the CHI604E electrochemistry workstation.

Catalytic measurements

The photothermal catalytic reduction of CO_2 was carried out with 100 mg of the sample powdered, which was uniformly placed at the bottom of a Pyrex glass cell. The whole catalysis reaction temperature was set at 350℃ with visible light irradiation on (photothermal). The temperature control was realized by a heating jacket surrounded the quartz reactor. And the light source used was a 300 W Xe lamp equipped with a UV- light filter (λ>420nm). The light illumination intensity is measured using CEL-NP2000-2 Full Spectral Optical Power Meter. And the measured optical power density value is 145 mW/cm^2. Before the reaction, the reactor was vacuumed with a pump and then was filled with high purity CO_2 (99.999 wt %) at a flow rate of 27 mL/min for 5min. This process was repeated for 5 times in order to guarantee that no other possible impurity gases will be involved during the catalytic reaction. The catalytic experiments were carried out in a gas-tight circulation system, distilled water (0.3 mL) was injected into the system when the temperature was higher than 120℃. The catalytic performance characterization was started once the reactor reached 350oC. The light source will be only swiched on the time reactor reached 350^{o}C. Samples were then taken hourly and qualitatively analyzed by GS-Tek (Echromtek A90) with gas chromatograph equipped with a flame ionization detector (FID). Finally, the quantification of CH_4 and CH_3OH yield was based on calibration curve method.

S2. The studies of catalytic properties assessment about Yield and STM efficiency of the photothermal catalysis



定量基准 面积 定量方法 归一化法

峰序	组分名	保留时间[min]	峰高[pA]	峰面积[pA*s]	峰面积%	含量[%]	峰类型
1		5.848	1211.50	5616.89	96.4043	96.4043	+ BB
2		27.515	9.49	209.50	3.5957	3.5957	BB
---	总计	--------	1220.99	5826.39	100.0000	100.0000	---

50.679min, 354.525 pA 请选择拟删除峰的起始时间 数据处理方法: 某方法 (17-06-29 21:07:25 > 17-05-09 13:48:09)

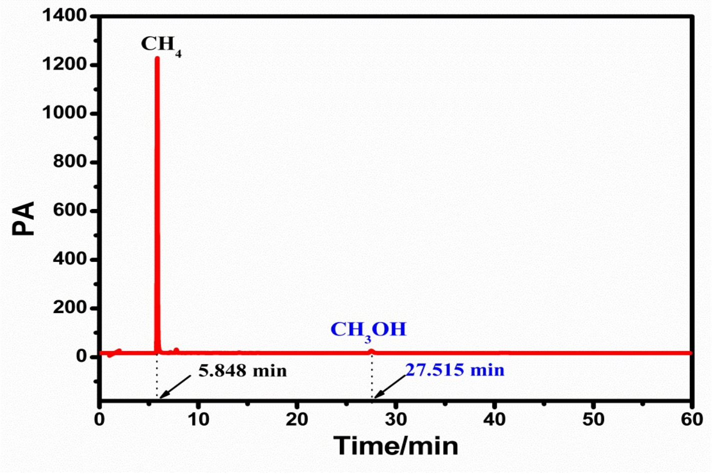


Figure S2. The original GC data

Energy efficiency discussion

A 300 W high-pressure Xe lamp (CEL-HXUV300, spectral output 420-760nm, overall radiant output 50 W) was used as the light source and the distance from a point source of light to the catalyst surface is 10 cm. The power of incident light was obtained by a CEL-NP2000 (Beijing CEAU Light, China). Solar-to-Methane (or Methanol) (STM) energy conversion efficiency was estimated using the following equation:

$$STM\ efficiency\ (\%) = \frac{Methane\ (mol)(Or\ Methanol(mol)) \times \Delta G^{\circ}\ (kJ \cdot mol^{-1})}{P_{total}\ (W\ cm^{-2}) \times Electrode\ area\ (cm^{2})}$$

Where ΔG° is the Gibbs free energy for conversion of gaseous CO_2 to Methane (or Methanol) (801 kJ $\cdot$ mol^{-1}, 690 kJ $\cdot$ mol^{-1}), Electrode erea (4 cm^2) and P_{total} is the power of incident light (145 $mW \cdot cm^{-2}$). ΔG° was estimated based on the following chemical reaction:

$$CO_2\ (g) + 2H_2(g) \rightarrow CH_4\ (g) + 2O_2\ (g),\ \Delta G^{\circ} = 801\ (\ kJ \cdot mol^{-1}\ )$$

$$CO_2\ (g) + 2H_2(g) \rightarrow CH_3OH(g) + 3/2O_2\ (g),\ \Delta G^{\circ} = 690\ (\ kJ \cdot mol^{-1}\ )$$

The yield of Calculation:

For example: CO_2: V (input)=130ml, n=130ml/22.4mol=5803.5714 μmol;

Reactor volume=210ml

The quantification of CH_4 and CH_3OH yield was based on the external standard and the use of calibration curve. The average area of CH_4 (100%) is 756900 (V=0.1ml), the average area of CH_3OH (100%) is 13093 **(V=0.1μl*(1ml/11ml)/1000(ml), 1ml of methanol and mixed 10ml H_2O extracting the mixture 0.1μl)**. At the same conditions, the average area of CH_4 and CH_3OH evolved from $LaCo_{0.6}Fe_{0.4}O_3$ is 3530.4 and 203.67 under photothermal catalytic conditions after 6h **(Every time, the volume of taking samples injected into the system is V=0.5ml (The volume of gas is mingle gas volume.))**. The total volume of CH_4 (100%) and CH_3OH (100%) evolved from $LaCo_{0.6}Fe_{0.4}O_3$ is 9.795 and 0.308 μl under photothermal catalytic conditions through mathematical and computation.

Yield (Moles of product CH_4 or CH_3OH per 100 moles of carbon dioxide)

=97.95μl/22.4/5803.5714*100=7.53459% (or 3.08 μl/22.4/5803.5714*100=0.23688%)

Table. S2 The yield and STM efficiency of photothermal reduction of CO_2 with H_2O vapor to CH_4 and CH_3OH over $LaCo_xFe_{1-x}O_3$ catalyst

Sample(x)	Yield[a] (%)		STM efficiency (%)		Selectivity(%)		Total Yield (%)
	CH_4	CH_3OH	CH_4	CH_3OH	CH_4	CH_3OH	
0.0	2.39	0.06	0.19	0.005	97.57	2.43	2.45
0.2	5.56	0.16	0.44	0.013	97.11	2.89	5.72
0.4	6.12	0.22	0.49	0.018	96.47	3.53	6.34
0.6	7.53	0.24	0.60	0.019	96.95	3.05	7.77
0.8	3.87	0.09	0.31	0.007	97.35	2.65	3.96
1.0	3.34	0.08	0.26	0.006	97.94	2.06	3.42

[a] Moles of product (CH_4 or CH_3OH) per 100 moles of CO_2.

References

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S3. Reaction molecular formula

Thermal-catalysis:

$$LaCo_xFe_{1-x}O_{3-\delta} + H_2O \rightarrow LaCo_xFe_{1-x}O_3 + H_2 \quad (1)$$

$$LaCo_xFe_{1-x}O_{3-\delta} + CO_2 \rightarrow C + LaCo_xFe_{1-x}O_3 \text{ (high } V_o) \quad (2)$$

$$LaCo_xFe_{1-x}O_{3-\delta} + CO_2 \rightarrow CO + LaCo_xFe_{1-x}O_3 \text{ (low } V_o) \quad (3)$$

$$C + 2H_2 \rightarrow CH_4 \quad (4)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad (5)$$

Photo-catalysis:

$$LaCo_xFe_{1-x}O_{3-\delta} + hv \rightarrow LaCo_xFe_{1-x}O_3(e^-) + LaCo_xFe_{1-x}O_3(h^+) \quad (6)$$

$$2H_2O \rightarrow 4H^+ + O2 + 4e^- \quad (7)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (8)$$

Photothermal catalysis:

$$CH_4 + O_2 \rightarrow CH_3OH \quad (9)$$

$$H^+ + e^- \rightarrow H^\cdot \quad (10)$$

$$H^\cdot + H^\cdot \rightarrow H_2 \quad (11)$$

The total reaction under Photothermal:

$$CO_2 + 2H_2O \rightarrow CH_4 + CH_3OH + 2O_2 \quad (12)$$