

Efficient photothermal catalytic methane dry reforming over rich oxygen vacancy catalysts

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Experimental Section

Catalyst synthesis

Catalyst Synthesis: The Ni/La₂Zr₂O₇ was prepared by sol-gel method. La(NO₃)₃·6H₂O, Zr(NO₃)₄·5H₂O, citric acid and urea were dissolved in 30 ml of deionized water to form a precursor solution. The molar ratio of citric acid, urea and metal ions was 2:2:1. The solution was homogeneously mixed and dried at 100°C until a gel was formed. The gel was then calcined at 800°C for 3 h to obtain La₂Zr₂O₇. Ni(NO₃)₂ solution and La₂Zr₂O₇ (Ni/(La+Zr)=0.1) were mixed and dried at 180°C. The powder was then calcined at 500°C for 4 h and reduced by 5 vol% H₂/Ar (30 ml min⁻¹) at 700 °C for 1 h to obtain 10% Ni/La₂Zr₂O₇. Samples of Ni nanoparticles loaded on La₂O₃ and ZrO₂ (10% Ni/La₂O₃ and 10% Ni/ZrO₂) were prepared using the same method. Ni nanoparticles loaded on TiO₂ (10%Ni/TiO₂) and SiO₂ (10%Ni/SiO₂) were prepared by impregnation method

Characterization:

The X-ray diffraction (XRD) patterns of the samples were obtained using a RigakuDmax X-ray diffractometer. A JEM-ARM200F electron microscope equipped with energy dispersive X-ray spectroscopy (EDX) was used to obtain transmission electron microscopy (TEM) and elemental mapping images. An inductively coupled plasma/optical emission spectroscopy (ICP-OES, Optima 4300DV) was used to determine elemental compositions. Diffuse absorption spectra were measured using a uv-3600i plus spectrophotometer. XPS spectra were measured using an X-ray photoelectron spectrometer (ESCALAB 250Xi). Thermogravimetric analysis was performed using an STA449F3 thermal analyzer. Raman spectra were obtained on a Renishaw in Via Raman microscope using 514.5 nm excitation. Electron paramagnetic resonance (EPR) measurements were performed by a Bruker ELEXSYS-II E500. Temperature programmed reactions were conducted on a multifunctional adsorption apparatus (TP-5080) by using a quartz tubular reactor that was linked with a quartz window.

Temperature programmed reduction of H₂ (H₂—TPR). 50 mg samples were placed in a reaction tube and treated with He gas (50 ml min⁻¹) at 300 °C for 1 h to remove adsorbed water and gases. The sample was cooled to 50 °C and then heated to 900 °C with a 10% H₂/He gas mixture at 10 °C min⁻¹. The effluent was detected using TCD.

Temperature programmed desorption of CO₂ (CO₂—TPD). CO₂-TPD was performed in a multifunctional adsorption apparatus connected to an online mass spectrometer. 50 mg of sample was added to the reaction tube and treated with He gas (50 ml min⁻¹) at 300 °C for 1 h to remove adsorbed water and gas. After cooling to ambient temperature, the gas flow rate was changed to 10% CO₂/He (50 ml min⁻¹), and the sample was pre-adsorbed for 1 h. The gas flow was switched to He gas (50 ml min⁻¹) for 30 min to remove the weakly adsorbed CO₂ on the surface. The sample was heated up to 800 °C with a He gas stream (50 ml min⁻¹) at 10 °C min⁻¹. Simultaneously, the outflow gas was recorded by an on-line mass spectrometer.

Temperature programmed disproportionation reaction (CO —TPD). 8 mg sample was reduced in situ at 700°C with a flow of 5% H₂/Ar. After cooling to ambient temperature, the reactor was cleaned with a stream of 5% CO/He (30 ml min⁻¹). The reactor was then heated to 700 °C at 10°C

min⁻¹.

Temperature programmed desorption of CH₄ (CH₄-TPD). 8 mg of sample was added to the reaction tube and treated with He gas (50 ml min⁻¹) at 300 °C for 1 h to remove adsorbed water and gas. After cooling to ambient temperature, the gas flow rate was changed to 10% CH₄/He (50 ml min⁻¹), and the sample was pre-adsorbed for 1 h. The gas flow was switched to He gas (50 ml min⁻¹) for 30 min to remove the weakly adsorbed CH₄ on the surface. The sample was heated up to 800 °C with a He gas stream (50 ml min⁻¹) at 10 °C min⁻¹ under dark and light illuminated. Simultaneously, the outflow gas was recorded by an on-line mass spectrometer.

Temperature programmed desorption of H₂ (H₂-TPD). 8 mg of sample was added to the reaction tube and treated with He gas (50 ml min⁻¹) at 300 °C for 1 h to remove adsorbed water and gas. After cooling to ambient temperature, the gas flow rate was changed to 10% H₂/He (50 ml min⁻¹), and the sample was pre-adsorbed for 1 h. The gas flow was switched to He gas (50 ml min⁻¹) for 30 min to remove the weakly adsorbed H₂ on the surface. The sample was heated up to 800 °C with a He gas stream (50 ml min⁻¹) at 10 °C min⁻¹ under dark and light illuminated. Simultaneously, the outflow gas was recorded by an on-line mass spectrometer.

Catalytic Performance Evaluation:

Thermal catalytic DRM Tests: The thermal catalytic activities of 10% Ni/La₂Zr₂O₇, 10% Ni/La₂O₃ and 10% Ni/ZrO₂ were determined on a fixed-bed reactor. A mixture of 50 mg of samples and 300 mg of quartz sand were placed on a quartz cotton support in the middle of the quartz reactor. Samples were reduced in situ with 5 vol% H₂/Ar at 700 °C for 1 h at a flow rate of 30.0 ml min⁻¹, and then switched to a gas mixture of 10.0/10.0/80.0 vol% CH₄/CO₂/Ar to determine the thermal catalytic activity from 700 °C to 400 °C. During the test, the temperature of the reaction was controlled by a tubular electric furnace. Concentrations of reactants and products were determined by a GC-9560 gas chromatograph. The DRM activity of 10% Ni/La₂Zr₂O₇ was carried out at different temperatures under dark or focused irradiation on a stationary reactor with a quartz window on the top. Here, 10 mg of the sample was reduced in situ with 5 vol% H₂/Ar at 700 °C for 1 h. After reduction by H₂, the gas mixture was switched to 10.0/10.0/ 80.0 vol% CH₄/CO₂/Ar for DRM at different temperatures in the dark or under focused irradiation.

Photothermal catalytic DRM tests: Activity tests of 10% Ni/La₂Zr₂O₇, 10% Ni/La₂O₃ and 10% Ni/ZrO₂ were carried out in a customized quartz-windowed reactor, and the stability of the first three was determined. 10 mg of the sample was taken in a quartz window reactor, and the surface of the sample was irradiated with light from a 500W xenon lamp focused by a convex lens. The samples were reduced in situ with 5 vol% H₂/Ar at 700 °C for 1 h at a flow rate of 90.0 ml min⁻¹, and then switched to a gas mixture of 20.0/20.0/60.0 vol% CH₄/CO₂/Ar for photothermal catalytic DRM.

Photocatalytic DRM tests: The reactor was placed in an ice water to maintain a mild temperature for testing the photocatalytic activity of the samples.

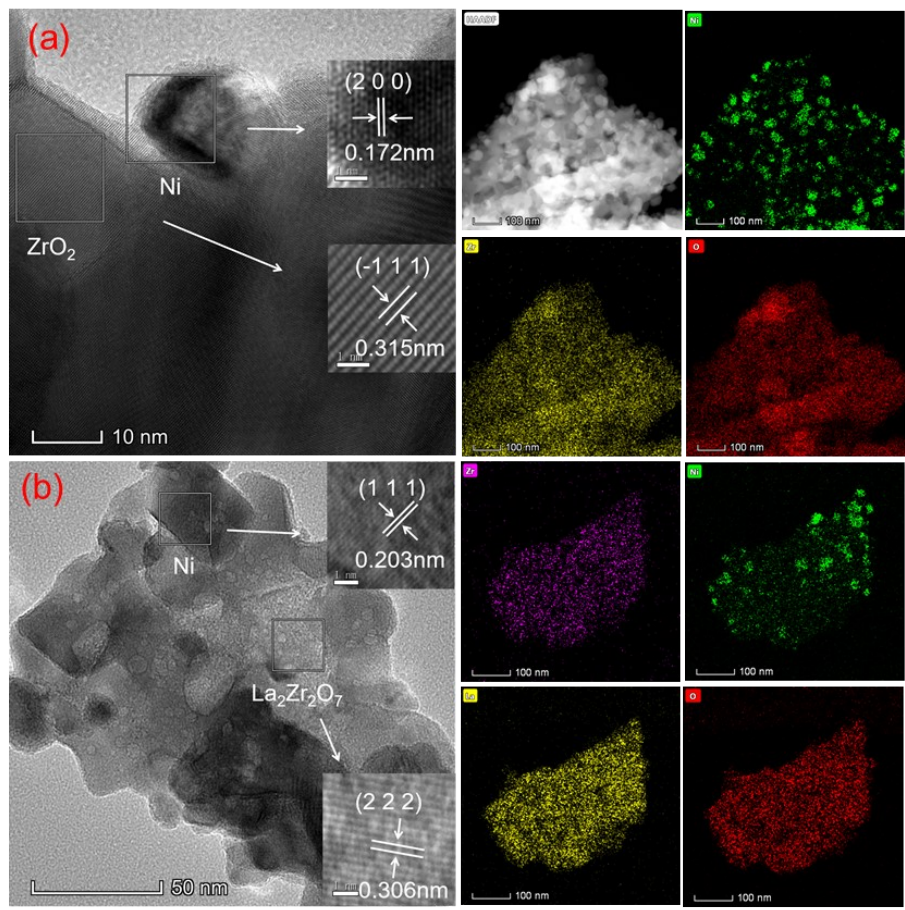
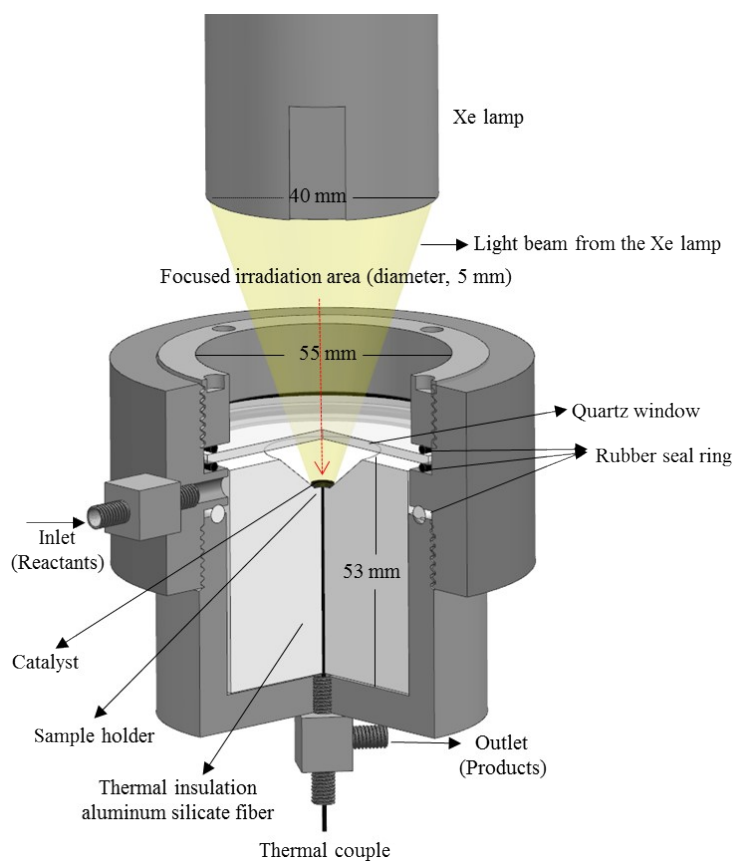


Fig. S1 TEM image, HRTEM image and the elemental mapping images of 10Ni/ZrO₂ (a) and 10Ni/La₂Zr₂O₇ (b).



Scheme S1. Schematic illustration of a stainless steel photothermal reactor for conducting DRM.

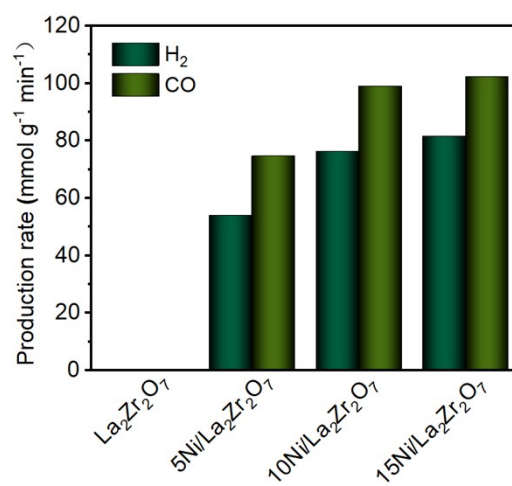


Fig. S2 Photothermal activity of La₂Zr₂O₇ with different Ni loadings.

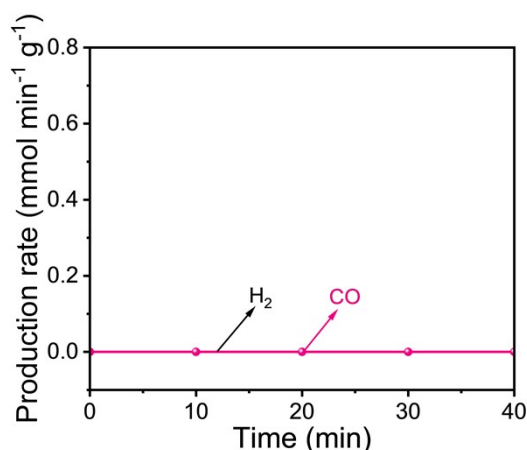


Fig. S3 Time course of P_{H_2} and P_{CO} for photocatalytic DRM on 10Ni/TiO₂

Table S1 Comparison of photothermal catalytic performance of DRM reactions

Entry	Sample	Photothermal temperature	Conditions	Production rates of CO and H ₂ (P_{CO} and P_{H_2})	Stability	Carbon deposition rate	Ref.
1	10Ni/La ₂ O ₃	728°C	385 kW m ⁻² ; 20.0 vol% CH ₄ - 20.0 vol % CO ₂ - 60.0 vol% Ar; Total feed flow rate is 90 mL/min	P_{CO} = 81.035 mmol g ⁻¹ min ⁻¹ P_{H_2} = 59.611 mmol g ⁻¹ min ⁻¹	50 h	8.12×10^{-4} g _c h ⁻¹ g _{catalyst} ⁻¹	This work
2	Co/Al ₂ O ₃	665°C	353.9 kW m ⁻² ; 30.0 vol% CH ₄ - 29.3 vol % CO ₂ - 40.7 vol% Ar; Total feed flow rate is 89.2 mL/min	P_{CO} = 37.97 mmol g ⁻¹ min ⁻¹ P_{H_2} = 31.42 mmol g ⁻¹ min ⁻¹	4h	1.65×10^{-1} g _c h ⁻¹ g _{catalyst} ⁻¹	Energy Environ. Sci., 2019, 12, 2581–2590
3	Co/Co-Al ₂ O ₃	697°C	353.9 kW m ⁻² ; 30.0 vol% CH ₄ - 29.3 vol % CO ₂ - 40.7 vol% Ar; Total feed flow rate is 89.2 mL/min	P_{CO} = 43.46 mmol g ⁻¹ min ⁻¹ P_{H_2} = 39.42 mmol g ⁻¹ min ⁻¹	70h	2.4×10^{-2} g _c h ⁻¹ g _{catalyst} ⁻¹	Energy Environ. Sci., 2019, 12, 2581–2590
4	SCM-Ni/SiO ₂	646°C	343.6 kW m ⁻² ; 11.7 vol% CH ₄ - 11.5 vol% CO ₂ - 76.8 vol% Ar; Total feed flow rate is 118.7 mL/min	P_{CO} = 19.9 mmol g ⁻¹ min ⁻¹ P_{H_2} = 17.1 mmol g ⁻¹ min ⁻¹	100h	/	Adv. Energy Mater., 2018, 8, 1702472
5	Ni/CeO ₂	807°C	363.4 kW m ⁻² ; 9.8 vol% CH ₄ - 10.0 vol% CO ₂ - 80.2 vol% Ar; Total feed flow rate is 122 mL/min	P_{CO} = 6.27 mmol g ⁻¹ min ⁻¹ P_{H_2} = 6.53 mmol g ⁻¹ min ⁻¹	100 h	1.25×10^{-2} g _c h ⁻¹ g _{catalyst} ⁻¹	Appl. Catal. B-Environ., 2018, 239, 555–564
6	1.0 wt% Pt/	767°C	371.1 kW m ⁻² ; 10.2 vol%	P_{CO} = 5.7 mmol g ⁻¹ min ⁻¹	100h	/	Green Chem.,

	CeO ₂ -MNR		CH ₄ - 10.2 vol% CO ₂ – 79.6 vol% Ar; Total feed flow rate is 120.5 mL/min	mmol g ⁻¹ min ⁻¹ P _{H2} = 6.0 mmol g ⁻¹ min ⁻¹				2018, 20, 2857–2869
7	10Ni/Al ₂ O ₃	550°C	1.07 W cm ⁻² ; Total feed flow rate is 20.0 mL/min (CH ₄ /CO ₂ = 1:1)	P _{CO} = 130 umol g ⁻¹ min ⁻¹ P _{H2} = 120 umol g ⁻¹ min ⁻¹	/	/		Appl. Catal. B- Environ., 2017, 209, 183–189
8	Pt-Au/SiO ₂	400°C;	0.6 W cm ⁻² ; Total feed flow rate is 20.0 mL/min (CH ₄ /CO ₂ = 1:1)	P _{CO} = 120 umol g ⁻¹ min ⁻¹ P _{H2} = 90 umol g ⁻¹ min ⁻¹	6h	/		ACS Appl. Mater. Inter., 2018, 10, 408– 416
9	Ni ₅ Cu ₅ /Al ₂ O ₃	748°C	20.0 vol% CH ₄ - 20 vol% CO ₂ – 60.0 vol% Ar; Total feed flow rate is 90 mL/min	P _{CO} = 40.45 mmol g ⁻¹ min ⁻¹ P _{H2} = 31.80 mmol g ⁻¹ min ⁻¹	50h	4.70 × 10 ⁻³ g _c h ⁻¹ g _{catalyst} ⁻¹		Catal Sci Technol, 2023, 13,2500-2507
10	Ni ₅ Cu ₂ /Al ₂ O ₃	739°C	20.0 vol% CH ₄ - 20 vol% CO ₂ – 60.0 vol% Ar; Total feed flow rate is 90 mL/min	P _{CO} = 63.80 mmol g ⁻¹ min ⁻¹ P _{H2} = 61.69 mmol g ⁻¹ min ⁻¹	50h	4.56 × 10 ⁻⁴ g _c h ⁻¹ g _{catalyst} ⁻¹		Catal Sci Technol, 2023, 13,2500-2507

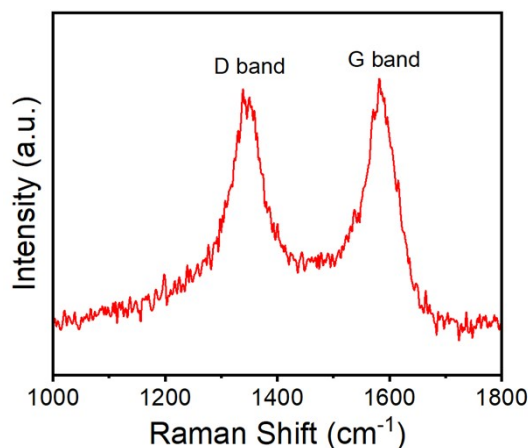


Fig. S4 Raman spectra of the used 10Ni/La₂Zr₂O₇.

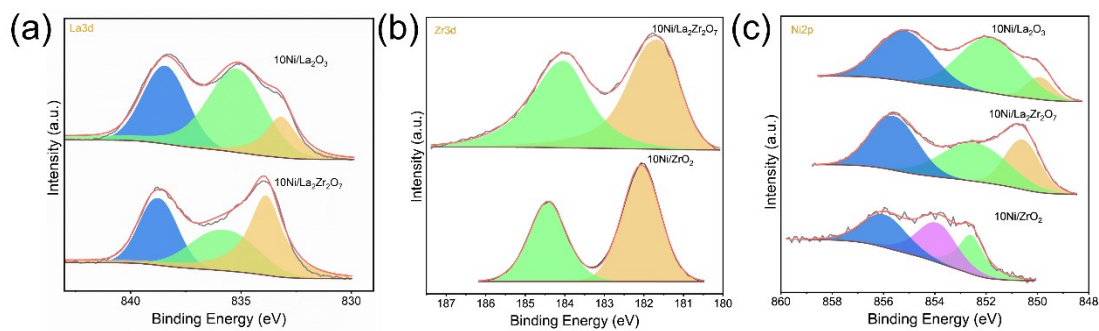


Fig. S5 XPS spectra of La 3d (a), Zr 3d (b), Ni 2p (c).

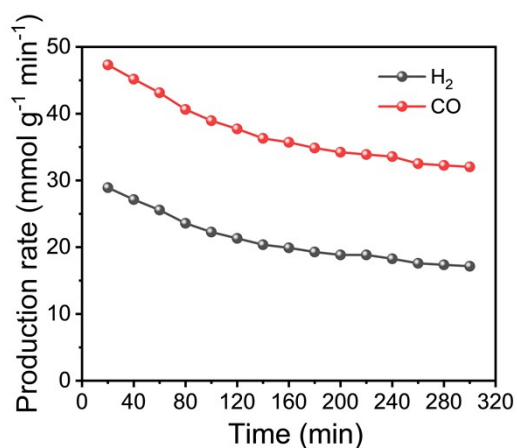


Fig. S6 Time course of P_{H₂} and P_{CO} for thermal catalytic DRM on 10Ni/SiO₂.

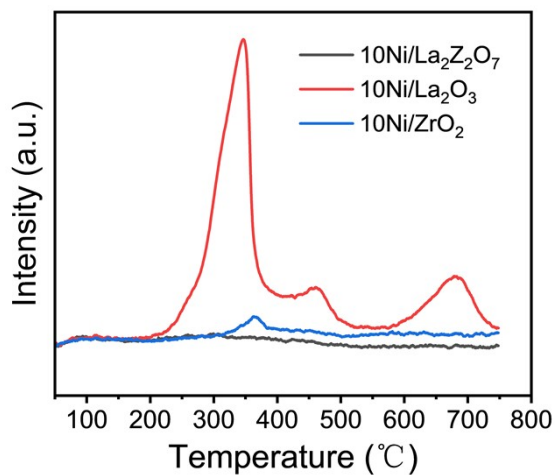


Fig. S7 CH₄-TPD of 10Ni/La₂O₃, 10Ni/ZrO₂ and 10Ni/La₂Zr₂O₇.

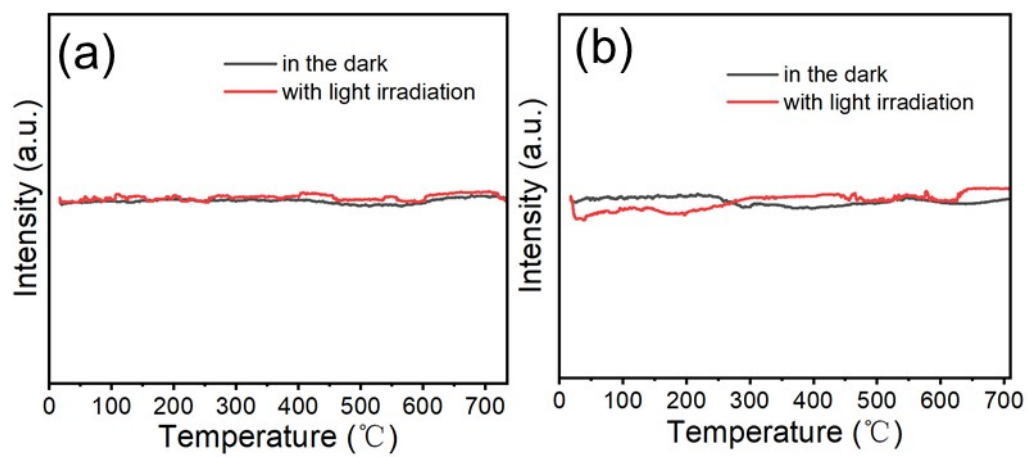


Fig. S8 CO-TPD (a) and H₂-TPD (b) of 10Ni/La₂O₃ in the dark and upon light irradiation.