

**Non-thermal plasma enabled catalytic dry reforming of methane over ceria nanorods
supported NiO catalyst: the role of Ru as coke resistant active sites**

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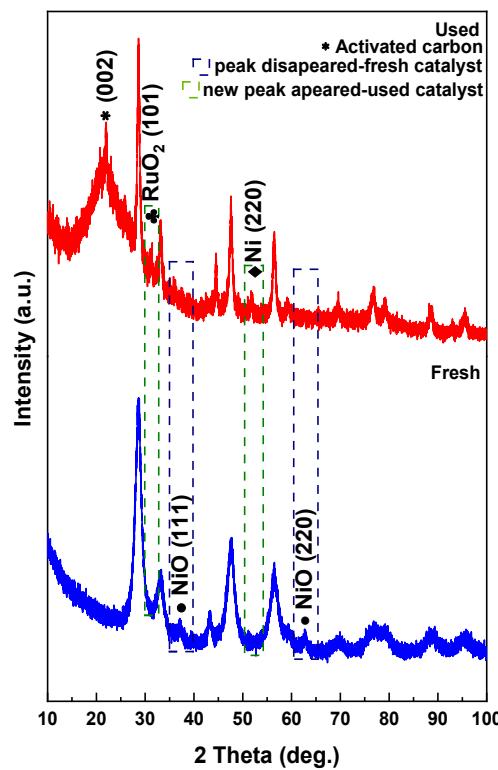


Fig. S1 XRD patterns of the fresh and spent 14 wt% Ni - 1 wt% Ru/CeO₂ NR catalysts.

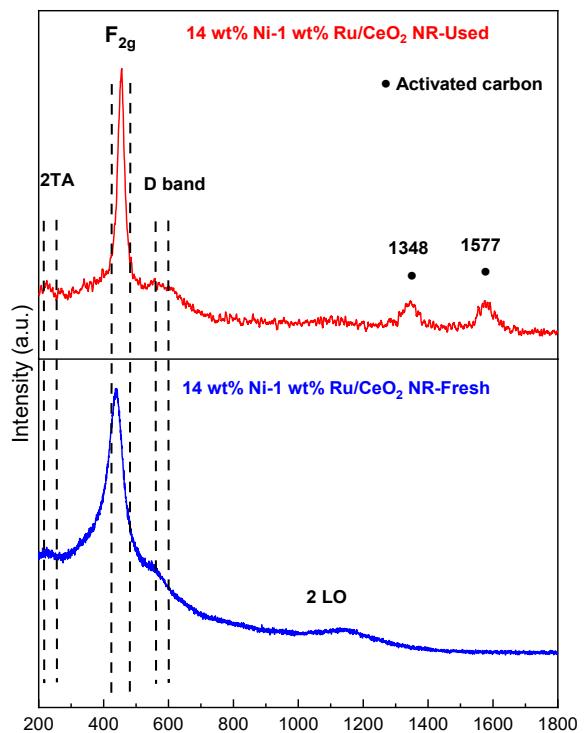


Fig. S2 Raman spectra of the fresh and spent 14 wt% Ni -1 wt% Ru/CeO₂ NR catalysts.

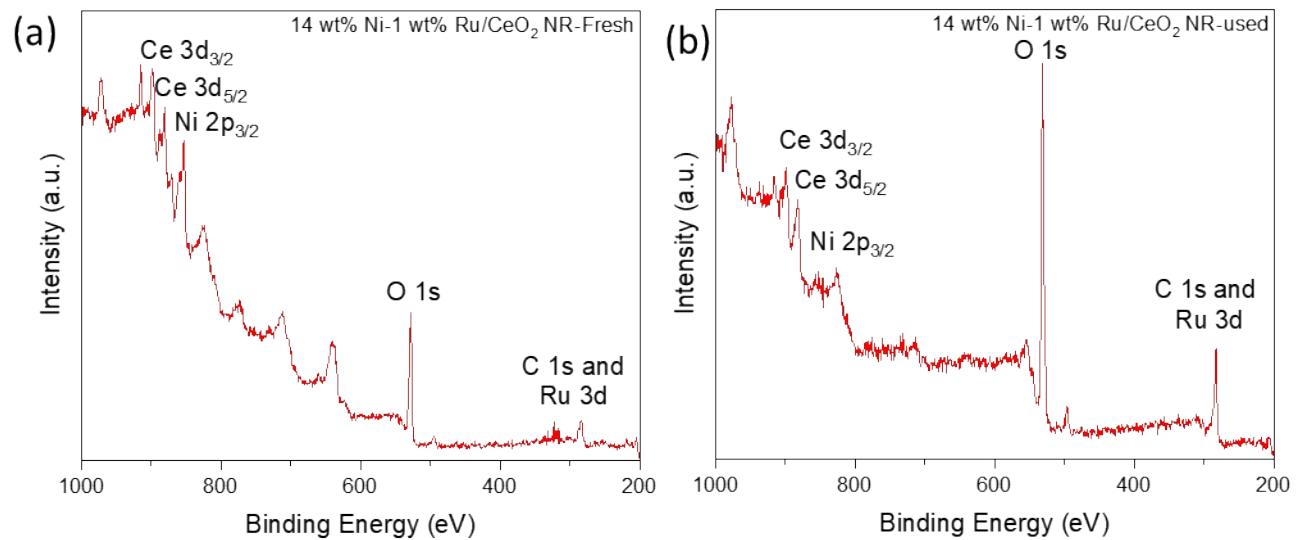


Fig. S3 XPS survey of the fresh and spent 14 wt% Ni -1 wt% Ru/CeO₂ NR catalysts.

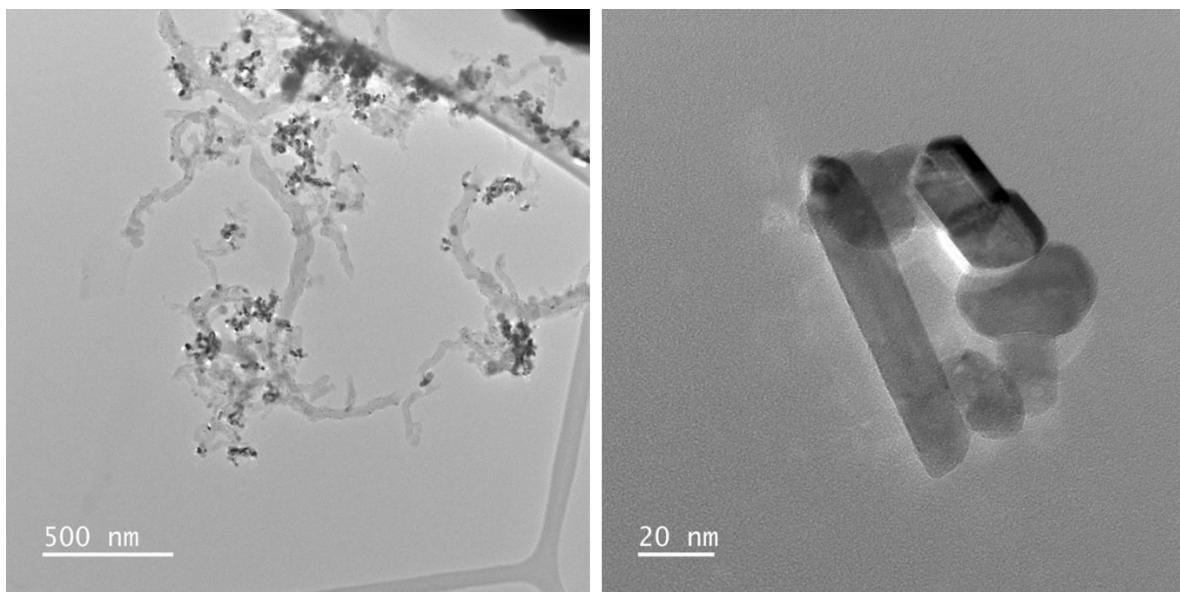


Fig. S4 TEM images of the spent 14 wt% Ni -1 wt% Ru/CeO₂ NR catalyst.

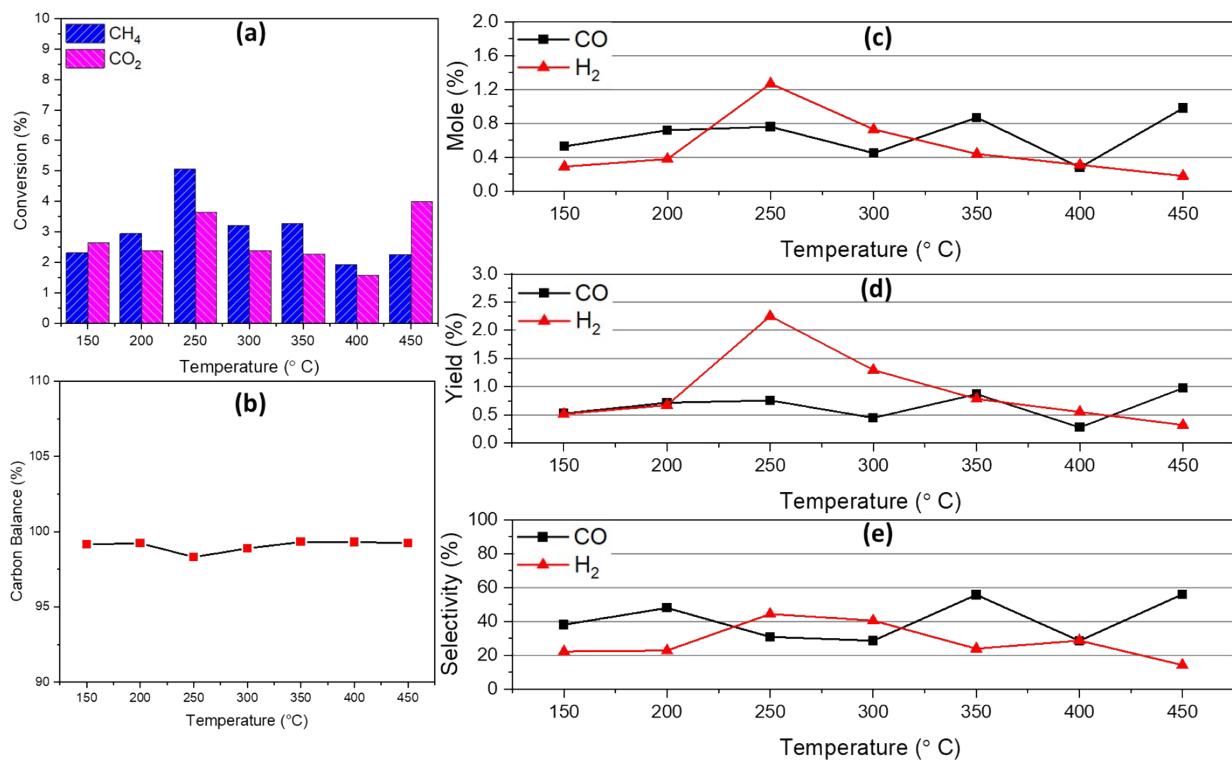


Fig. S5 DRM reaction performance under plasma only (without catalyst) condition: (a) CH₄ and CO₂ conversion, (b) Carbon balance, (c) CO and H₂ mole concentration, (d) yield and selectivity, from 150 °C to 450 °C. (Catalyst weight: ~200 mg, Power: 17.66 to 22.73 W, Flow rate: CO₂: 250 sccm and CH₄: 100 sccm, and Frequency: 20 kHz).

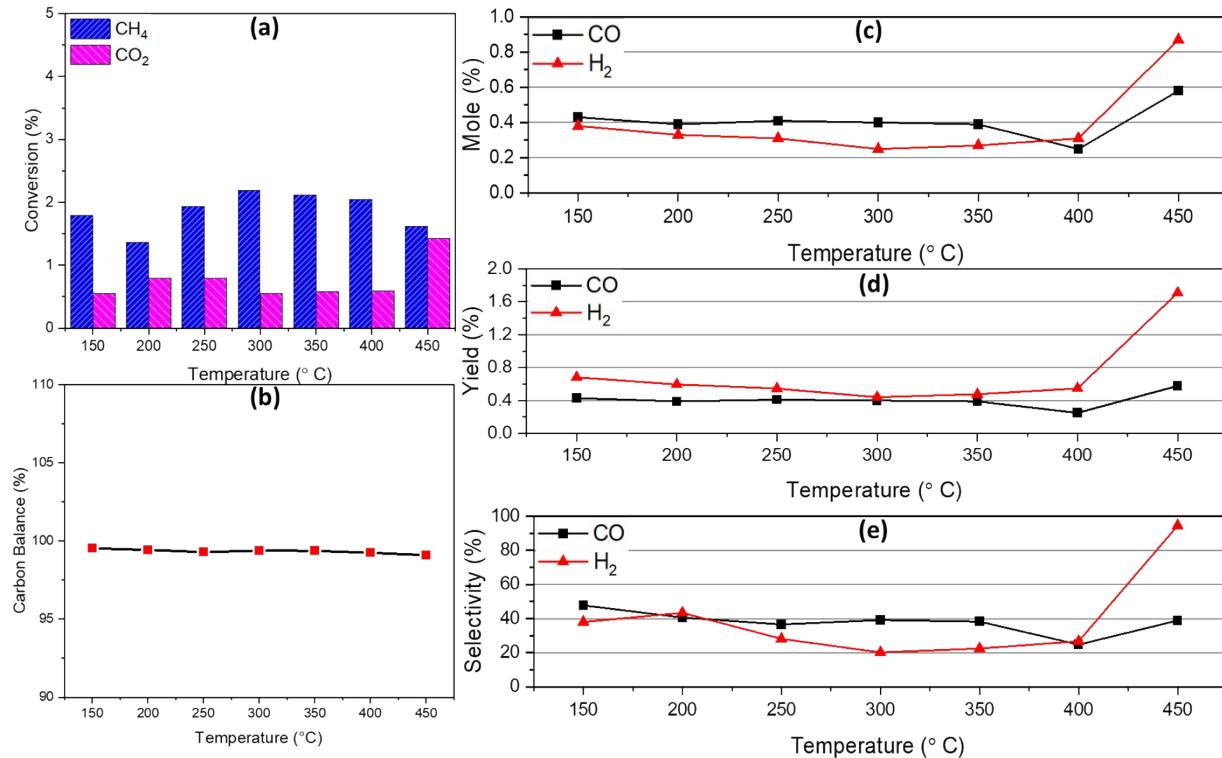


Fig. S6 DRM reaction performance under plasma + bare CeO₂ NR condition: (a) CH₄ and CO₂ conversion, (b) Carbon balance, (c) CO and H₂ mole concentration, (d) yield and selectivity, from 150 °C to 450 °C. (Catalyst weight: ~200 mg, Power: 17.66 to 22.73 W, Flow rate: CO₂: 250 sccm and CH₄: 100 sccm, and Frequency: 20 kHz).

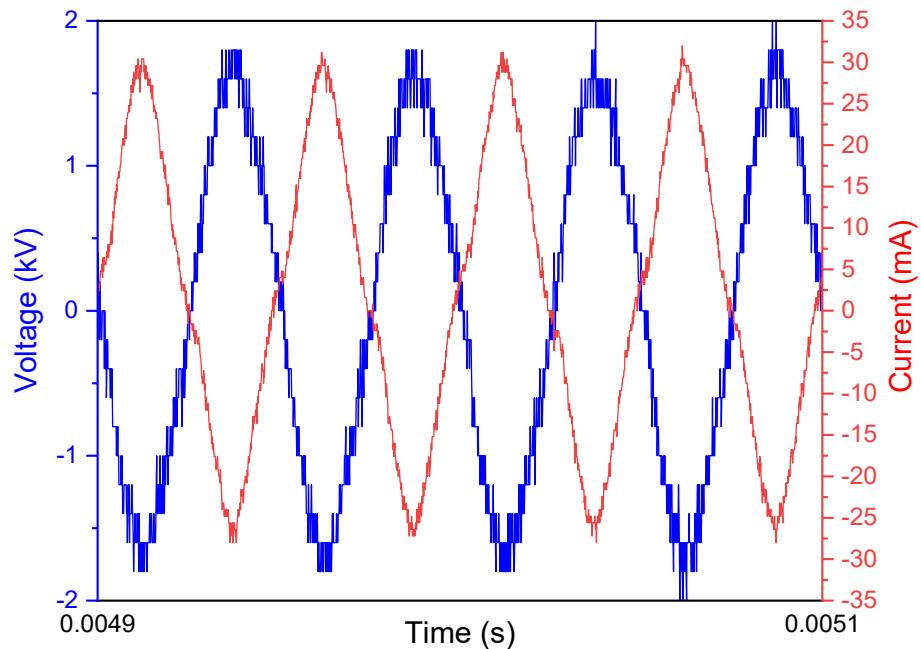


Fig. S7 Applied voltage and current signals in the plasma catalytic system.

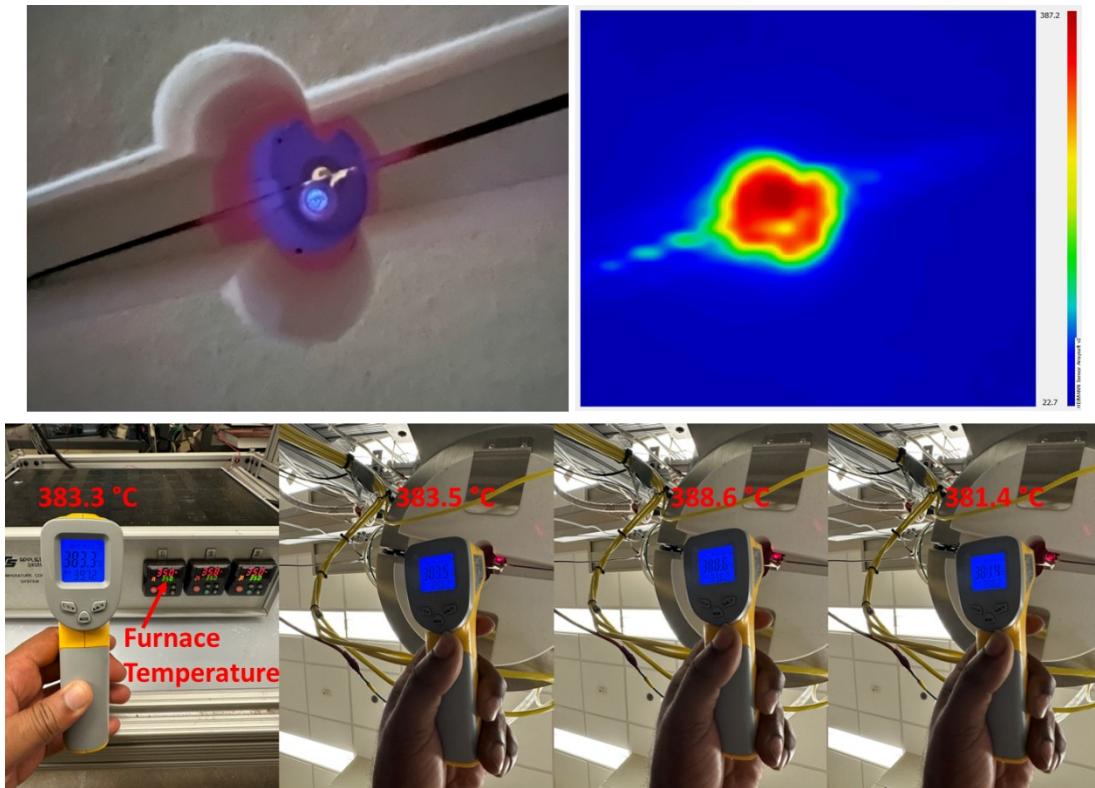


Fig. S8 Temperature measurement at plasma catalytic reaction zone with thermopile infrared array sensor and infrared thermometer.

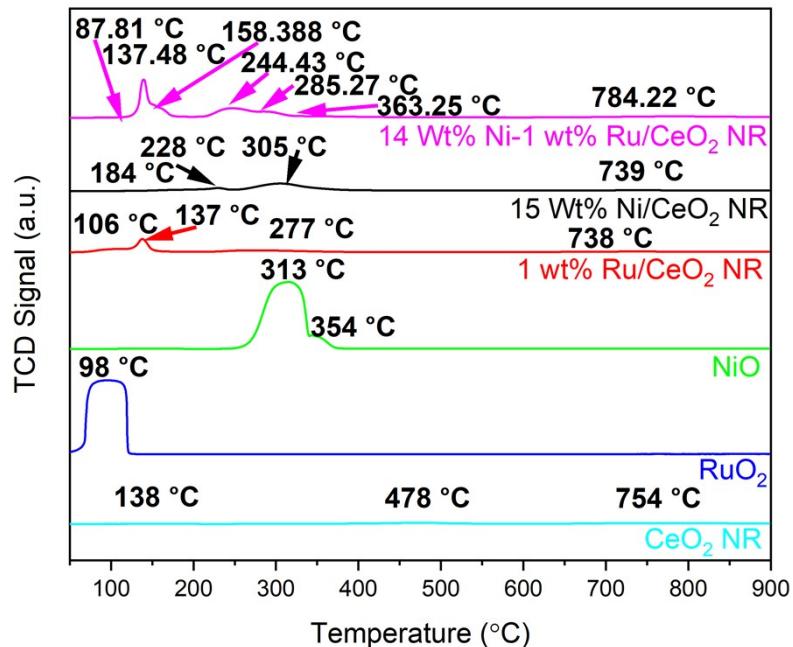


Fig. S9 H₂-TPR profiles of the CeO₂ NR, RuO₂, NiO, 1 wt% RuO_x/CeO₂ NR, 15 wt% NiO/CeO₂ NR and bimetallic 14 wt% Ni-1 wt% Ru/CeO₂ NR catalysts.

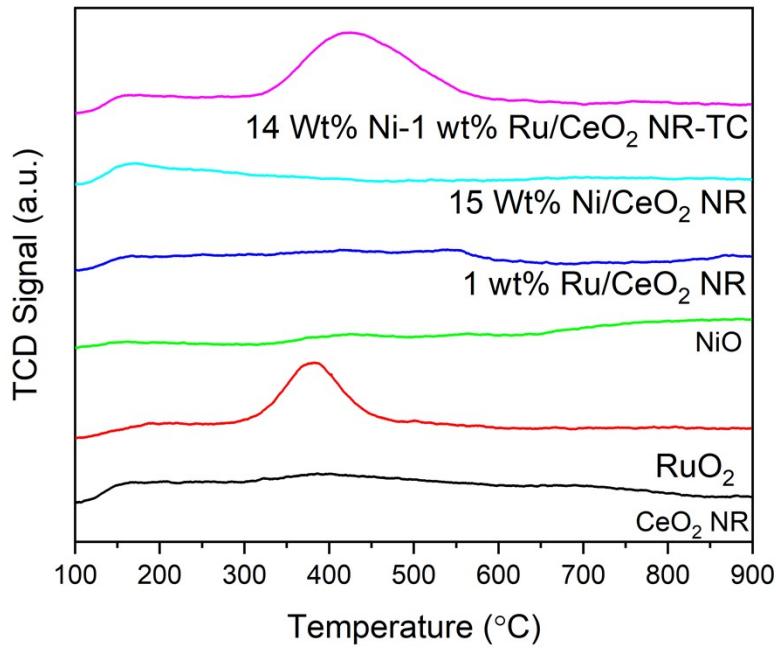


Fig. S10 CO_2 -TPD profiles of the CeO_2 NR, RuO₂, NiO, 1 wt% $\text{RuO}_x/\text{CeO}_2$ NR, 15 wt% NiO/ CeO_2 NR and bimetallic 14 wt% Ni-1 wt% Ru/ CeO_2 NR catalysts.

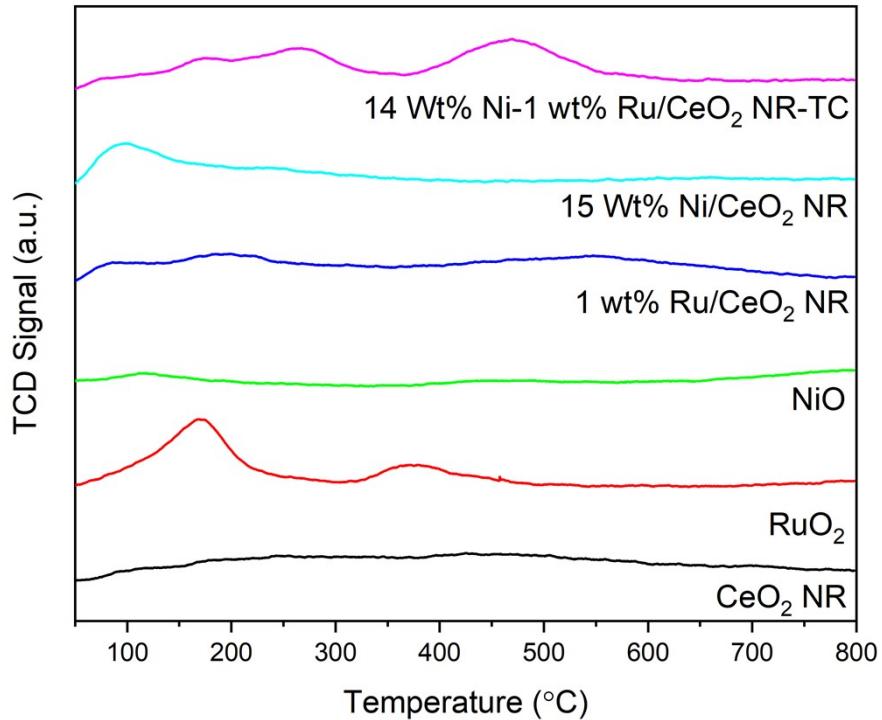


Fig. S11 CO-TPD profiles of the CeO_2 NR, RuO₂, NiO, 1 wt% $\text{RuO}_x/\text{CeO}_2$ NR, 15 wt% NiO/ CeO_2 NR and bimetallic 14 wt% Ni-1 wt% Ru/ CeO_2 NR catalysts.

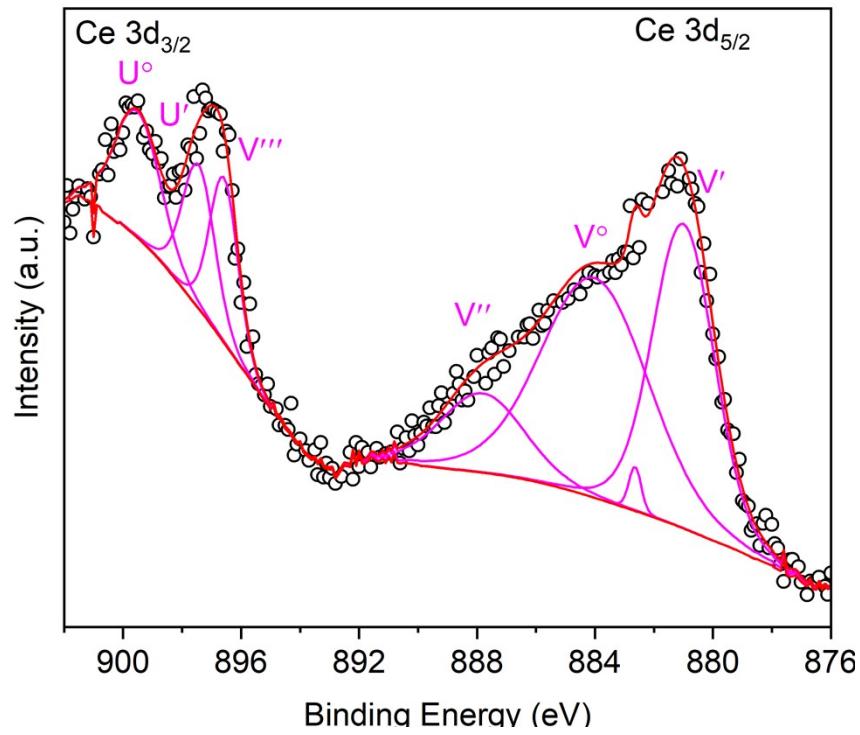


Fig. S12 XPS profile of Ce 3d for the spent 14 wt% Ni-1 wt% Ru/CeO₂ NR catalyst.

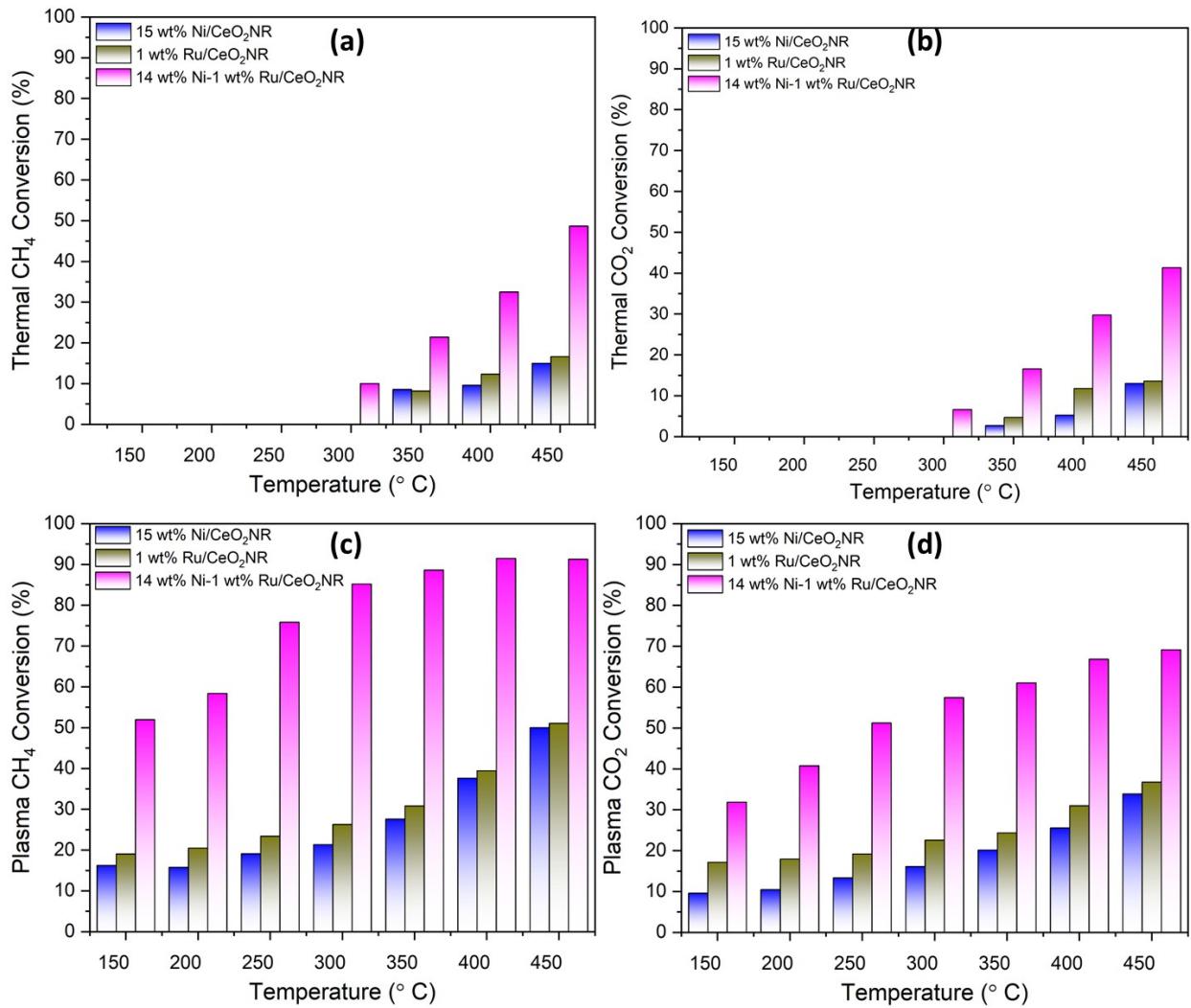


Fig. S13 (a-b) Thermal and (b-c) plasma assisted catalytic CH_4 and CO_2 conversion at various temperatures with 15 wt% Ni/CeO₂ NR, 1 wt% Ru/CeO₂ NR and 14 wt% Ni-1 wt% Ru/CeO₂ NR (Catalyst weight: ~200 mg, Flow rate: CO_2 : 250 sccm and CH_4 : 100 sccm, and Frequency: 20 kHz).

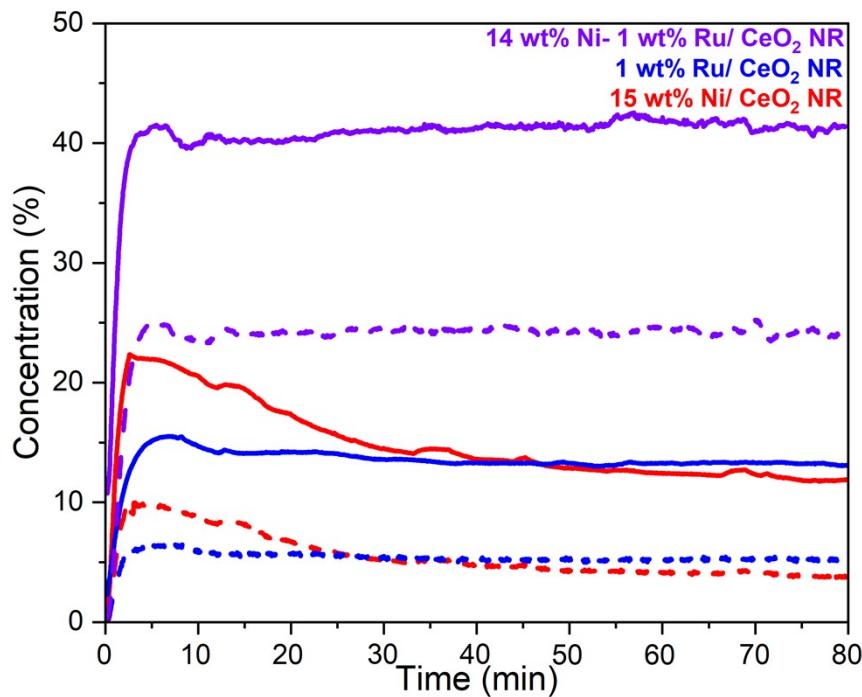


Fig. S14 Stability of 15 wt% Ni/CeO₂ NR, 1 wt% Ru/CeO₂ NR and 14 wt% Ni -1 wt% Ru/CeO₂ NR catalyst at 350 °C for plasma catalytic DRM (solid line: CO and dashed line: H₂).

Table S1. Plasma properties and experimental parameters for the plasma catalytic systems.

Plasma properties & Experimental parameters	
Plasma power	17.66 W – 22.73 W
Plasma type	Sinusoidal
Frequency	20 KHz
Gas flow rate	350 sccm
CH ₄ : CO ₂	100:250
Furnace temperature range	150 °C – 450 °C

Table S2. Comparison of plasma-assisted DRM activity over different catalysts.

Catalyst	Plasma type	Temperature (° C)	CH ₄ Conversion (%)	CO ₂ Conversion (%)	References
Commercial Ni/Al ₂ O ₃	DBD	500	59	42	[1]
15 wt% Ni/CeO ₂ NR	DBD	500	66	40	[2]
1 wt% Ru /CeO ₂ NR	DBD	450	51	37	[3]
14 wt% Ni- 1 wt% Ru/CeO ₂ NR	DBD	450	92	70	This work

References

- [1] Q. Wang, B.-H. Yan, Y. Jin, Y. Cheng, Dry reforming of methane in a dielectric barrier discharge reactor with Ni/Al₂O₃ catalyst: interaction of catalyst and plasma, *Energy & Fuels.* 23 (2009) 4196–4201.
- [2] M.R. Ahsan, M.M. Hossain, Z. Barlow, X. Ding, R. Wang, Low-Temperature Plasma-Assisted Catalytic Dry Reforming of Methane over CeO₂ Nanorod-Supported NiO Catalysts in a Dielectric Barrier Discharge Reactor, *ACS Appl Mater Interfaces.* (2023).
- [3] M.R. Ahsan, M.M. Hossain, X. Ding, R. Wang, Non-equilibrium plasma-assisted dry reforming of methane over shape-controlled CeO₂ supported ruthenium catalysts, *J Mater Chem A Mater.* 11 (2023) 10993–11009.