Supplementary Information

Advancing catalytic oxidation of lean methane over cobalt-manganese oxide via phase-engineered amorphous/crystalline interface

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Experimental section

All chemicals (analytical grade) were used directly without further purification in the synthesis process. The preparation process refers to the literature[1]. $Co(NO_3)_2 \cdot 6H_2O$ (5 mmol), $Mn(CH_3COO)_2 \cdot 4H_2O$ (1 mmol), and Polyethylene glycol-2000 (PEG-2000) (0.1875 mmol) were dissolved in 20 mL of deionized water to prepare the precursor solution A. NH_4HCO_3 (6 mmol) was prepared in 10 mL of deionized water as the precipitant to form the solution B, which was transferred to a flat bottom flask. NH_4HCO_3 (6 mmol) was prepared in 10 ml of deionized water as a precipitant to form solution B, which was then transferred to a flat-bottom flask. Solution A was then added to solution B and reacted in anultraviolet ultrasonic microwave three-in-one reaction instrument,(MC8S-3, Nanjing, China) for 30 minutes. The suspension was then washed three times with anhydrous ethanol and the precipitate was dried at 70 °C for 6 h and then calcined at 350 °C for 4 h. The ultrasonic power was fixed at 300 W. The precipitate was then dried at 70 °C for 6 h

and calcined at 350 °C for 4 h. To explore the optimal microwave power, the ultrasonic power was fixed at 300 W. The $CoMnO_x$ samples were referred to as MW-X US-300W (MW is the microwave power and X is the power in watts. The X = 50W, 100W, 150W, 200W, 250W, 300W and 400W)

After determining the optimal power of 250 W, the microwave power was fixed at 250 W and the ultrasonic power was adjusted to obtain a sample called MW-250 W US-Y (US is the ultrasonic power, Y = 90 W, 180 W, 300 W, 450 W and 540 W)

Catalyst characterizations

The XRD patterns were determined by an X-ray diffractometer (Rigaku Smartlab, Japan). The thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) was conducted on a Setsys Evolution thermal analyzer (Simultaneous, France). SEM analysis was performed on a Supra 55 scanning electron microscope (Germany). TEM and HRTEM were conducted by Tecnai G2 TF20 high-resolution transmission electron microscope (Philips-FEI) to observe the micromorphology and crystal structure of the catalysts. The Brunauer-Emmett-Teller (BET) surface area was measured on an SSA-4000 pore specific surface area analyzer. Fourier transform infrared (FTIR) spectra were carried out using an FTIR-8400S spectrometer (Shimadu, Japan). XPS was measured on the Escalab 250 X-ray photoelectron spectrometer (Thermo VG, USA). Hydrogen temperature programmed reduction analysis (H_2-TPR) was performed on a BELCAT instrument (BEL Japan, Inc.). In situ DRIFTS was carried out on Bruker equipment (Germany).

Catalytic activity test

The catalytic activities of catalysts for methane combustion were carried out in a quartz reaction tube (diameter = 6 mm, length = 550 mm) which was used as a quartz micro-fixed bed reactor at atmospheric pressure. The middle of the quartz tube is fixed by a sand core. For each measurement, 100 mg of the catalysts were loaded into the center of the quartz micro-fixed bed reactor. A gas mixture composed of 1 vol.% CH_4, 20 vol.% O_2, 5 vol.% or 10 vol.% H_2O (when used) and balanced N_2 was fed

into the micro-reactor, and the total flow rate was held at 60 mL min^{-1} via a mass flow controller, corresponding to the space velocity (GHSV) of 36,000 mL g^{-1} h^{-1}. The gas composition of the inlet and outlet of the reaction tube was analyzed on-line by a gas chromatograph (GC-7890) equipped with TCD and a flame ionization detector (FID) detector.

The methane gas conversion was calculated by the following equation：

$$CH4\ \ conversion(\%) = \frac{[CH4]_{in} - [CH4]_{out}}{[CH4]_{in}} \times 100(\%)$$

Where CH$_4$ conversion (%) represents the conversion of methane, [CH$_4$]$_{in}$ represents the initial concentration of methane, and [CH$_4$]$_{out}$ represents the concentration of methane after catalytic combustion.
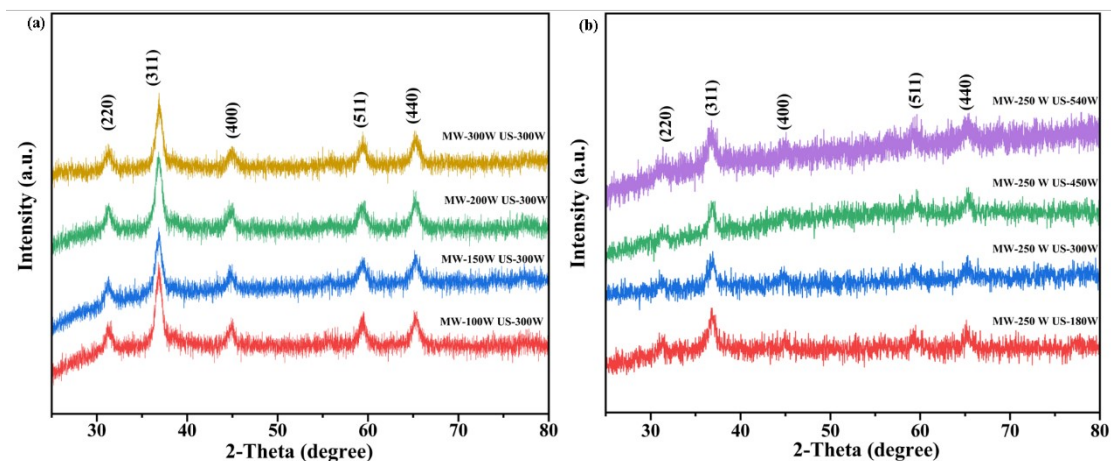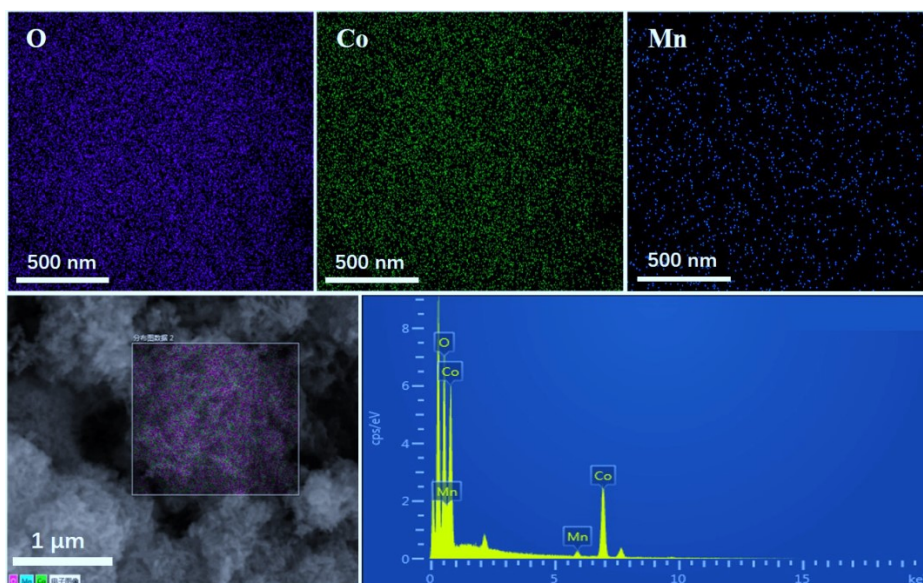

Fig. S1 (a) XRD patterns of different sample.

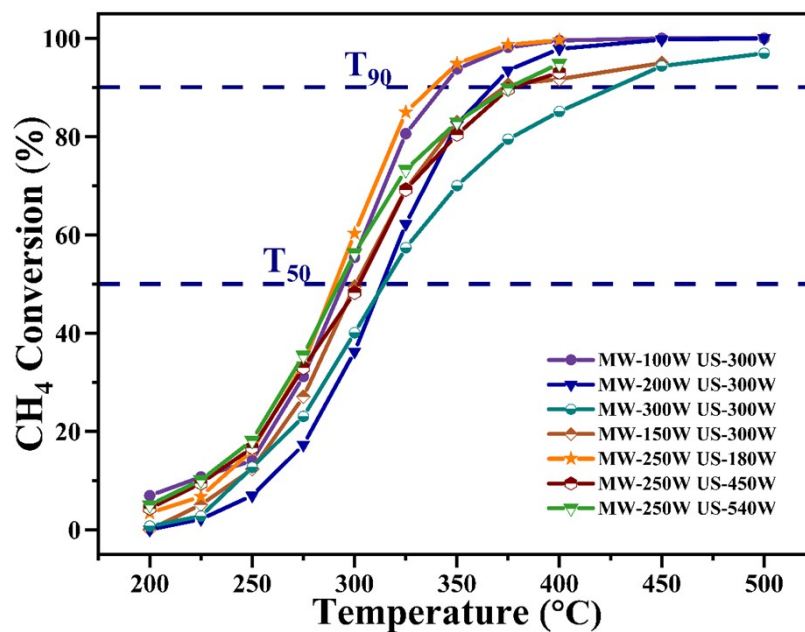**Fig. S2** SEM-EDS of the typical MW-250 W US-300 W catalyst.

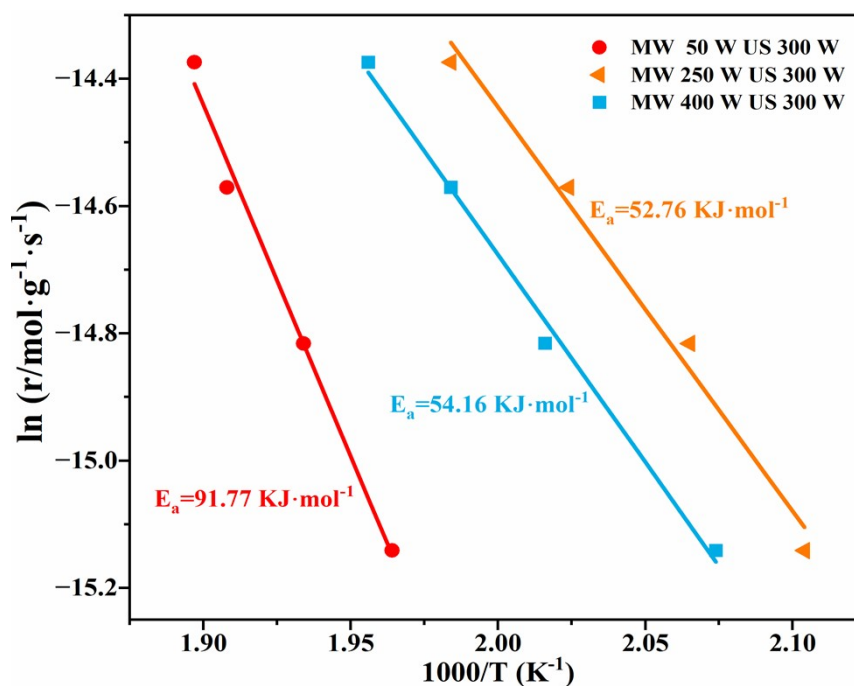**Fig. S3** CH$_4$ oxidation activity for different samples as a function of temperature.

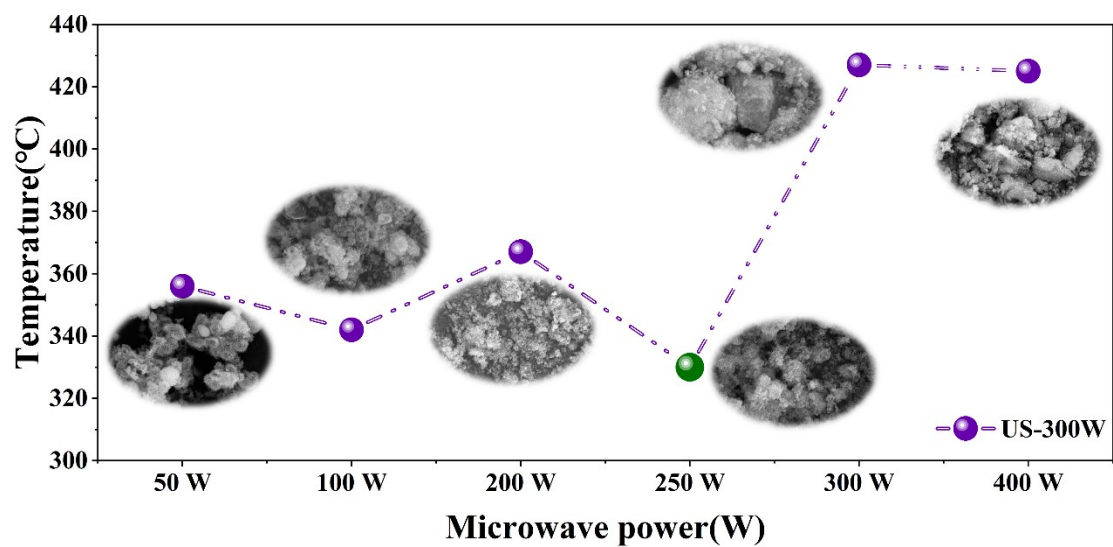**Fig. S4** Arrhenius plots for methane oxidation over different samples.

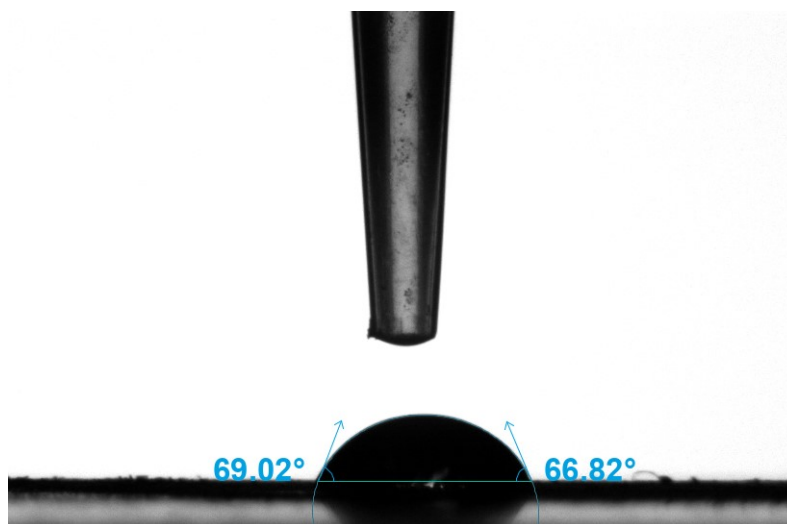**Fig. S5** The relationship between microwave, morphology, and performance of catalysts.

Fig. S6 Static water droplets contact angles of MW-250W US-300W catalyst

Table S1 BET surface areas, pore sizes, pore volumes for the different samples

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	Average pore size (nm)
MW-50W US-300W	94.95	0.54	22.56
MW-250W US-300W	87.69	0.84	38.02
MW-400W US-300W	96.43	0.50	19.86
MW-400W US-90W	91.21	0.57	25.12

Table S2 Comparison of the catalytic activities of various reported catalysts with those in present work

Catalysts	Reaction Conditions	T_{50} /°C	T_{90} /°C	Ref.
MB-Co_3O_4	1% CH_4, 20% O_2, 30,000 mL·g^{-1}·h^{-1}	355	434	[2]
$NiCo_2O_4$ bubbles	1 % CH_4, 20% O_2, 30,000 mL·h^{-1}·g^{-1}	346	401	[2]
60%$MnCo_2O_4$/SiC	1% CH_4, 20% O_2, SV = 45000·mL/(g·h)	375	444	[3]
Co_3O_4-ZrO_2(2%)	0.5% CH_4, 8.0% O_2, 40 mL·min^{-1}	—	335	[4]
Co-In-0.2	1% CH_4, 10% O_2, 48,000 mL·g^{-1}·h^{-1}	—	380	[5]
N-Co_3O_4-110	2vol.% CH_4, 20 vol.% O_2, 46,800 mL·g^{-1}·h^{-1}	342	412	[6]
CoGO50	1vol% CH_4,10 vol% O_2, 30,000 mL·g^{-1}·h^{-1}	295	370	[7]
Pd(PdO)/Co_3O_4@SiO_2	1% CH_4, 21% O_2, 30,000 mL·g^{-1}·h^{-1}	357	445	[8]
Pd-Co_3O_4	1% CH_4, 20% O_2, 30,000 mL·g^{-1}·h^{-1}	291	337	[9]
$CoMnO_x$ MW-250W	1% CH_4, 20% O_2, 36,000 mL·g^{-1}·h^{-1}	281	330	This work

Notes and references

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