

## Fibrous NiO/CeO<sub>2</sub> nanocatalysts for the partial oxidation of methane at microsecond contact times

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### Experimental details:

*Catalyst preparation:* NiO/CeO<sub>2</sub> catalysts were synthesized using ESM as a template. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>99.99 %) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (>99.9 %) were dissolved in deionized water to obtain 300 ml 0.5 M metal ion (Ni<sup>2+</sup> + Ce<sup>3+</sup>) solutions with the Ni<sup>2+</sup>/Ce<sup>3+</sup> molar ratios of 1:8, 1:4, 1:1, 4:1 and 8:1 respectively. The ESM template was derived from commercial chicken eggs. After the removal of CaCO<sub>3</sub> shell from the eggshells by soaking into 1M HNO<sub>3</sub> solution for 5 min, the ESM was washed with deionized water and dried in an oven set at 95 °C for 2 h. 3 g of the dried ESM was immersed into each solution at room temperature for 3 h. Then, the ESM-metal composites were dried at 95 °C for 2 h, and heated at 1000 °C for 2 h in air to crystallize catalysts. All chemicals were purchased from Sigma Aldrich Australia, and used as received.

*Catalyst characterization and test:* The crystalline structure of template catalysts was confirmed by using CuK $\alpha$  radiation with a Bruker D8 Advance diffractometer equipped with a LynxEye detector (Bruker-AXS, Karlsruhe, Germany) at a scan rate of 2 °C/min and a step size of 0.02°. The microstructures of the catalysts were observed by a microscope (Zeiss Neon 40EsB FIBSEM). Due to the low conductivity of NiO/CeO<sub>2</sub> catalysts, the samples were set on electron-conductive stick tape, and then coated with 3 nm Pt film to avoid charging . The accelerating voltage applied is 15 KV. The composition of the templated catalysts was tested by a induced coupled plasma (ICP, Optima 7300 DV, PerkinElmer) using the mixture of hydrochloric acid (36 wt%), sulphuric acid (98 wt%) and hydrogenperoxide with the same volume ratio to dissolve the ceramic catalysts. Nitrogen adsorption–desorption experiment was carried out at 77 K using a Micrometrics ASAP 2020MC analyzer, and the specific

surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method. Temperature programed reduction (TPR) was performed on ChemBET3000 (Quantachrome Instruments) from 25 °C to 900 °C using 0.03g catalysts.

*Catalyst test:* The templated NiO/CeO<sub>2</sub> catalysts were firstly crushed into flakes with uniform sizes of 1 to 2 mm by using 10-mesh and 18-mesh sieves. Then, 0.2 g of flake catalyst was put on the quartz filter in the middle of a quartz tube reactor, and the inner diameter of the quartz tube is 20 mm. The reactor was heated by a tubular furnace, and the temperature on the surface of catalyst bed was indicated by a K-type thermocouple. The NiO/CeO<sub>2</sub> catalysts were reduced by a mixed gas of 20 vol% H<sub>2</sub>/Ar at 800 °C for 1 h, and then a gas mixture of 10CH<sub>4</sub>: 5O<sub>2</sub> : 85Ar (volume) was introduced into the reactor to conduct the CPOM at temperatures ranging from 600 to 900 °C. GHSV was adjusted by mass flow controllers (AALBORG). GHSV and contact time were calculated according to the below formulas:

$$\text{GHSV} = \frac{\text{Volumetric flow rate of feeding gas at room temperature}}{\text{Catalyst real volume (exclusive void volume)}}$$

$$\text{Contact time} = \frac{\text{Catalyst real volume (exclusive void volume)}}{\text{Volumetric flow rate of feeding gas at } 850 \text{ } ^\circ\text{C}}$$

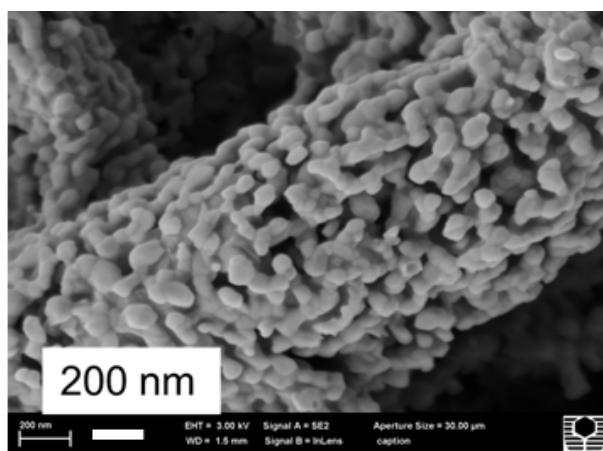
The composition of the exit gas from the reactor is analyzed by a Gas Chromatography (Agilent 6890), and reforming performances were evaluated using the following defined parameters:

$$\text{CH}_4 \text{ conversion} = \frac{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}}{\text{CH}_{4,\text{in}}} \times 100\%$$

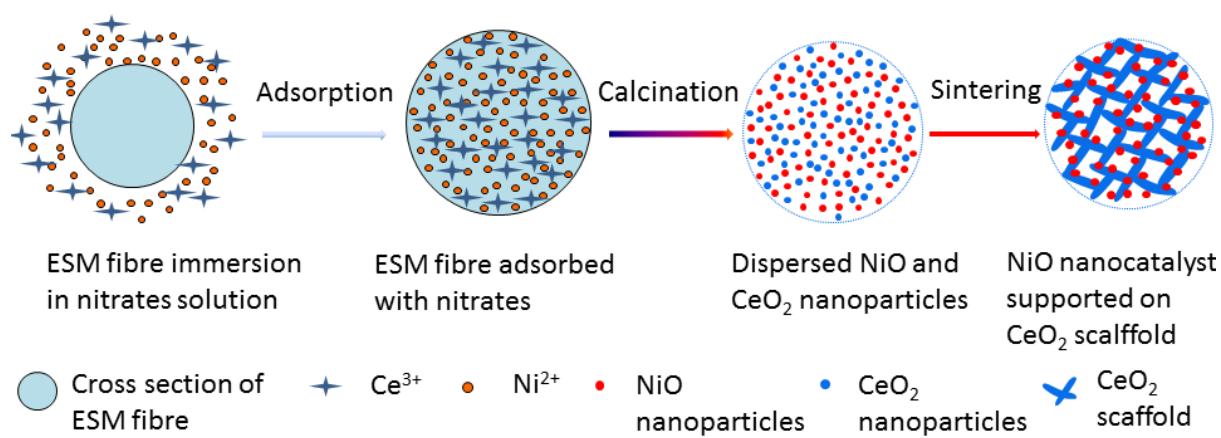
$$\text{H}_2 \text{ selectivity} = \frac{\text{H}_{2,\text{out}}}{2(\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}})} \times 100\%$$

$$\text{CO selectivity} = \frac{\text{CO}_{\text{out}}}{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}} \times 100\%$$

## Supporting experimental data

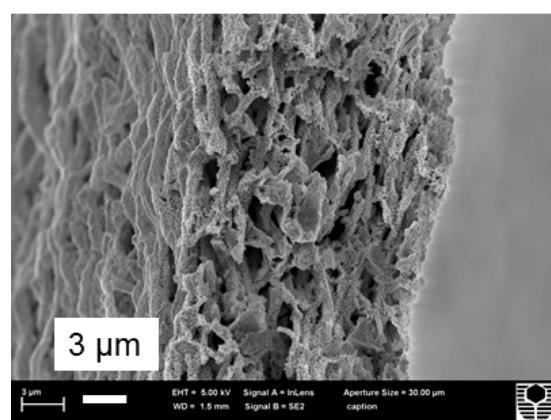


**Fig. S1** SEM image of CeO<sub>2</sub> scaffold. In order to show the CeO<sub>2</sub> scaffold, the NiO/CeO<sub>2</sub> catalyst with a NiO content of 47.8 wt% was reduced in hydrogen and the resulting Ni was then removed by immersing into 1M nitric acid. The Ni/CeO<sub>2</sub> ceramic was kept into the nitric acid only for 20 minutes because nitric acid can erode CeO<sub>2</sub> scaffold slowly. Thereby, we removed Ni nanoparticles mainly on ceramic fibre surface. The connected CeO<sub>2</sub> particles constructed a scaffold for supporting NiO nanocatalysts.

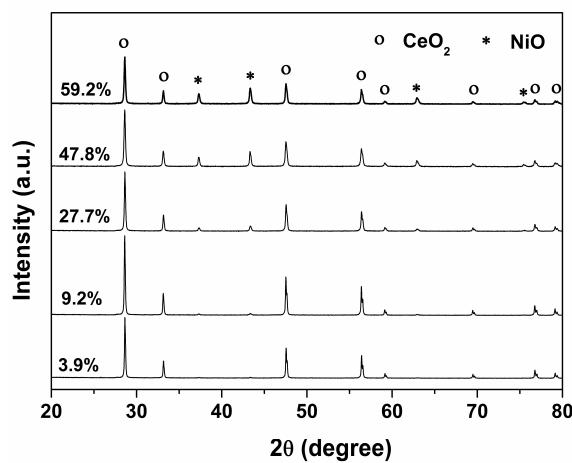


**Fig. S2** Schematic representation of the formation of NiO nanocatalyst supported on CeO<sub>2</sub> scaffold using a one-step template synthesis process. When protein fibres were immersed in nitrate solution, metal ions uniformly adsorbed within the protein fibres. During the

calcination of the protein/nitrates composites, nitrates were converted into metal oxide particles, which compact together to keep fibre morphology after protein was burned off at around 500 °C, producing well-dispersed and uniform NiO and CeO<sub>2</sub> nanoparticles. The subsequent heating at high temperatures led to nanoparticle sintering, and the sintering of each metal oxide is restrained by the other metal oxide. Compared with NiO nanoparticles, CeO<sub>2</sub> nanoparticles have high sinterability, which can be confirmed by the bigger particle size of CeO<sub>2</sub> particles than that of NiO particles in all catalysts. The sintered CeO<sub>2</sub> particles form a scaffold supporting NiO nanoparticles.

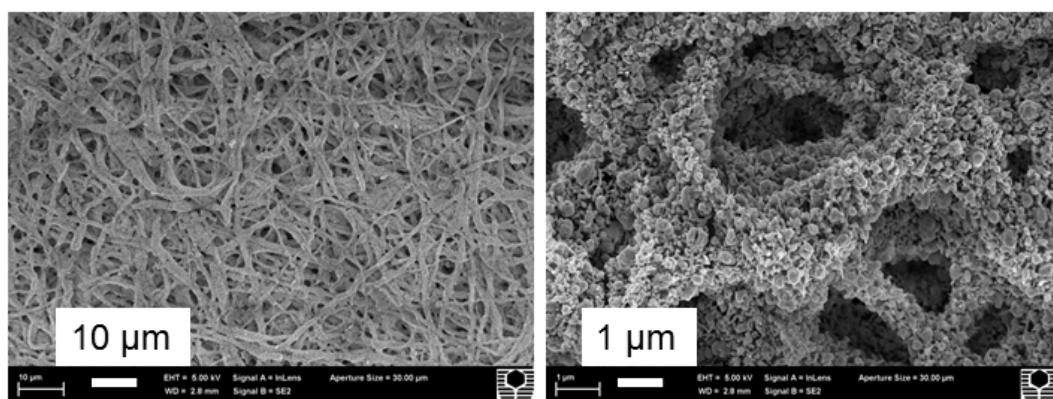


**Fig. S3** SEM images of the cross section of NiO/CeO<sub>2</sub> flake catalyst at different magnifications. The thickness of flake catalyst with a NiO content of 47.8 wt% is about 16 μm, and the interconnected ceramic fibres constructs a three-dimensional structure.

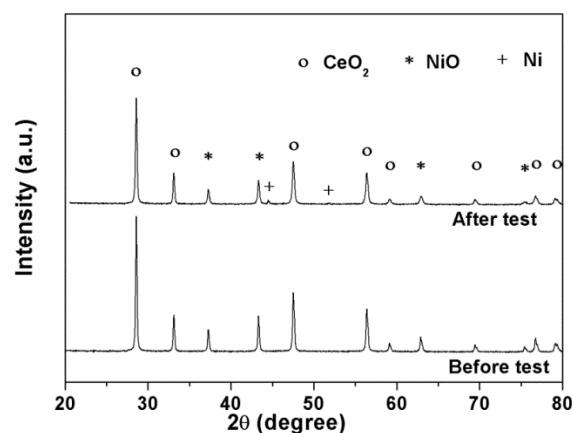


**Fig. S4** XRD patterns of the NiO/CeO<sub>2</sub> catalysts with different NiO contents and prepared at

1000 °C.



**Fig. S5** SEM images of the fibrous 47.8 wt% NiO/CeO<sub>2</sub> catalyst after the CPOM for 12 h at different magnifications. The fibrous structure of the catalyst is stable during the CPOM, and nanocatalysts are retained. No catalyst aggreation and coke formation is found in the catalyst after test.



**Fig. S6** XRD patterns of the 47.8 wt%NiO/CeO<sub>2</sub> catalysts before and after test. There is a small amount of Ni presenting in the used catalyst after test. As argon flew through the reactor after stopping reforming until it was cooled down, the state of Ni should keep changing among Ni<sup>0</sup> and Ni<sup>2+</sup> during the CPOM. After test, no increase in particle size occurred according to the XRD peak intensities of NiO, indicating the resistance to catalyst sintering.