

**Supplementary Information for**

**Facet Effect of Ceria Nanoparticles on Platinum  
Dispersion and Catalytic Activity of Methanol Partial  
Oxidation**

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## **Experimental details**

### **Catalyst synthesis.**

The ceria nanocube and nanosphere were synthesized according to the hydrothermal method, as reported elsewhere.<sup>1-2</sup> Briefly, for the synthesis of ceria NC, 8.4 g of sodium hydroxide (NaOH) and 0.868 g of cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) were separately dissolved in beakers containing 35 ml and 5 ml distilled water. These two stock solutions were later mixed in a 50 ml Teflon bottle and stirred at room temperature (RT) for 30 min. Finally, the Teflon bottle was placed in a stainless-steel autoclave and treated at 180 °C for 24 h. For  $\text{CeO}_2$  NS synthesis, 1 g of cerium nitrate hexahydrate was dissolved in 1 ml of distilled water. Subsequently, 1 ml of glacial acetic acid and 30 ml of ethylene glycol were added under continuous stirring. The resulting solution was placed in a 50 ml Teflon tube autoclave and treated at 180 °C for four hours. For both  $\text{CeO}_2$  NC and  $\text{CeO}_2$  NS, a white solid precipitate was obtained at the bottom of the Teflon bottle. The resultant white solid was washed several times with distilled water, followed by ethanol to remove the excess salts and dried at 70 °C in the oven overnight.

The platinum supported (~1.0 wt % Pt) on the nano-shaped ceria catalysts were prepared by incipient wetness impregnation using a hexachloroplatinic acid as a precursor. The nano-shaped  $\text{CeO}_2$  powder (0.6 g) and distilled water (10 ml) were added and stirred vigorously for 30 min in a 100 ml beaker. The required quantity of chloroplatinic acid was dissolved in deionized (DI) water (30 mL) and added dropwise into the above solution. The resulting solution mixture was kept under overnight stirring at RT, followed by increased temperature to 90 °C until evaporation of the solvent. The obtained bottom solid product was collected and finally calcined under air at 400 °C for two hours with a 2 °C/min ramp rate.

### **Characterisation.**

The diffraction pattern of as-synthesized catalysts was collected using an x-ray diffractometer (XRD; D-MAX 2500, Rigaku) equipped with Ni filtered Cu k-alpha x-ray source operating at 40 kV and 300 mA. The data were collected at a scan rate of 2.4°/min,

and step size of 0.01 Å between the 2θ scan range of 10-80°. Raman spectra were obtained using Horiba JY lab RAM HR 800 spectrometer with a 514 nm laser source. The different morphology and size of the catalysts were examined using transmission electron microscopy (TEM; Tecnai F30 ST, FEI). The TEM samples were prepared on a 300-mesh copper grid by the drop-casting of ethanol-catalyst suspension. The atomic weight percentage of platinum was determined by using the Inductively Coupled Plasma-Optical Emission Spectrometer 720 (ICP-OES720; Agilent). X-ray photoelectron spectroscopy (XPS; k-alpha, Thermo VG Scientific) measurements were performed using an Al k-alpha monochromator x-ray source (1486.3 eV) on the pre-reduced PtCeO<sub>2</sub> catalyst (250 °C for one hour, 10 % H<sub>2</sub>). The single-point BET surface area was determined by N<sub>2</sub> adsorption/desorption isotherms at liquid nitrogen temperature using an ASAP 2020 instrument (Micrometrics). The Pt metal dispersion on the ceria supports was acquired using CO-Temperature programmed desorption (CO-TPD, BELCAT-B, BEL JAPAN Inc.) instrument operated in the CO pulse chemisorption regime with a stoichiometry factor of Pt: CO = 1:1. Initially, the catalyst was pre-treated in 5 % H<sub>2</sub> (50 ml/min) at 250 °C for one hour, followed by CO pulse measurements (5 % CO) at 50 °C. H<sub>2</sub>-TPR experiments were carried out using BELCAT-B, BEL JAPAN Inc. Briefly, 50 mg of the catalyst was pre-treated with 20 % O<sub>2</sub> and 80 % N<sub>2</sub> at 400 °C for one hour and cooled down to 50 °C in the same environment. After purging with He for 30 minutes, temperature-programmed reduction with 5 % H<sub>2</sub> (30 ml/min.) was performed until 1000 °C with a ramp rate of 10 °C/min.

Diffuse Reflectance Infrared Fourier-Transform (DRIFT) Spectroscopy measurements were performed by using an Agilent Carry 660 FTIR spectrophotometer consisting of a mercury cadmium telluride (MCT) detector and diffusivity reflectance cell (Harrick Scientific Products). In brief, about 10 mg of the sample was placed on a stainless-steel mesh by mechanical pressing and introduced into the Harrick cell for analysis. Initially, samples were pre-treated at 250 °C in 10 % H<sub>2</sub> for an hour, followed by helium purging for a few hours to remove the surface contaminants. CO chemisorption-DRIFT experiments were conducted at 50 °C using 2 % of CO gas (balanced with He) and purging with helium, respectively. For the methanol adsorption-DRIFT studies, methanol was sent

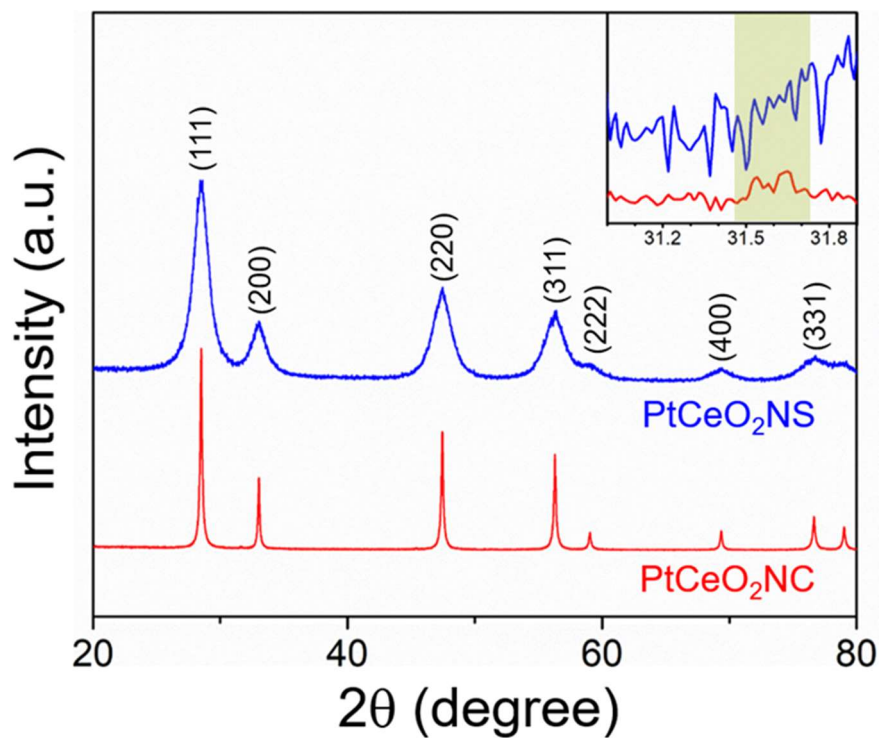
via helium (50 ml/min.) at RT for 15 min, followed by 30 minutes of helium purging and temperature-programmed desorption studies (3 °C/min).

### Evaluation of catalytic activity

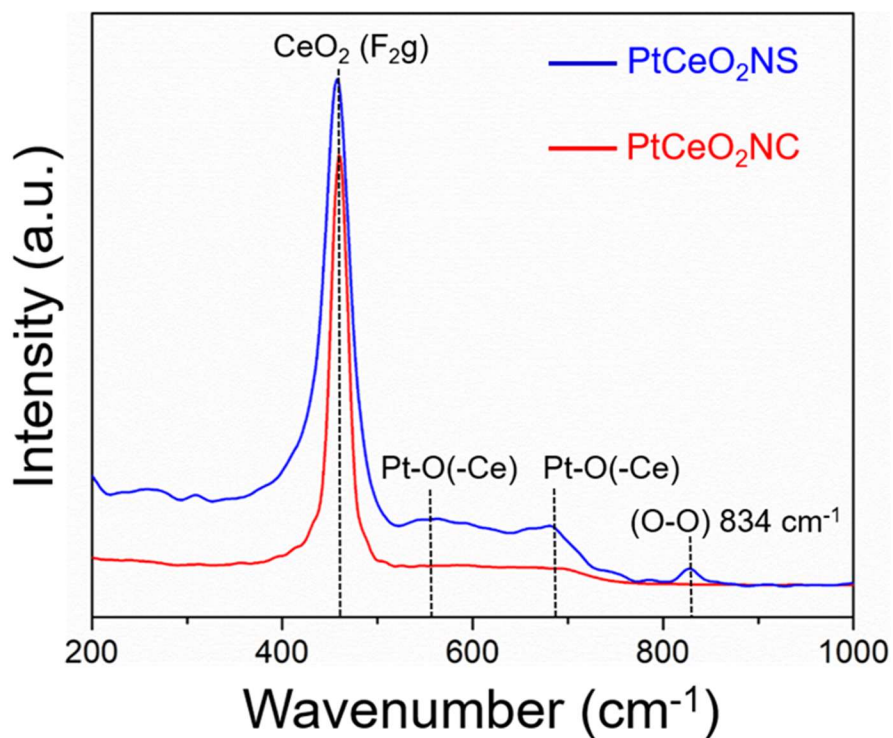
Initially, the synthesized catalyst was sieved into the 350-micron size and diluted with a quartz sand in 1:3 ratios, respectively. Prior to the reaction, 200 mg of diluted catalyst was loaded into the fixed bed reactor and reduced at 250 °C for 1 h in 10 % H<sub>2</sub> gas. For the methanol partial oxidation, the oxygen and methanol were mixed (CH<sub>3</sub>OH: O<sub>2</sub> = 2: 1) in a preheated gas lines using a mass flow controller (MFC) and a liquid syringe pump. Reactant mixture was passed through the catalyst, and the subsequent products were analyzed by the gas chromatograph (GC, DS Science), consisting of TCD and FID detector. Using N<sub>2</sub> as a diluent gas, the catalyst testing was conducted at a total flow rate of 100 ml/minute from 30 to 100 °C. Before taking the GC measurements, the reactant mixture was allowed through the reactor for 3 hours at RT and followed temperature-dependent experiments. At each 15 °C interval, the reaction temperature was stabilized for one hour before taking the GC measurements. The active Pt sites were determined by CO-chemisorption, used for calculating the turnover frequency (TOF).

**Table 1** ICP-OES analysis, BET surface area, CO-TPD metal dispersion and XPS oxidation states of PtCeO<sub>2</sub> catalysts.

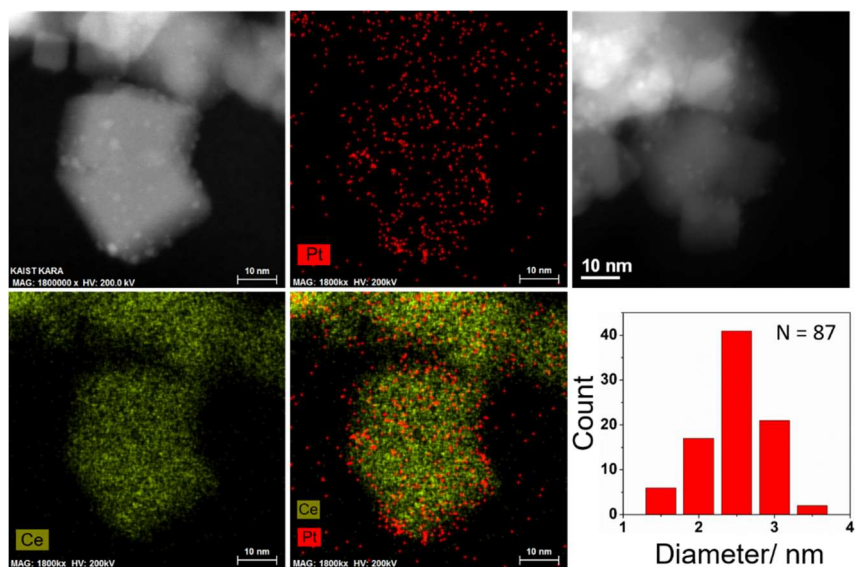
Sample name	Pt content wt. % (ICP-OES)	BET Surface Area (m <sup>2</sup> /g)	D <sub>Pt</sub> (%) CO-TPD	XPS Analysis (%)			
				Ce <sup>3+</sup>	Pt <sup>0</sup>	Pt <sup>2+</sup>	Pt <sup>4+</sup>
PtCeO <sub>2</sub> NC	1.14	37	53.4	27.6	30	60.9	9.1
PtCeO <sub>2</sub> NS	1.19	164	66.8	32.1	11.8	75.4	12.8



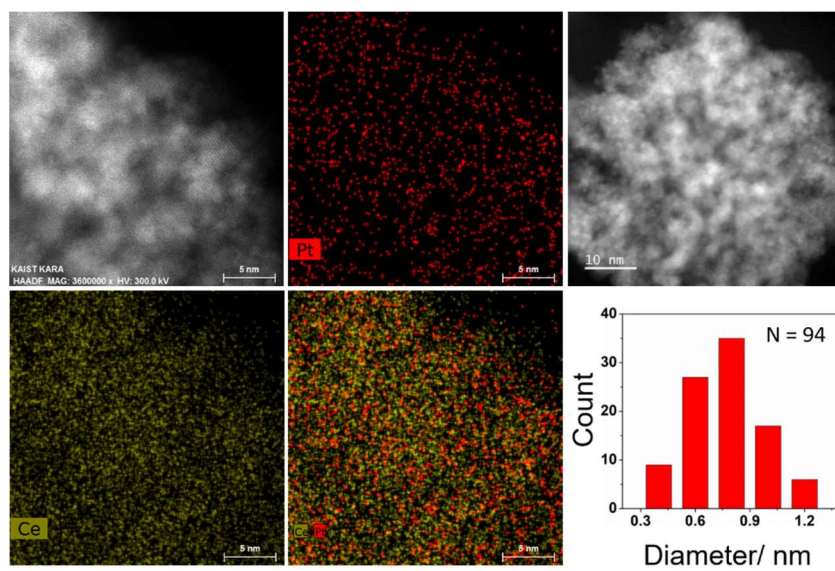
**Fig. S1** XRD spectra of nano-shaped PtCeO<sub>2</sub> catalysts.



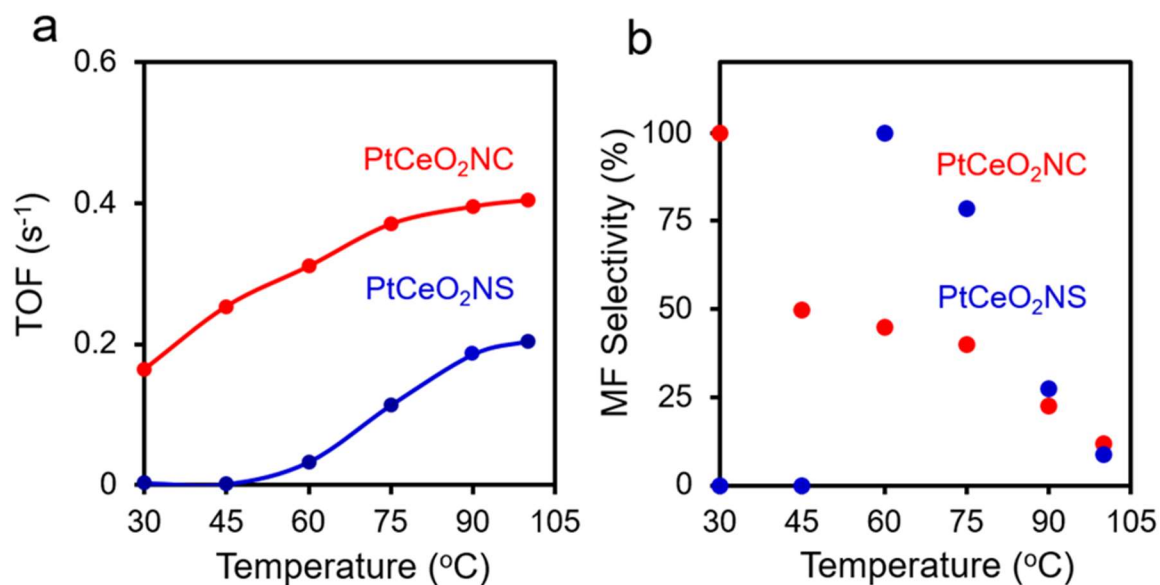
**Fig. S2** Raman analysis of nano-shaped PtCeO<sub>2</sub> catalysts.



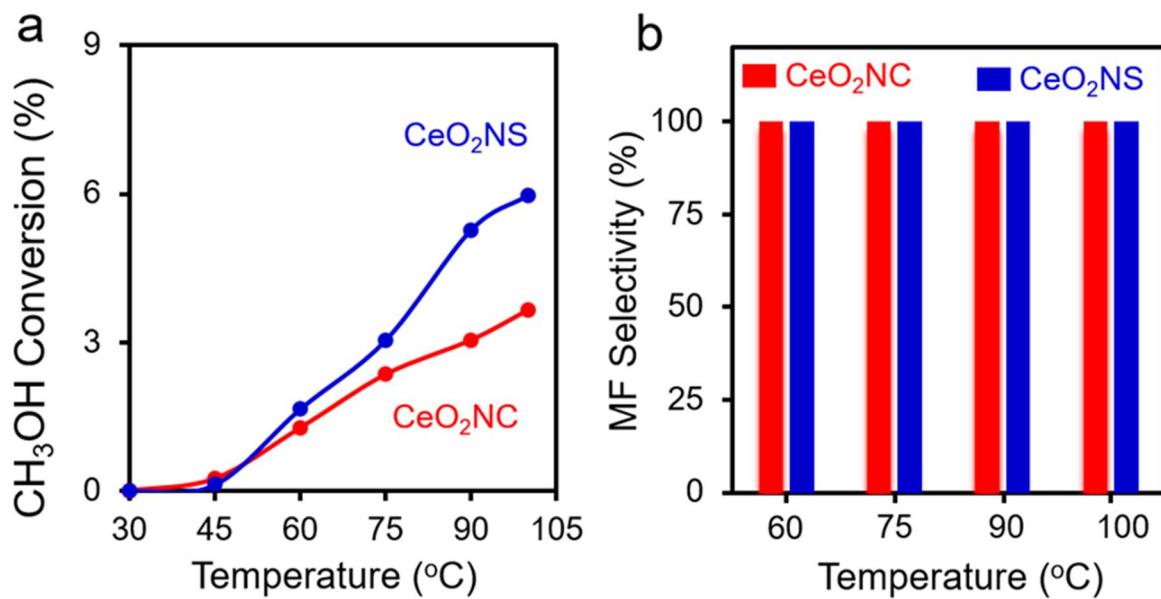
**Fig. S3** STEM-EDS and HAADF-STEM analysis of PtCeO<sub>2</sub>NC.



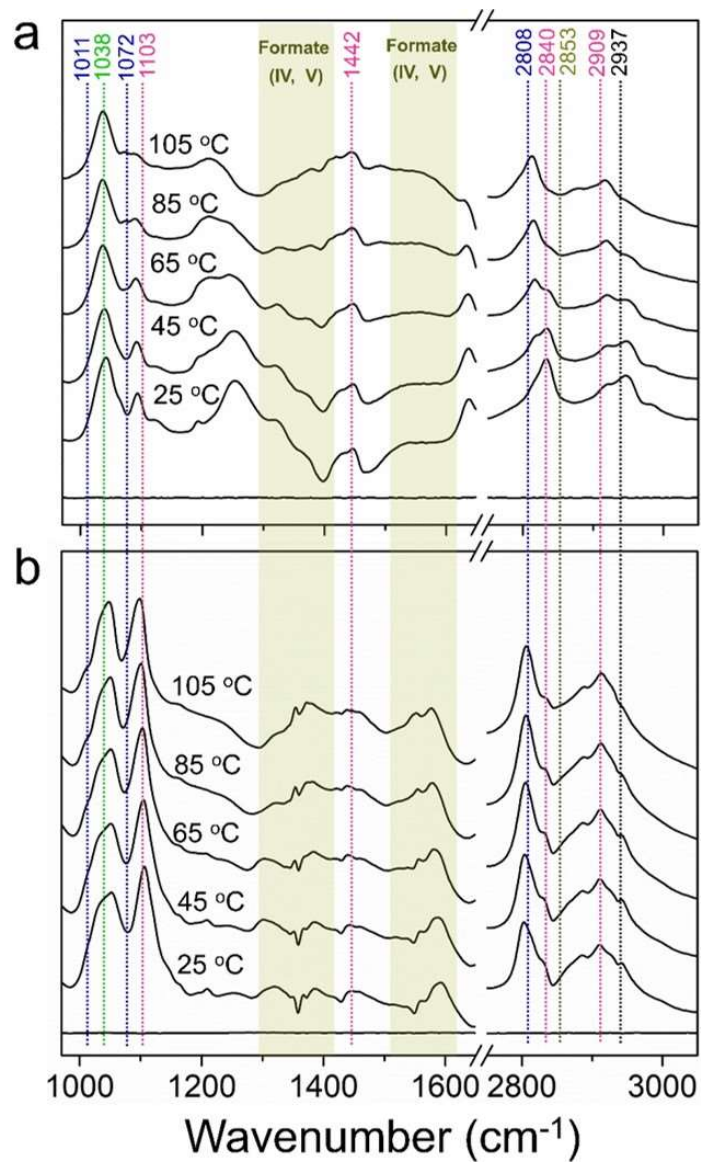
**Fig. S4** STEM-EDS and HAADF-STEM analysis of PtCeO<sub>2</sub>NS.



**Fig. S5** Second Cycle (a) Methanol turn over frequency (TOF) vs. Temperature and (b) Methyl formate (MF) selectivity vs. Temperature plots of the nano-shaped PtCeO<sub>2</sub> catalysts.



**Fig. S6** (a) Methanol conversion vs. temperature and (b) Methyl formate (MF) selectivity vs. temperature plots of the nano-shaped CeO<sub>2</sub> catalysts.

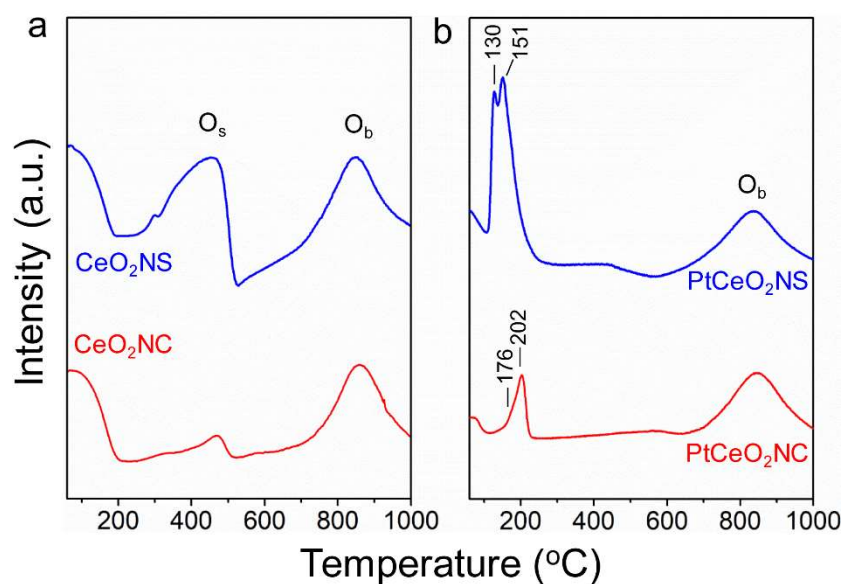


**Fig. S7** CH<sub>3</sub>OH-DRIFT studies on (a) CeO<sub>2</sub>NC (b) CeO<sub>2</sub>NS supports at different desorption temperatures.

**H<sub>2</sub>-TPR.** The CeO<sub>2</sub> NC and NS have shown the reduction peaks between 200-500 °C and 600-1000 °C due to the CeO<sub>2</sub> surface (O<sub>s</sub>) and bulk oxygen (O<sub>b</sub>) reduction. The reduction temperatures of CeO<sub>2</sub>NS are slightly lower than those for the CeO<sub>2</sub>NC, which might be due to its small size and the higher surface area of CeO<sub>2</sub>NS. After 1 wt. % Pt deposition on the CeO<sub>2</sub> surface, no changes in the bulk oxygen reduction temperature (O<sub>b</sub>) were observed. However, surface oxygen reduction



temperatures ( $O_s$ ) decreased to a different extent in both the catalysts (PtCeO<sub>2</sub>NC and PtCeO<sub>2</sub>NS), resulting in the H spillover from Pt to surface oxygen. Among, PtCeO<sub>2</sub>NS exhibit a low-temperature peak at 130 and 151 °C, which may be due to the PtOx species and the surface O of CeO<sub>2</sub> in the vicinity of Pt nanoclusters, respectively. On the other hand, the corresponding peak for PtCeO<sub>2</sub>NC is located at 176 (small hump) and 202 °C. These findings show that PtCeO<sub>2</sub>NC has lower reducibility, likely due to weaker metal-support interaction caused by decreased Pt dispersion.<sup>3</sup>



**Fig. S8** H<sub>2</sub>-TPR analysis of nano-shaped a) CeO<sub>2</sub> b) PtCeO<sub>2</sub> catalysts.

#### Notes and references

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2. X. Liang, J. Xiao, B. Chen, Y. Li, *Inorg. Chem.* 2010, **49**, 8188-8190.
3. T. Wu, X. Pan, Y. Zhang, Z. Miao, B. Zhang, J. Li and X. Yang, *J. Phys. Chem. Lett.* 2014, **5**, 2479-2483.