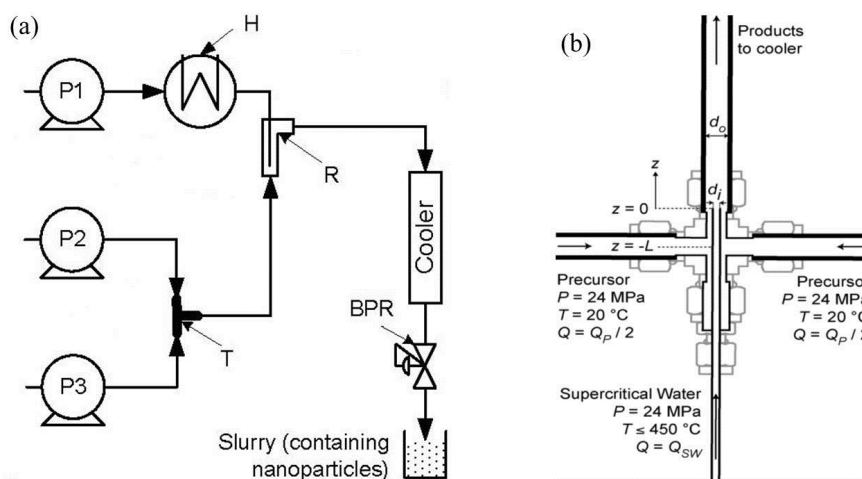


## Supplementary Information

### 1. sc-H<sub>2</sub>O route syntheses

The Pt/CeO<sub>2</sub> hybrid crystallite was manufactured in our laboratory using a three pump-hydrothermal flow system (CHFS). The reactor, tubing and components were all made of 316 stainless steel (Swagelok™). The apparatus (see supplementary Fig. S1) consists of a metal salt(s) solution HPLC pump (P2), a base solution HPLC pump (P3, only used in case) and a water HPLC pump (P1). Deionized water was pumped through an electrical pre-heating coil (2.5 kW) and heated to the appropriate temperature (450 °C), which then meets a aqueous metal salt solution and/or a flow of NaOH solution (1 M) at a mixing point (a 3/8" counter-current mixer that was assisted by a 450 °C band heater), whereupon rapid co-precipitation of crystalline products occurred. The aqueous suspension was cooled via a water jacket cooler, passed through a 7 μm-line filter and was collected from the exit of a back-pressure regulator (BPR). Flow rates of 10, 10 and 20 mL min<sup>-1</sup> were used for metal salt solution, base solution and water stream, respectively. The system pressure was maintained at ca. 23.0 MPa. Solids were recovered by centrifuging the suspension and then freeze-dried to yield the final products. It was noted that ca. 92% Ce precursor had been effectively converted into CeO<sub>2</sub> based on the ICP measurement on collected solution.



**Fig. S1** (a) Schematic representation of the three-pump (P1–P3) continuous hydrothermal flow synthesis system that was used to prepare nanoparticles catalysts. Key: P = pump, BPR = back-pressure regulator, R = reactor, H = heater, T = T junction; (b) Schematic diagram of the confined jet reactor (R. I. Gruar, C. J. Tighe and J. A. Darr, Industrial & Engineering Chemistry Research, 2013, 52, 5270-5281).

### 2. Characterizations

Freeze-drying was performed using a Vacuum Freeze Dryer, Model LGJ-10C, supplied from Beijing

Boyikang Laboratory Instruments Co., Ltd; the solids were frozen for 4 h at  $-50\text{ }^{\circ}\text{C}$  and then freeze-dried for 24 h at 10 Pa. XRD patterns were recorded by a Rigaku D/Max RA diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 0.15418\text{ nm}$ ) at 40 kV and 150 mA and at an angle of  $2\theta$  from 10 to  $80^{\circ}$ . The morphology of crystallite was evaluated using a model JEM-ARM200F (JEOL Company, Japan) high-resolution transmission electron microscope (200 kV accelerating voltage) instrument equipped with a spherical aberration STEM. Laser Raman spectra were obtained using a LABRAM-HR Raman-scope fitted with a Spectraphysics argon ion laser ( $\lambda = 514\text{ nm}$ ) at a power of 20 mW. BET surface areas (SBET) were determined using  $\text{N}_2$  physisorption at 77 K with a Micromeritics ASSP 2020 equipment. Sample pre-treatment was conducted at  $150\text{ }^{\circ}\text{C}$  for 2 h under vacuum. Surface elemental analysis was conducted by using a Thermo ESCALAB 250 XPS instrument with a Al-K $\alpha$  radiation ( $h\nu = 1486.6\text{ eV}$ ) operated at 150W. The signal of adventitious carbon (a binding energy of 284.6 eV) had been used to calibrate the binding energy scale. Curve fits were performed using a Shirley background and a Gaussian peak shape with 30 % Lorentzian character. In CO-TPR, samples (0.05 g) were heated to  $200^{\circ}\text{C}$  with a dwelling time of 1 h and then cooled down to room temperature. The process was operated with a purge of flowing Hegas at the rate of 50 mL/min. Thereafter, samples were pre-treated at  $30\text{ }^{\circ}\text{C}$  for 40 min and then heated up from 30 to  $900^{\circ}\text{C}$  under a purge of flowing CO/Ar (6%  $\text{H}_2$  in Ar) at 35 mL/min. The variation in  $\text{H}_2$  concentration was recorded by a thermal conduction detector (TCD) and a HIDEN QGA portable mass spectrometry (MS). An Optima 7300 DV ICP supplied from Perkin Elmer Corporation(USA) was used to measure the metal ions content in the sample. For digestion, 0.05 g solid powders were first mixed with NaOH and then heated in a muffle furnace at  $300\text{ }^{\circ}\text{C}$  for 1 h and  $650\text{ }^{\circ}\text{C}$  for 0.5 h. After that, 20 mL HCl was added to complete the digestion.

### **3. Activity measurements**

The activities for toluene oxidation were measured in a fixed bed reactor. The 6-mm i.d. quartz reactor tube was loaded with 0.50 g catalyst powder (40 - 60 mesh, mixed with quartz sand to yield the totally volume at 1mL) and placed in an electrically heated furnace. The flow rate was set to maintain the gas hourly space velocity (GHSV) at  $19200\text{ mL}/(\text{g h})$  for all the runs. The nitrogen streams were bubbled through a saturator filled with liquid toluene (flow rate =  $1.6\text{ mL}/\text{min}$ ), which were then mixed with 10 %  $\text{O}_2/\text{N}_2$  gas stream to keep the inlet concentration of gaseous toluene at ca. 500ppm. Prior to the tests, all samples were pre-treated under a purge of the mixed gas at  $120\text{ }^{\circ}\text{C}$  until the stabilization of the system. The reactants and products were monitored using GC analyzer (Agilent Technologies 7890A) equipped with a flame ionization detector (FID) and GS-Gaspro column. No other carbon-containing organic compounds were detected at  $T_{90}$  (i.e. 90 % conversion of toluene).

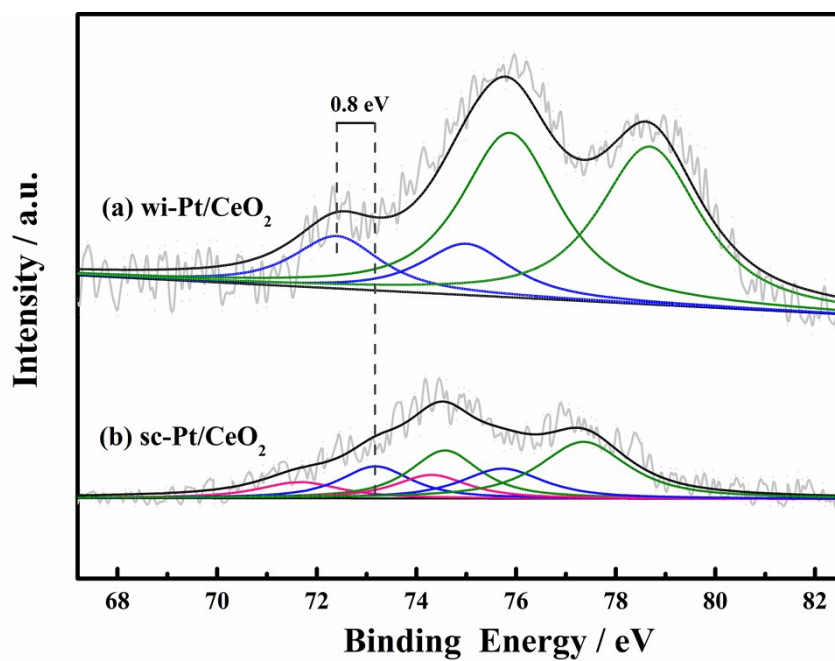


Fig. S2 Pt4f X-ray photoelectron spectra of (a) wi-Pt/CeO<sub>2</sub> and (b) sc-Pt/CeO<sub>2</sub>.

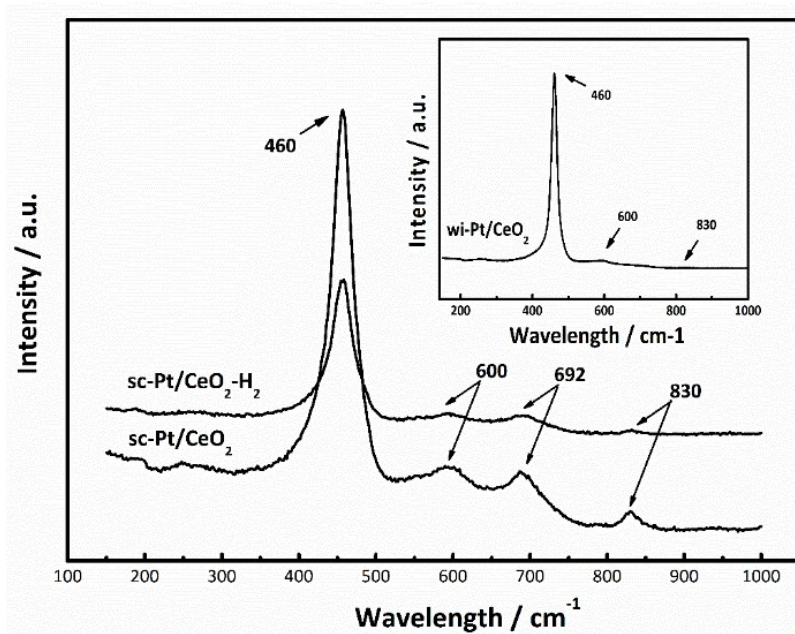


Fig. S3 Raman spectra of Pt/CeO<sub>2</sub> hybrid materials.

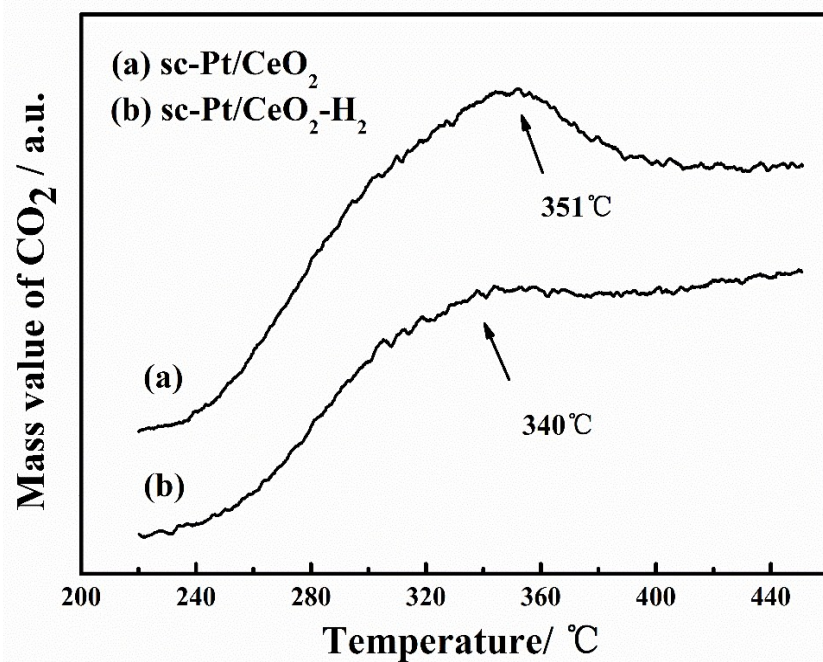


Fig. S4CO-TPR profiles of (a) sc-Pt/CeO<sub>2</sub> and (b) sc-Pt/CeO<sub>2</sub>-H<sub>2</sub>.

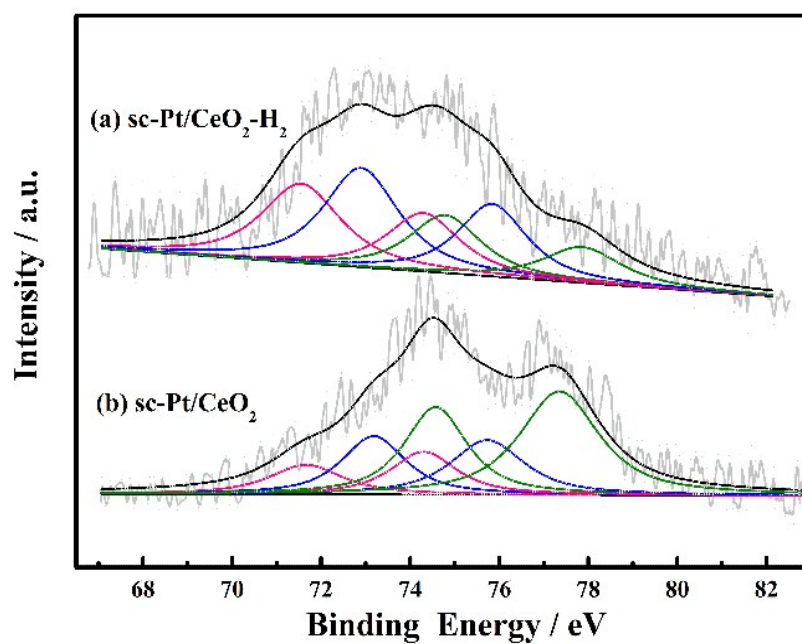


Fig. S5 Pt4f X-ray photoelectron spectra of (a) sc-Pt/CeO<sub>2</sub>-H<sub>2</sub> and (b) sc-Pt/CeO<sub>2</sub>.

Table S1 Elemental species over Pt/CeO<sub>2</sub> samples as analyzed by XPS.

Samples	Species	Binding Energy of 4f7/2 (eV)	Relative Intensities (%)
sc-Pt/CeO <sub>2</sub>	Pt <sup>0</sup>	71.6	18.23

	Pt <sup>2+</sup>	73.2	33.62
	Pt <sup>4+</sup>	74.6	48.15
	Pt <sup>0</sup>	71.5	35.04
sc-Pt/CeO <sub>2</sub> -H <sub>2</sub>	Pt <sup>2+</sup>	72.9	41.63
	Pt <sup>4+</sup>	74.7	23.33