Supporting Information

Pt-based Core-shell Nanocatalysts with Enhanced Activity and Stability for CO Oxidation

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1 Catalysts preparation

Synthesis of Pt@SiO_2: The process was carried out using the Stöber method by following the reported method with a modification.[1] For the synthesis of Pt nanoparticles, 15 ml of aqueous 10 mM K_2PtCl_4 (Aldrich, 99.9%) and 37.5 ml of 400 mM TTAB (Aldrich, 99%) were mixed with 88.5 ml of deionized water in a 500-ml round bottom flask at the room temperature. The mixture was stirred at the room temperature for 10 min and was heated at 50 ºC for 10 min., and then 9 ml of 500 mM ice-cooled $NaBH_4$ (Aldrich, 98%) solution was injected through the septum using a syringe to the above clear solution. The gas evolved inside the flask was released by inserting a needle through the septum for 20 min. The resultant solution was kept at 50 ºC for 15 h. The product was centrifuged at 8000 rpm for 30 min. The supernatant solution was separated and centrifuged again at 11000 rpm for 15 min, twice. The Pt nanoparticle colloids were collected and re-dispersed in 15 ml of deionized water by sonication. The as-prepared Pt nanoparticle colloid (1.5×10^{-4} mol) dispersed in 15 ml of deionized water was added to 35.5 ml of deionized water. A NaOH solution (3.0 ml of 0.05 M) was added to the aqueous Pt colloid solution with stirring to adjust the pH of the solution to around 10-11. To this basic solution, a controlled amount of 10 vol% TEOS (Tetraethylorthosilicate) diluted with methanol was added to initiate the silica polymerization. The as-synthesized Pt@SiO_2 was calcined at 400 ºC for 2 h in static air to remove TTAB surfactants to generate Pt@SiO_2 catalysts.

[1] S. H. Joo, J. Y. Park, C.-K. Tsung, Y. Yamada, P. Yang and G. A. Somorjai, *Nat Mater*, 2009, **8**, 126

Synthesis of Pt@SiO_2@CeO_2: Pt@SiO_2@CeO_2 was prepared by a chemical precipitation method in accordance with the following procedure. The obtained Pt@SiO_2 spheres after grinded and 664 mg $Ce(NO_3)_3\cdot6H_2O$ (JK Chemical, 99.9%) was dispersed or dissolved in 30 ml ethanol through an ultrasonic treatment process for 15 min. Subsequently, 2.2 g HMT (hexamethylenetetramine) (JK Chemical, 99%) dissolved in 20 ml deionized water was added to the fully dispersed particle solution with ultrasonic vibrations for another 15min. The mixture was then stirred for 2 h in a water bath maintained at 70 ºC. The obtained solids were washed by ethanol and water until PH=7. Then they were dried at 60 ºC overnight and calcined at 400 ºC for 2 h, thus get Pt@SiO_2@CeO_2 catalyst.

Synthesis of Pt@CeO_2: Pt@CeO_2 was prepared by a leaching method. The as prepared Pt@SiO_2@CeO_2 was dispersed in a concentrated NaOH solution (2M). The mixture was stirred at 60 ºC for 2 h, then the solids were washed with large amount of water until PH=7. The obtained solids were then dried at 120 ºC overnight, thus get Pt@CeO_2.

Synthesis of Pt/CeO_2: Pt/CeO_2 was prepared by a co-precipitation method used as a reference catalyst. Appropriate amount of H_2PtCl_6 and $Ce(NO_3)_3{\cdot}6H_2O$ ((Pt wt.) : (CeO_2 wt.) =1:100) was dissolved in 100 ml deionized water, and then solution of 5×10^{-2} mol/L NaOH was added into the above solution until PH value reaches 9. The resultant reaction mixture was aged for 1 h under agitation. After aging step, the reaction mixture was washed and filtered to attain the solid, which was subsequently dried overnight and calcined at 400 °C for 2 h to obtain 1%Pt/CeO_2.

2. Activity test:

Catalytic tests were conducted at the atmospheric pressure in a quartz fixed-bed reactor (Φ10 × 30 mm) loaded with 0.05 g catalysts (20-40 mesh) mixed with 1 ml of quartz particles. The catalysts were pre-reduced with 10%H_2/N_2 for 1 h at 400 ºC. After reduction the catalyst was purged with nitrogen for 30 min at the same temperature. The total feed flow rate was held constant at 100 ml/min, with flowing N_2. The activity tests were performed with molar ratio $O_2/CO/N_2$ = 1/1/3, at different temperatures, ranging from 100 to 350 ºC, the stability test was performed at 250 ºC.

The conversion of CO was defined as follows:

$$CO\ converion\ (\%) = \frac{[CO_2]_{out}}{[CO]_{in}} \times 100$$

3. Characterization:

BET (Brunauer-Emmett-Teller) surface areas and pore structure of catalysts were measured using a Micromeritics Tristar 3000 analyzer by nitrogen adsorption at -196 ºC. The specific surface areas were calculated from the isotherms using the BET method, and the pore distribution and the cumulative volumes of pores were obtained by the BJH (Barrett-Joyner-Halenda) method from the desorption branches of the adsorption isotherms.

Elemental analysis of catalysts was performed on an ICP-OES (Varian Vista-MPX) at a high frequency emission power of 1.5 kW and a plasma airflow of 15.0 L/min (λ_{Pt} = 214.424 nm, λ_{Si} = 251.611 nm, λ_{Ce} = 418.659 nm).

X-ray diffraction patterns (XRD) were recorded with a Bruker D8 Focus operated at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation (λ = 1.54056 Å) and a 2θ ranging from 10 to 85° at a scanning rate of 0.02°/step and 0.15 s/step.

Transmission electron microscope (TEM) images were obtained on a FEI Tecnai G2 F20 transmission electron microscope at 100 kV. The sample powder was dispersed in ethanol by sonification; drops of the suspension were applied onto a copper grid-supported transparent carbon foil and dried in air.

Table S1 Element composition (EDX analysis/ICP results)

Element weight / %	Pt	Si	Ce	O
Pt@SiO_2	45.9/17.6	17.5/38.4	–	36.6/43.9
Pt@SiO_2@CeO_2	8.0/11.9	2.4/25.9	68.3/26.5	21.4/35.7
Pt@CeO_2	10.3/21.9	0.6/1.6	70.2/49.0	18.9/21.4

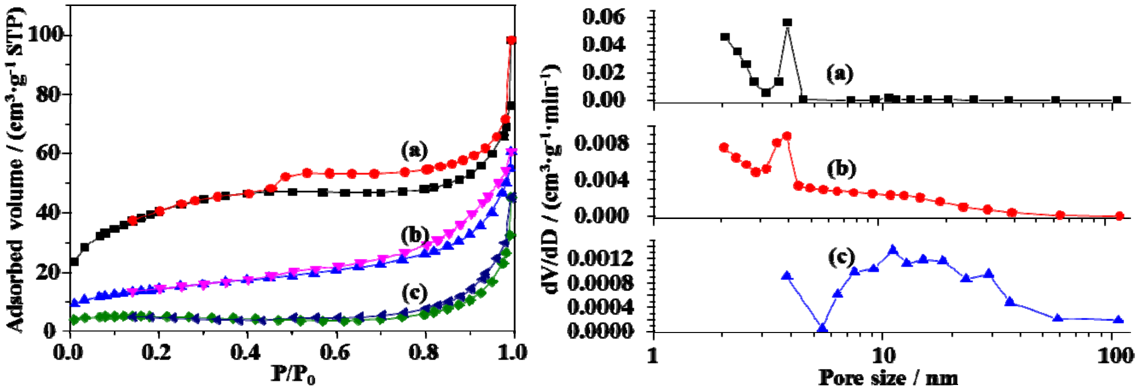


Figure S1 N_2 adsorption-desorption isotherms and pore size distribution curves calculated by the BJH equation in desorption branches of the core-shell catalysts (a) Pt@SiO_2, (b) Pt@SiO_2@CeO_2, (c) Pt@CeO_2.

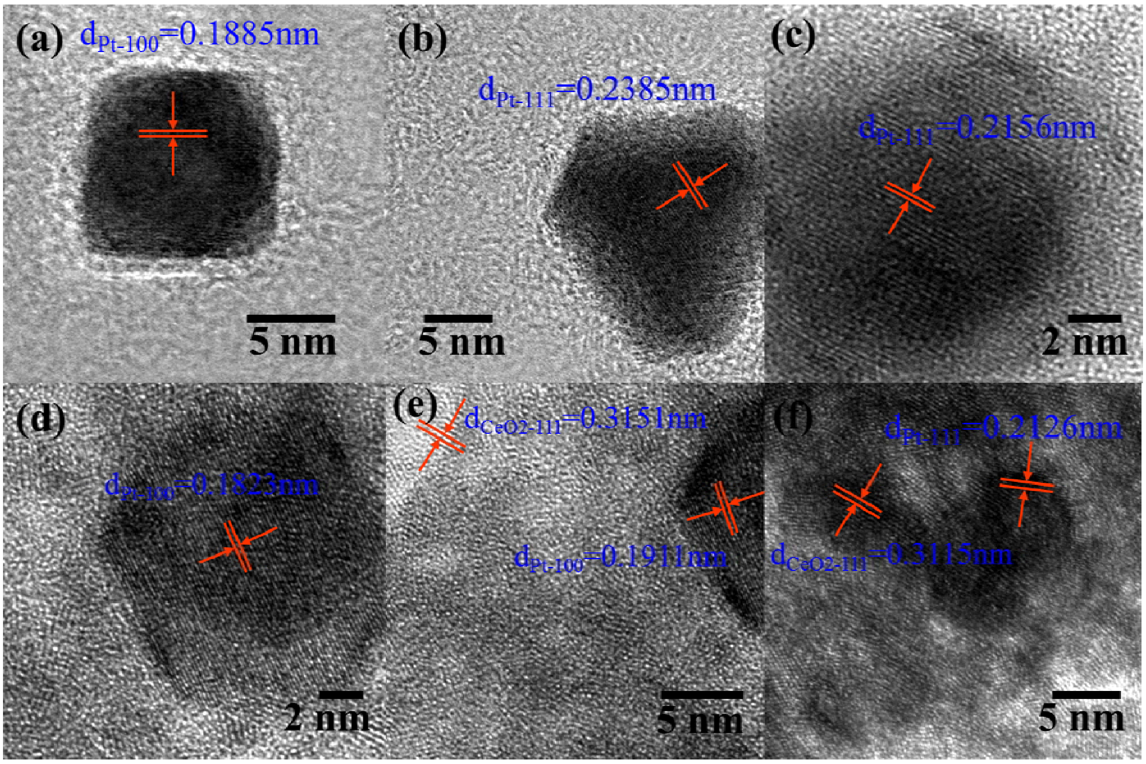


Figure S2 HRTEM image of the Pt-based core-shell catalysts, (a) (b): TTAB capped Pt particles, (c): Pt@SiO_2, (d) (e): Pt@SiO_2@CeO_2, (f): Pt@CeO_2

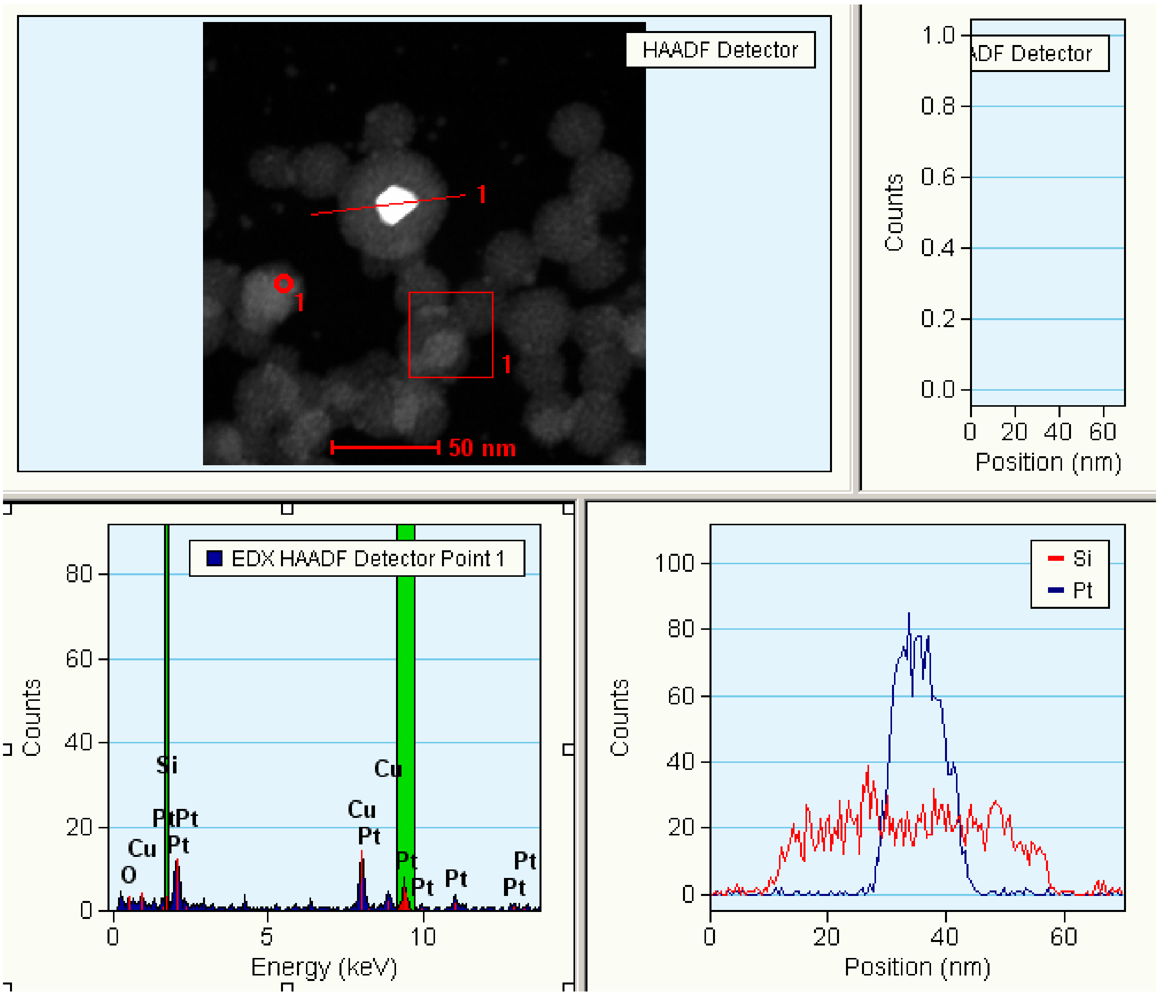


Figure S3 EDX-line scanning results of Pt@SiO_2

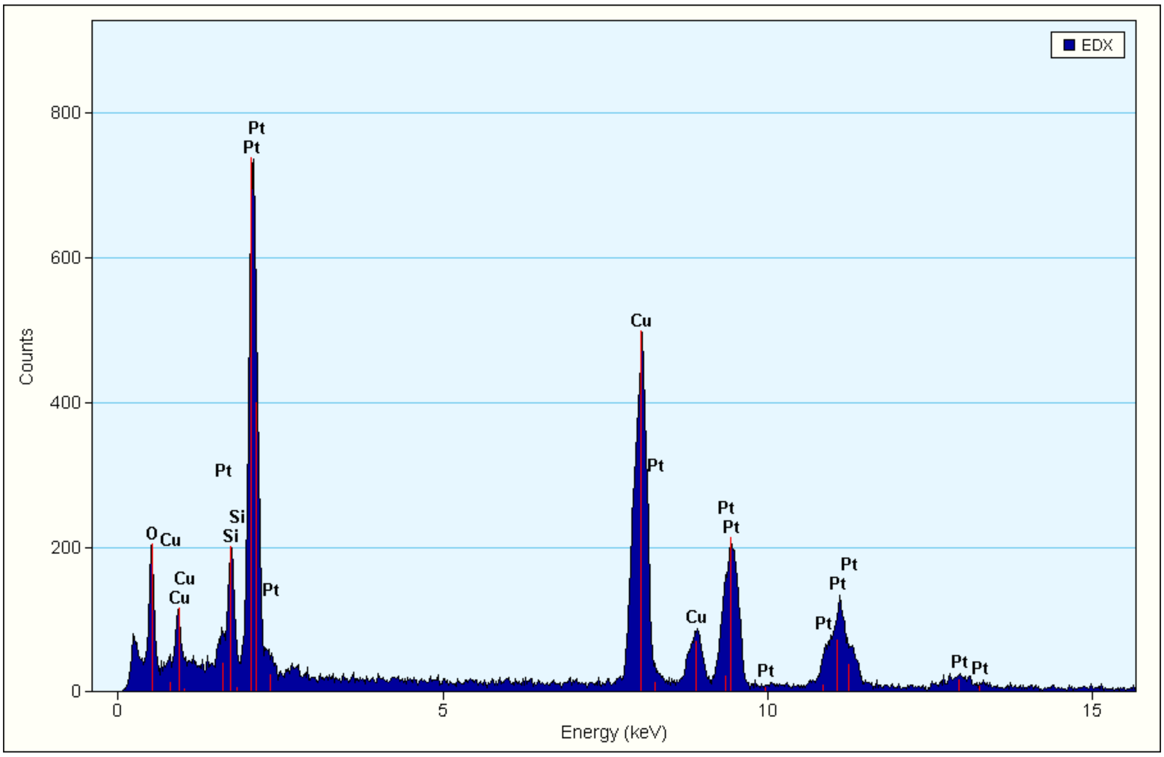


Figure S4 EDX scanning results of Pt@SiO_2

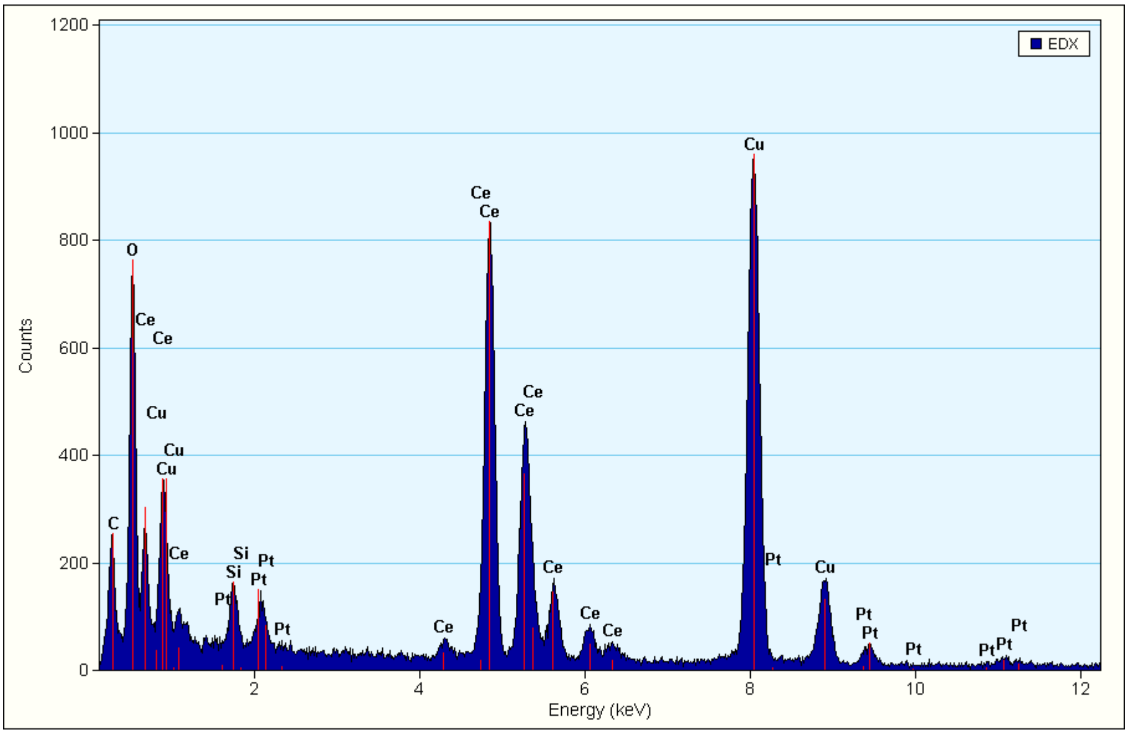


Figure S5 EDX scanning results of Pt@SiO_2@CeO_2

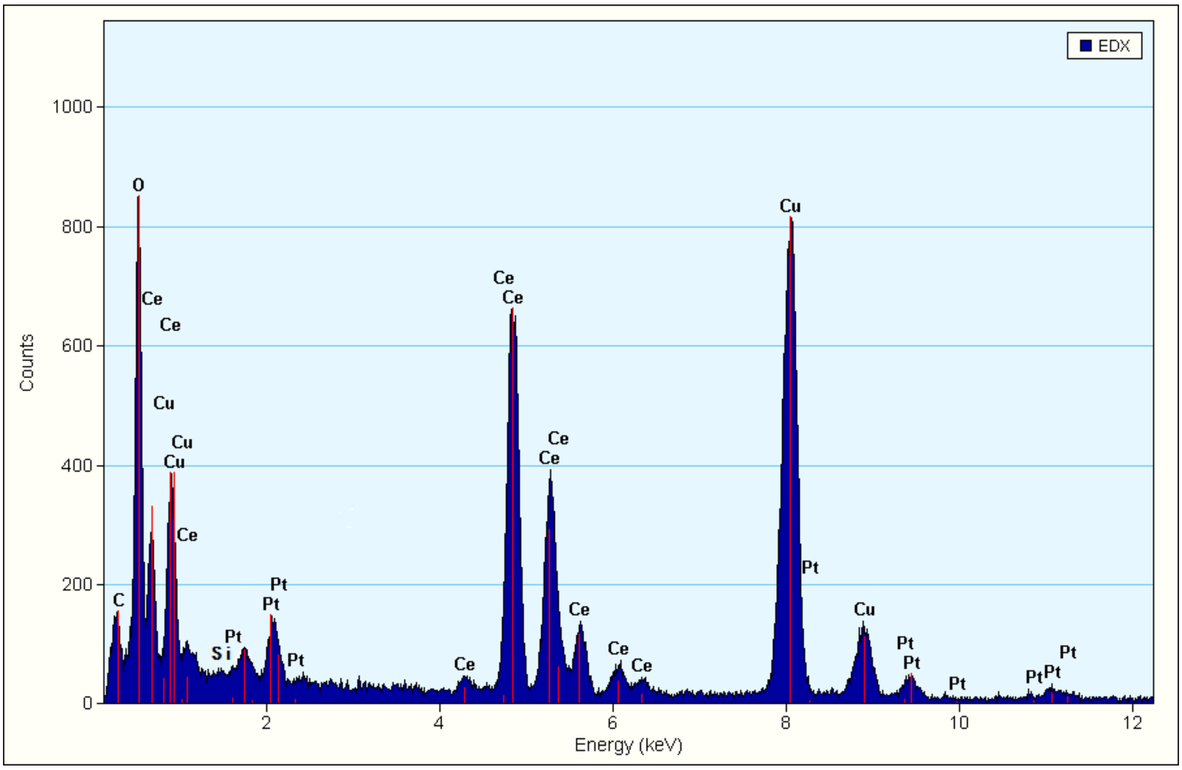
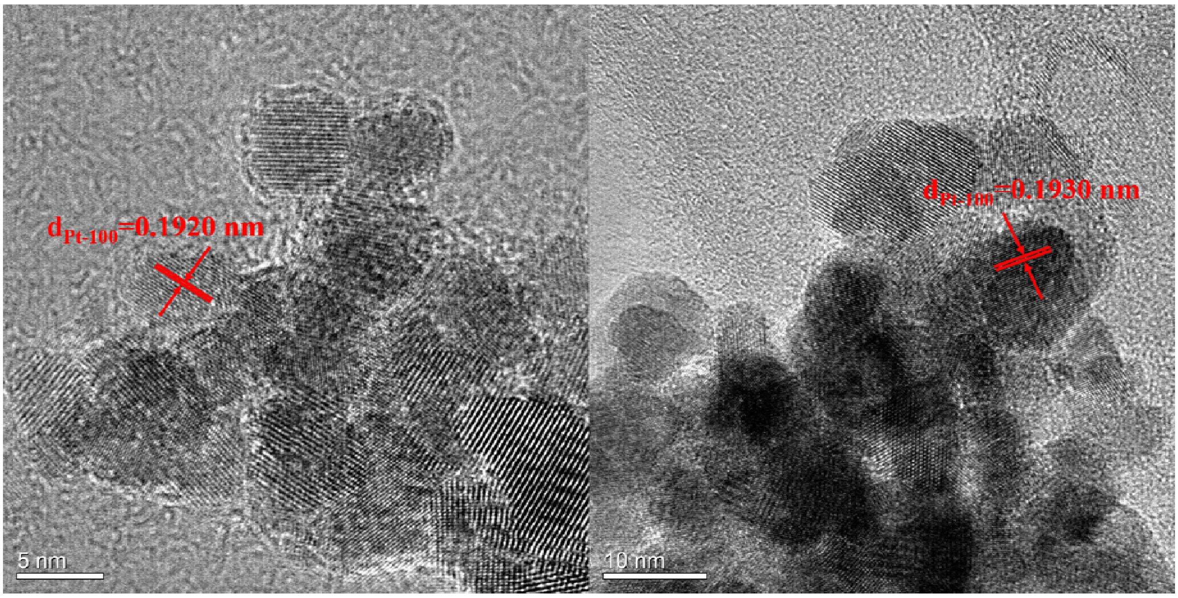


Figure S6 EDX scanning results of $Pt@CeO_2$



(a) (b)

Figure S7 TEM images of the Pt/CeO_2 catalyst before (a) and after (b) stability test