

Supplementary Information

The catalysts of 3D ordered macroporous ZrO₂-supported core-shell Pt@CeO_{2-x} nanoparticles: The effect of optimized Pt-CeO₂ interface on improving catalytic activity and stability for soot oxidation

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Experimental Section

1 Preparation of materials

1.1 Synthesis of monodispersed PMMA microsphere and assembly of template

Non-crosslinked, monodispersed polymethyl methacrylate (PMMA) microspheres were synthesized using an emulsifier-free emulsion polymerization technique with water-oil single-phase initiator. The Methyl methacrylate (MMA, 120 ml) as monomer was purified by reduced pressure distillation. Then, water (240 ml) were poured into a four-necked and round-bottomed flask. When the mixture was heated to 80°C by a hot water bath, the refined monomers were also added into it. A Teflon stirring paddle attached to the flask was driven by an electric motor after Ar was bubbled to deaerate the air for 2h. In a separate polyethylene bottle, 0.6 g of potassium persulfate ($K_2S_2O_8$, water phase initiator) were added into the water (50 ml). When the solution was heated to 80°C, it was added to the flask. Under the constant stirring rate (350 r min^{-1}) and the protection of nitrogen, the mixture was kept at 80°C for 2 h. After the reaction was finished, the reaction system was naturally cooled to room temperature, and the homogeneous latex with nearly monodispersed PMMA microspheres were obtained by the filtration with filter paper (pore sizes, $\sim 1 \mu\text{m}$). In the present studies, the average diameters of the obtained microspheres were 350 nm which were estimated by using laser particle size analyzer. The latex was centrifuged at 3000 r min^{-1} for 10 h to form colloidal crystal templates (CCT). The clear liquid was decanted, and the solid block was dried at room temperature. Finally, the highly ordered PMMA template was obtained. The SEM image of colloidal crystal templates are shown in Fig S1.

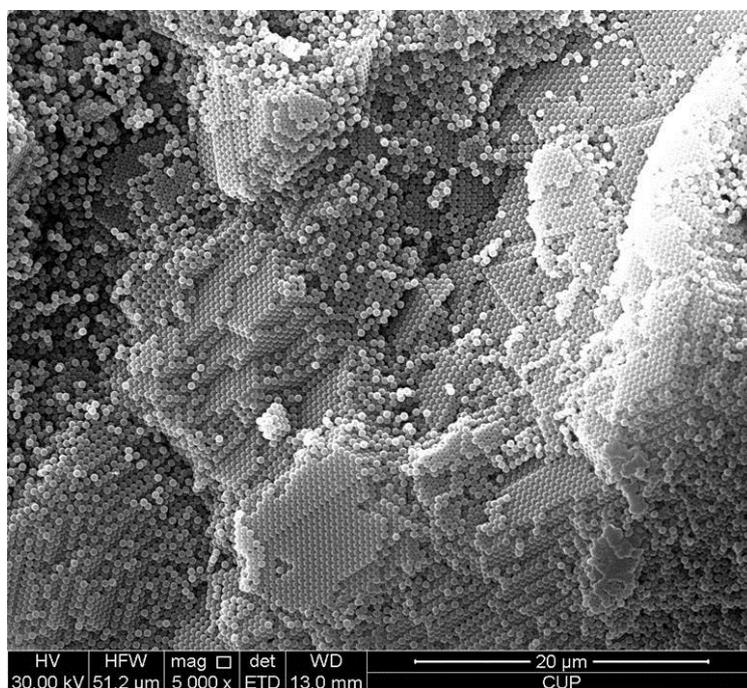


Fig.S1 SEM images of PMMA colloidal crystal template

1.2 Preparation of 3DOM ZrO₂ solid solution support

The 3DOM ZrO₂oxide was prepared by colloidal crystal template method using ethylene glycol (EG)-methanol solution of various metal nitrates (ZrOCl₂·8H₂O) as precursor solution as shown in Fig.S2. To obtain 3DOM metal oxides, the solidification of these salts is necessary before the bursts of template polymethyl methacrylate. As using EG-methanol solvent, the heteropolynuclear complex containing zirconium ions came into being at low temperature during the dry process, indicating that the solidification of the salt occurred before the decomposition of the template polymer. Methanol (6 ml) and EG were added to achieve the solution with desired concentration of methanol. Then the inorganic precursors were added to the CCT and permeated the voids between the close-packed spheres, and condensed into a hard inorganic framework upon drying. Excessive liquid was removed from the impregnated microspheres template via a Buchner funnel connected to vacuum. The infiltrated template was allowed to dry in a desiccator using anhydrous calcium chloride at 40°C for 24h. Finally, the dried sample was mixed with alumina balls (3~5 mm) and heated in a quartz tube at the rate of 1°C min⁻¹ from 20°C to 650°C in air for 6 h to remove the CCT, and then 3DOM ZrO₂ support possessing perfect crystal phases was obtained.

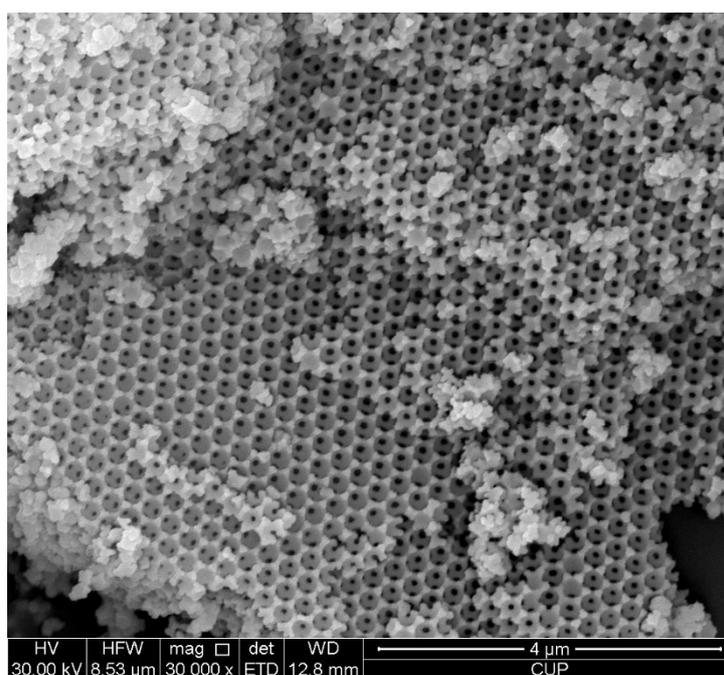


Fig.S2 SEM images of 3DOM ZrO₂ support.

1.3 Synthesis of 3DOM ZrO₂-supported Pt@CeO_{2-x} core-shell NP catalysts

3DOM Pt@CeO_{2-x}/ZrO₂-ncatalysts were synthesized via the precipitation method, where n is the mole ratio of CeO_{2-x} to Pt in catalysts. The reagent specifications are shown in Table 1. The typical preparation procedures were described as follows: The poly N-vinyl-2-pyrrolidone (PVP) solution as a stabilizer was added into the mixed solution (100 ml) of H₂PtCl₆. Then 3DOM ZrO₂ support was also introduced into the solution. Then the Ce(NO₃)₃ solution (50 ml) was introduced into the solution. The mixture solution was stirring for 1 h. A reductant solution (NaBH₄) (50 ml) was injected into the solution at flow rate of 1 ml min⁻¹. The synthesis stopped after complete consumption of the NaBH₄ solution. The reaction system was further stirring for 1 h, and subsequently kept static for 2 h. Then, the product was filtered and washed with distilled water at 50° until the Cl⁻ was completely removed according to a test with AgNO₃. The final products were calcined in a furnace at 450°C for 1 h and the desired 3DOM Pt@CeO_{2-x}/ZrO₂ catalysts were obtained, shown in Fig S3.

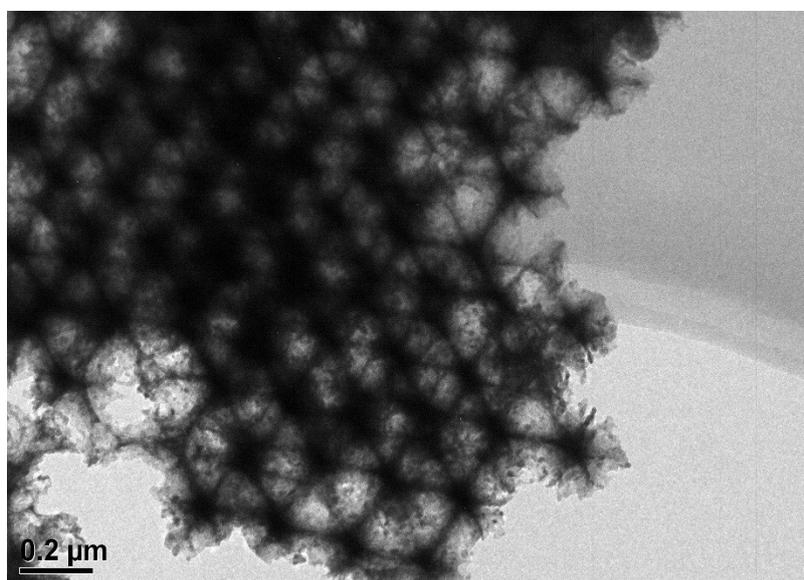


Fig.S3TEM images of 3DOM Pt@CeO_{2-x}/ZrO₂-1catalyst.

2. Characterization

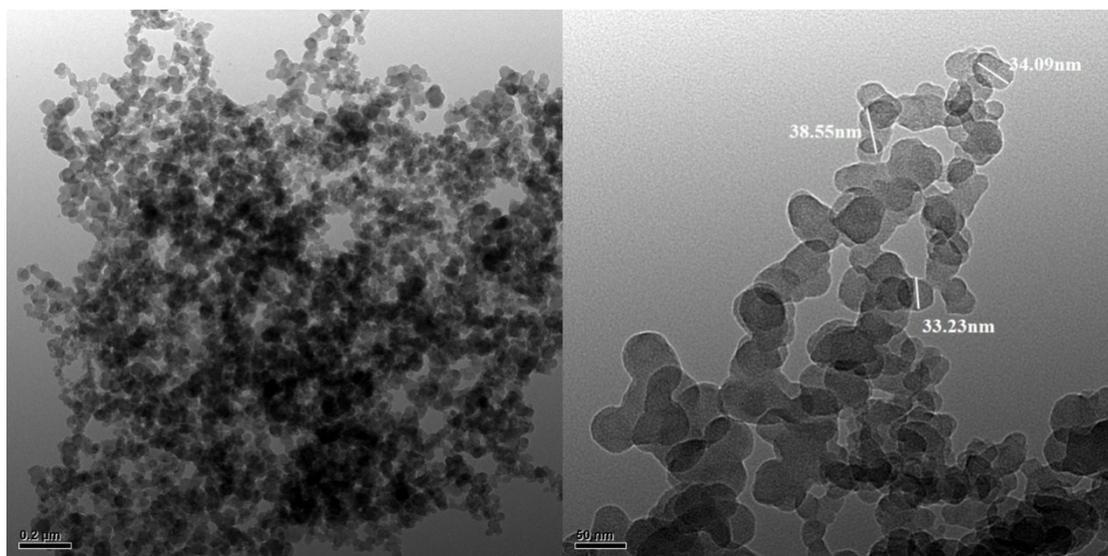


Fig.S4TEM images of the soot particles

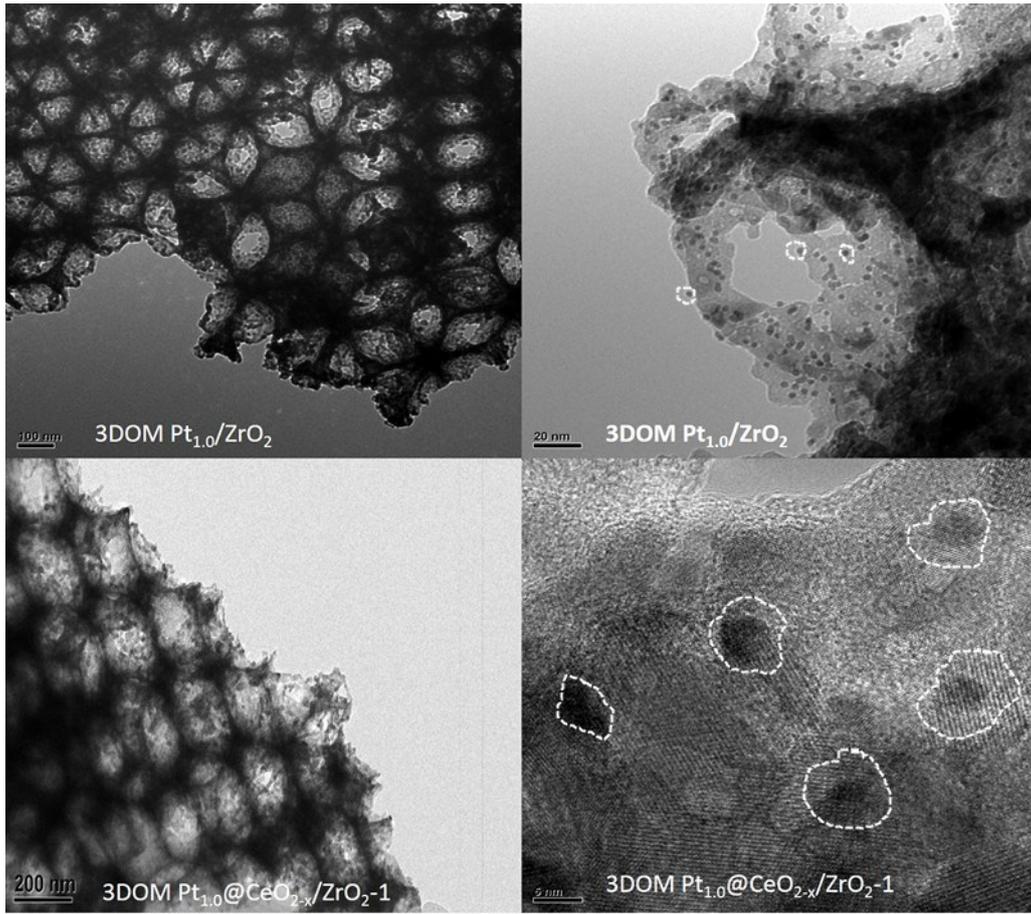


Fig.S5 TEM images of 3DOM Pt_{1.0}/ZrO₂ and Pt_{1.0}@CeO_{2-x}/ZrO₂-1

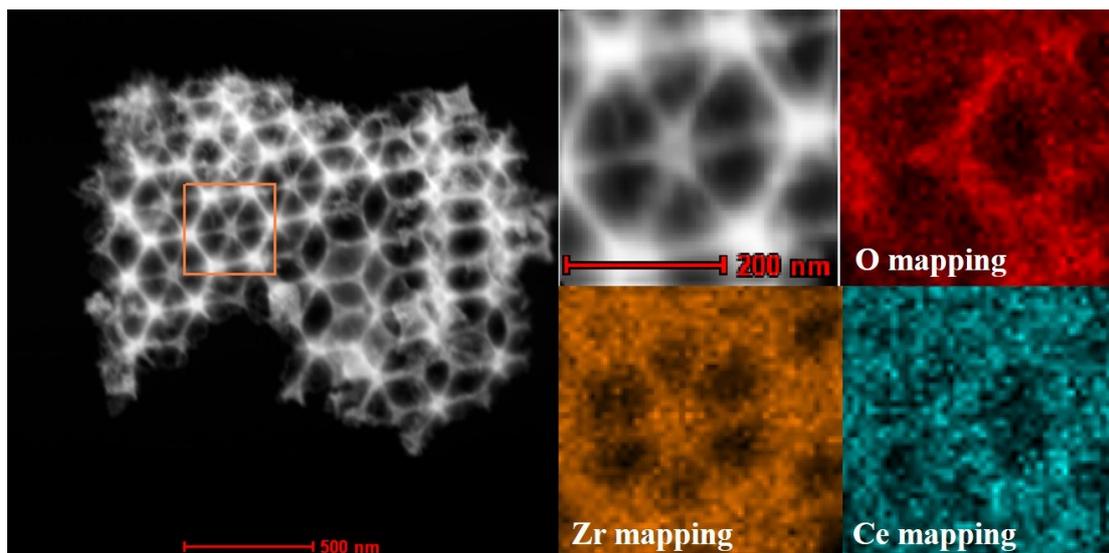


Fig.S6 the HAADF-STEM images and EDX scan analyses of the elements-mapping analysis for Ce, Zr and O over the typical 3DOM Pt@CeO_{2-x}/ZrO₂ catalyst.

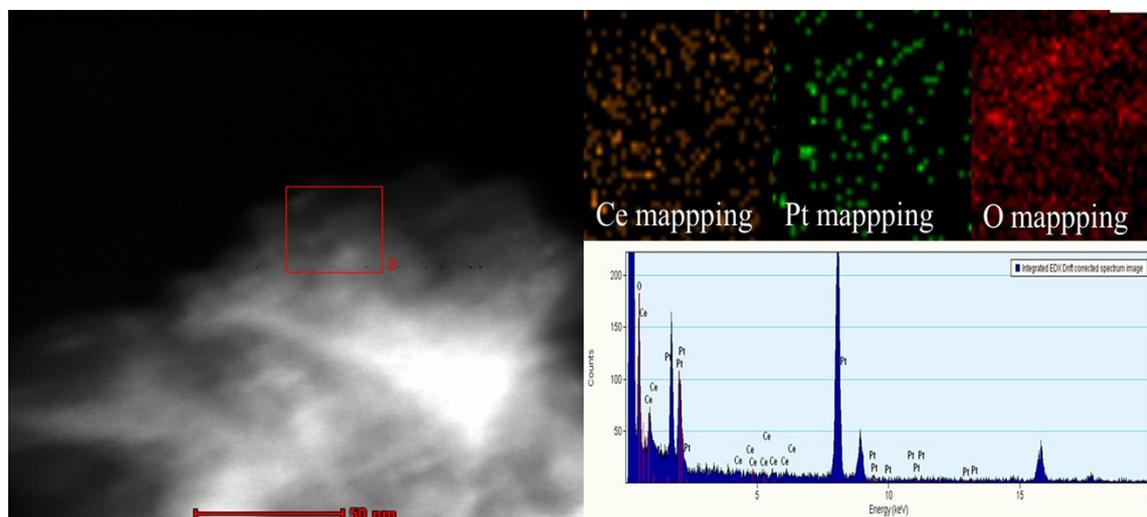


Fig.S7 HAADF-STEM images and EDX scan analyses of the elements-mapping analysis for Ce and Pt over the typical 3DOM Pt@CeO_{2-x}/ZrO₂ catalyst. The orange and green colors indicate Ce and Pt elementals of the rectangle area in inset determined by HAADF-STEM-EDX analysis (mapping images), respectively.

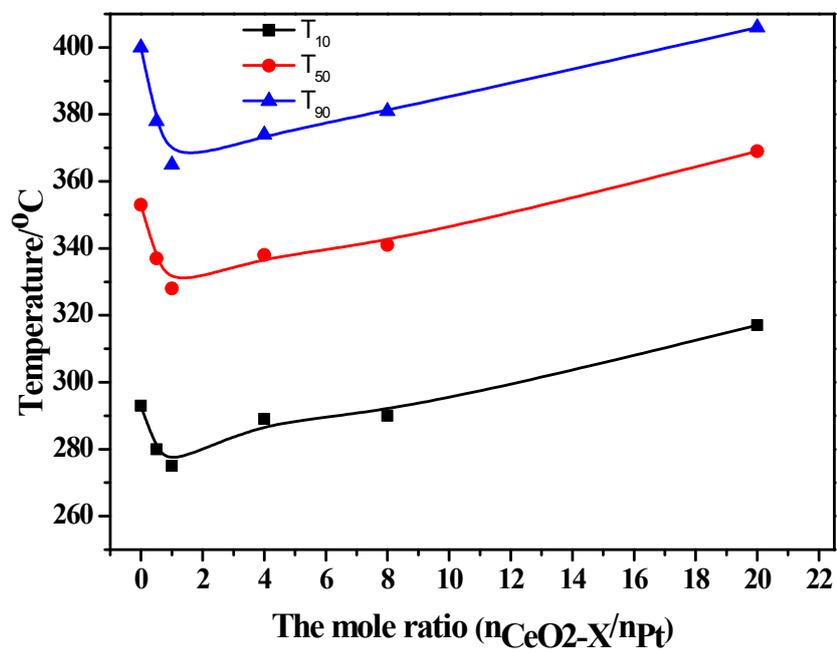


Fig.S8 The catalytic activity profiles for soot oxidation over the 3DOM Pt@CeO_{2-x}/ZrO₂ catalysts as a function of the mole ratio ($n_{\text{CeO}_2\text{-X}}/n_{\text{Pt}}$)

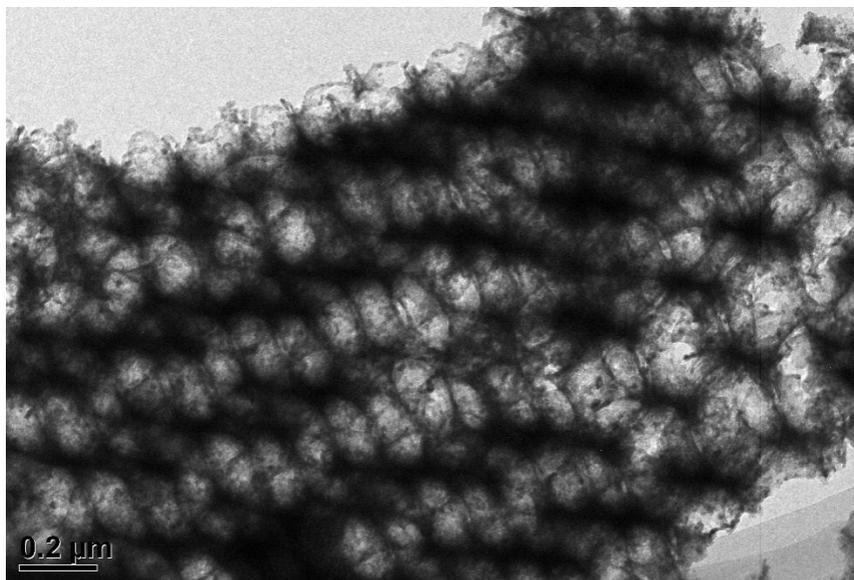


Fig.S9 TEM images of 3DOM Pt_{1.0}@CeO_{2-x}/ZrO₂-8catalyst after five-cycle tests of TPO.

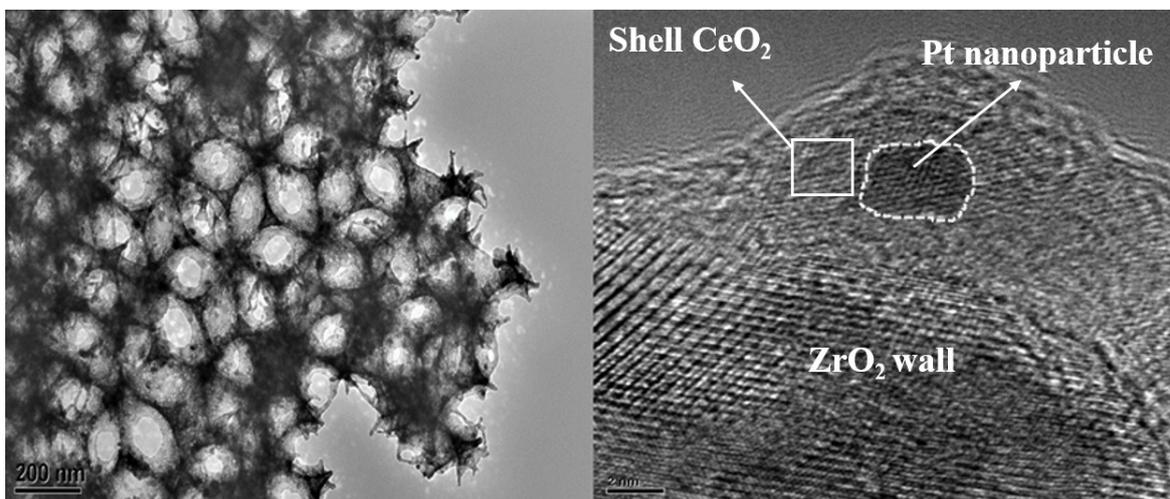


Fig.S10 TEM images of 3DOM Pt@CeO₂/ZrO₂-1 after use in the reaction

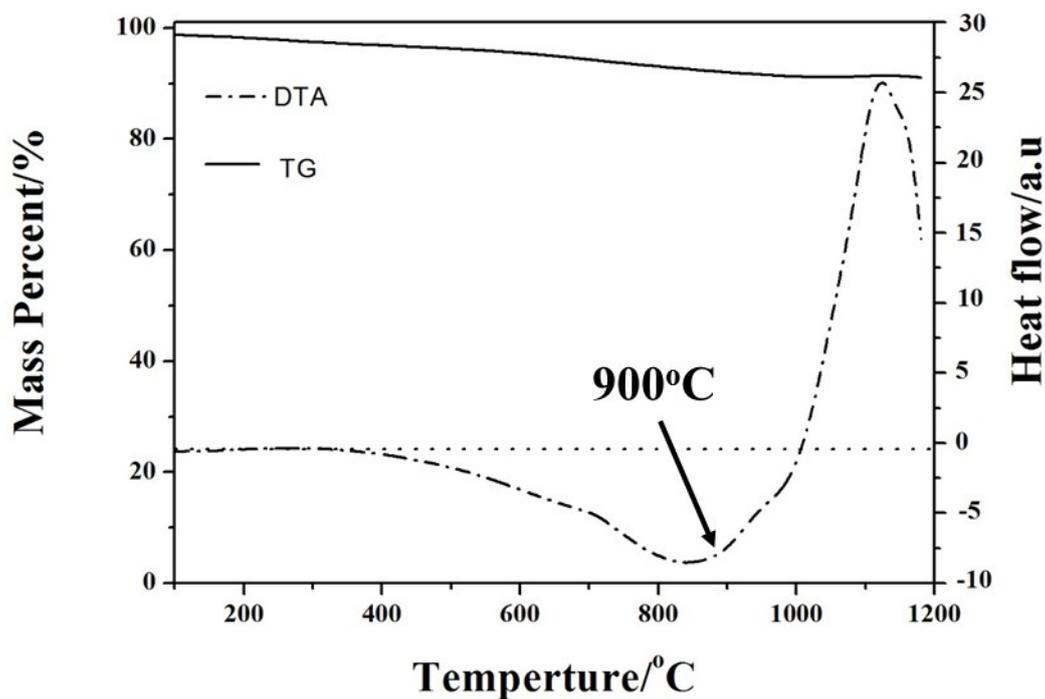


Fig.S11 TG-DTA curves of pure soot(with N₂, temperature rising rate 10°C/S).

The sample weight is only reduced by 10% from 0 to 1200 °C. The sample absorbed a small amount of heat from 400~800°C. It is probably because the evaporation of water in the sample. The sample started to liberate heat from 900°C. The decomposition reaction is exothermal reaction. The thermal decomposition temperature of soot is above 900°C.

Table.S1BET surface areas of 3DOM ZrO₂, Pt/ZrO₂ and Pt@CeO_{2-x}/ZrO₂ catalysts.

Catalyst (3DOM) ^o	BET(m ² /g) ^o
ZrO ₂ ^o	15.3 ^o
Pt _{1.0} /ZrO ₂ ^o	18.3 ^o
Pt _{1.0} @CeO _{2-x} /ZrO ₂ -0.5 ^o	20.6 ^o
Pt _{1.0} @CeO _{2-x} /ZrO ₂ -1 ^o	21.1 ^o
Pt _{1.0} @CeO _{2-x} /ZrO ₂ -4 ^o	22.4 ^o
Pt _{1.0} @CeO _{2-x} /ZrO ₂ -20 ^o	26.3 ^o

Table.S2 The results for element analysis of Printex U or diesel soot⁵⁰

Element content/%	Printex U/%
C	92.0
H	0.7
O	3.5
N	0.1
S	0.2
Si	-
Fe	-
Other*	3.5