Supporting Information

Synthesis of Highly Active Pt-CeO_2 Hybrids with Tunable Secondary Nanostructures for Catalytic Hydrolysis of Ammonia Borane

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Experimental Section:

Synthesis of Pt NPs:

3.0 nm Pt NPs were synthesized through a facile ultrasound-assisted method. Typically, 0.1 mmol H_2PtCl_6 was mixed with 0.5 mmol PVP in the presence of 15 mL ethylene glycol and 5 mL water, followed by ultrasound treatment for 10 minutes by using an ultrasonic cell crusher. The as-obtained products were purified by acetone, washed with water for three times, and then redissolved in 10 mL water.

In situ growth of the Pt-CeO_2 nanoflowers:

0.4 mmol of $Ce(NO_3)_3$ and 0.4 mmol L-lysine were added into a 10 mL aqueous solution contained 0.1 mmol the as-prepared 3.0 nm Pt NPs, then 50 μL tert-butylamine were added in the solution, followed by heating at 80 ^oC for 3 hours. The final products were purified by centrifugation at 12000 rpm in the presence of acetone.

In situ growth of the Pt-CeO_2 nanonecklaces:

The as-obtained 3.0 nm Pt NPs aqueous solution was mixed with 0.2 mmol $Ce(NO_3)_{3,}$ 0.2 mmol L-lysine, and 10 mL water. Then 50 μL tert-butylamine were added in the solution, followed by heating at 80 ^oC for 3 hours. The products were separated by centrifugation at 12000 rpm for 10 minutes and washed with water for three times. The sample was dried at 60 ^oC over night.

Synthesis of 8.0 nm CeO_2 NPs:

0.5 mmol $Ce(NO_3)_3$ and 0.5 mmol L-lysine were mixed together in 20 mL water to form a transparent solution. Then 50 μL tert-butylamine were dropped in the mixture, followed by ultrasound treatment at 1000 W for 5 minutes by using an ultrasonic cell crusher. The products were purified by centrifugation and washed with water for three times, then redissolved in 10 mL water.

Synthesis of 5.7 nm CeO_2 NPs:

In order to obtain much smaller CeO_2 NPs, we reduced the reaction temperature and decreased the tert-butylamine amount to slow down the growth rate of CeO_2. Experimentally, 0.5 mmol $Ce(NO_3)_3$ and 1 mmol L-lysine were mixed together in 40 mL water to form a transparent solution. Then 30 μL tert-butylamine were dropped in the mixture, followed by heated at 60 ^{o}C. The products were purified by centrifugation with the aid of acetone.

Self-assembly of 3.0 nm Pt with 8.0 or 5.7 nm CeO_2 NPs into the two Pt-CeO_2 nanosatellites respectively:

10 mL water containing 0.1 mmol 3.0 nm Pt NPs were dropped into the 10 mL aqueous solution of 0.1 mmol the as-prepared 5.7 or 8.0 nm CeO_2 NPs. The mixture was stirred for 2 hours, and then centrifugated at 12000 rpm in the presence of acetone for 10 minutes. After being washed with water for three times, the product was sintered at 200 ^{o}C in air to get the final nanosatellites.

Characterization:

The X-ray diffraction patterns of the products were collected on a Rigaku-*D*/max 2500 V X-ray diffractometer with Cu-K_{α} radiation ($\lambda = 1.5418$ Å), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. XPS measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K_{α} X-ray radiation as the X-ray source for excitation. The zeta potential values were tested on a zetasizer, ZEN 3600 of Marvern company.

Catalytic tests:

2 mmol NH_3BH_3 and 20 mL water were mixture together in a three-necked round-bottom flask. The catalysts were dispersed in 5 mL water, and then injected in

the reaction system. The molar ratio of [Pt]/[NH_3BH_3] is kept at a constant of 0.018. The evolution of H_2 was monitored using the gas burette. The reaction was carried out at room temperature under ambient atmosphere. The hydrolysis of NH_3BH_3 can be briefly expressed as follows:

$$NH_3BH_3 + 2H_2O \longrightarrow NH_4^+ + BO_2^- + 3H_2\uparrow$$

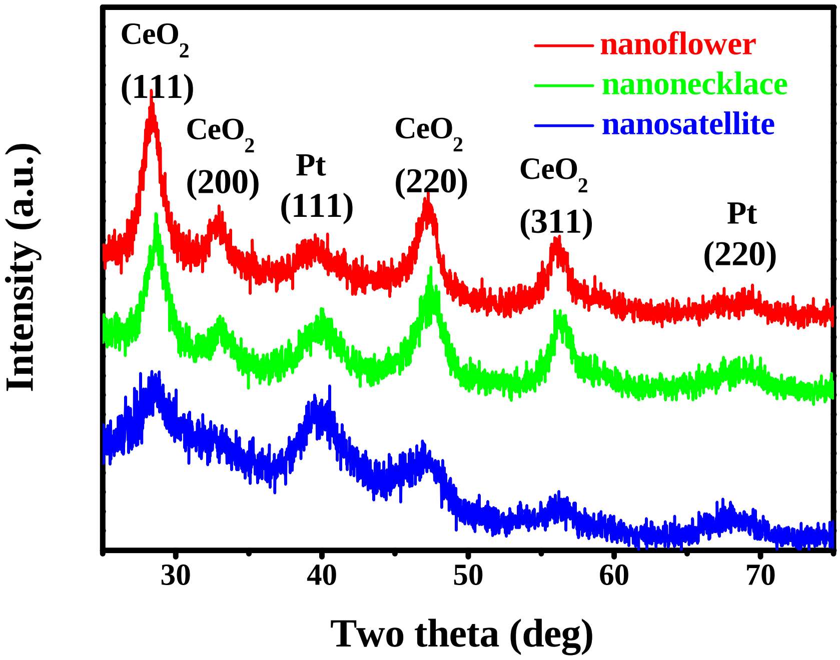

Fig. S1 The X-ray diffraction (XRD) patterns of the three kinds of Pt-CeO_2 hybrids. The two peaks at 2θ = 39.4° and 69.7° can be indexed into the face centered cubic Pt (111) and (220) reflections while the others should be indexed as the pure fluorite structured CeO_2. The molar ratio of [Pt]/[Ce] are determined by EDX analysis (Figure S2) as 1:7.0, 1:1.5, and 1:1.0 for the Pt-CeO_2 nanoflower, nanonecklace, and nanosatellite, respectively.

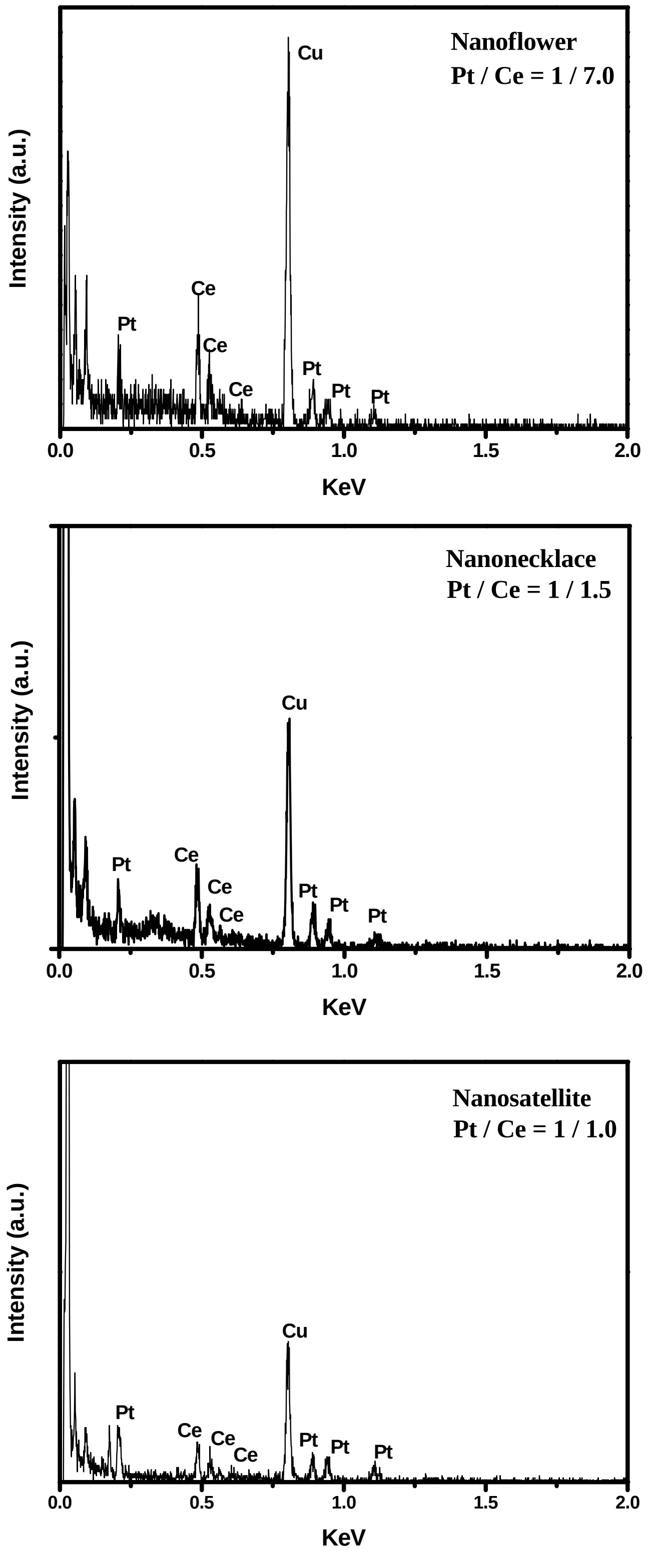

Fig. S2 EDX analysis of the three kinds of Pt-CeO_2 hybrids.

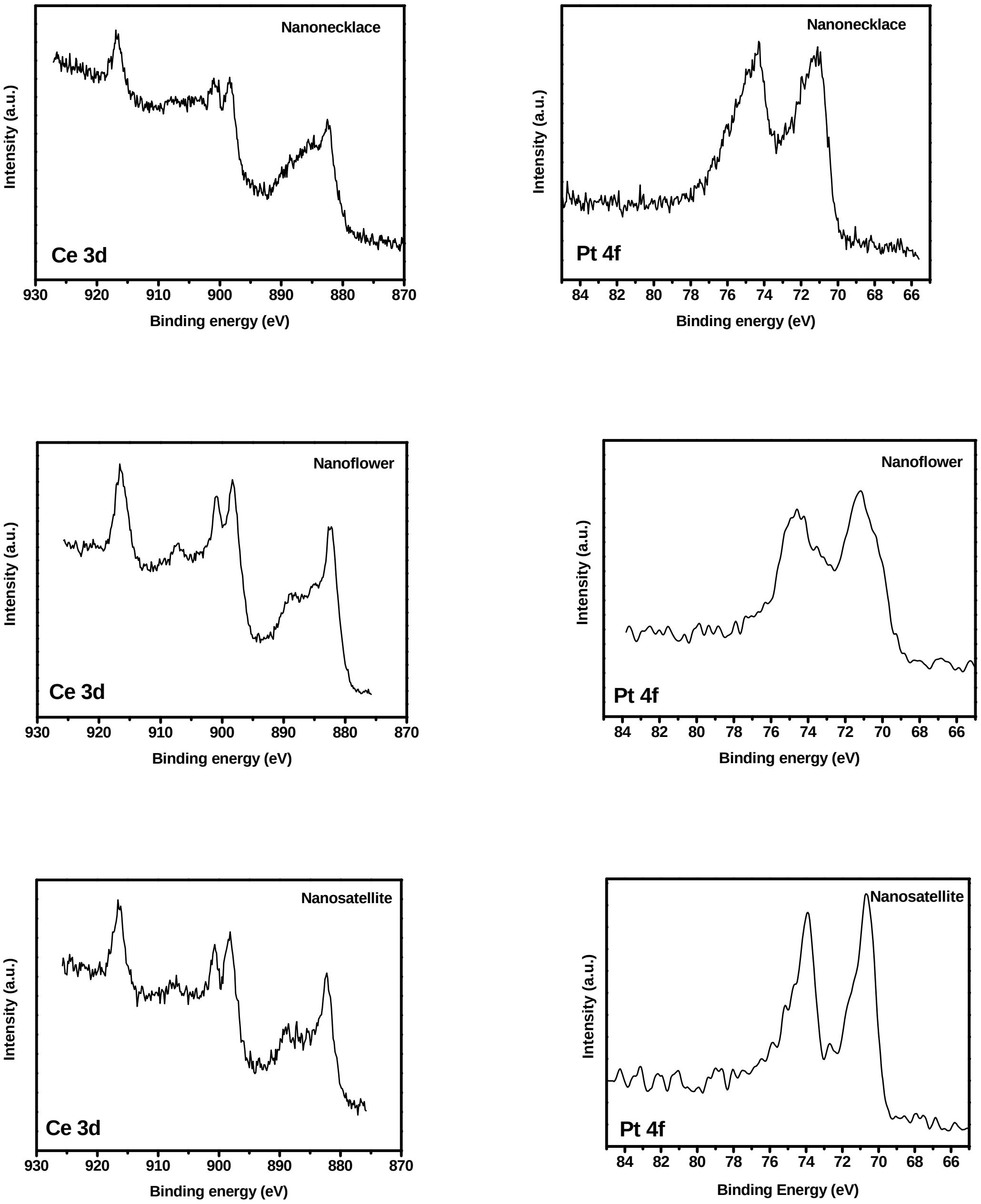

Fig. S3 XPS spectra of the Pt-CeO_2 hybrids.

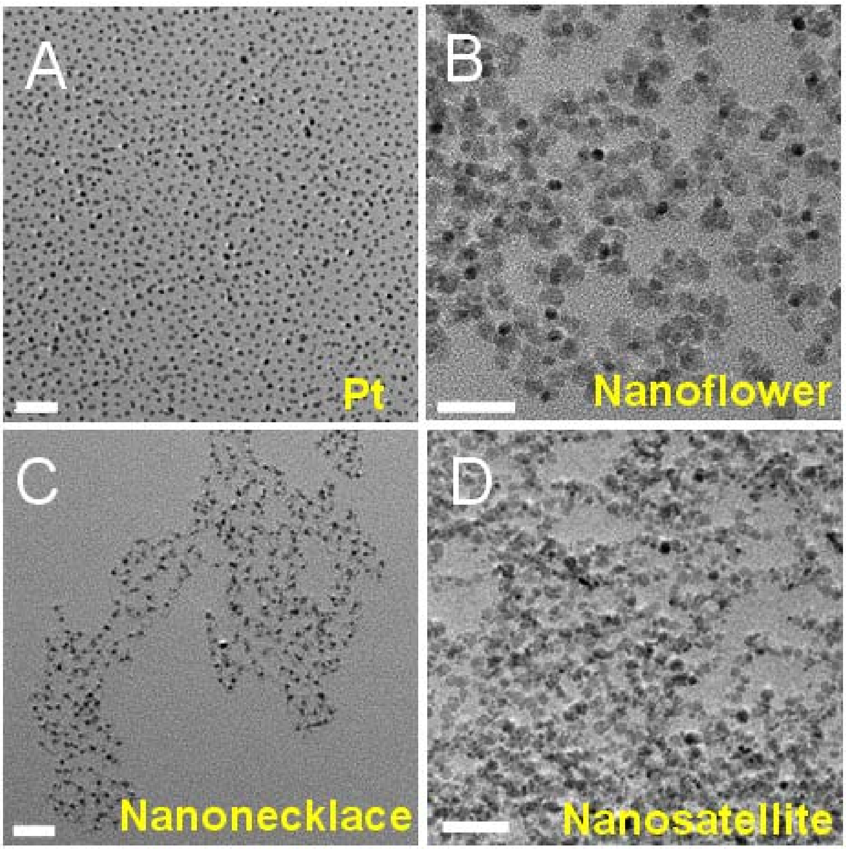

Fig. S4 The large-area TEM images of the Pt (A), the Pt-CeO_2 nanoflower (B), and the Pt-CeO_2 nanonecklace (C) and the Pt-CeO_2 nanosatellite. The scale bar is 20 nm.

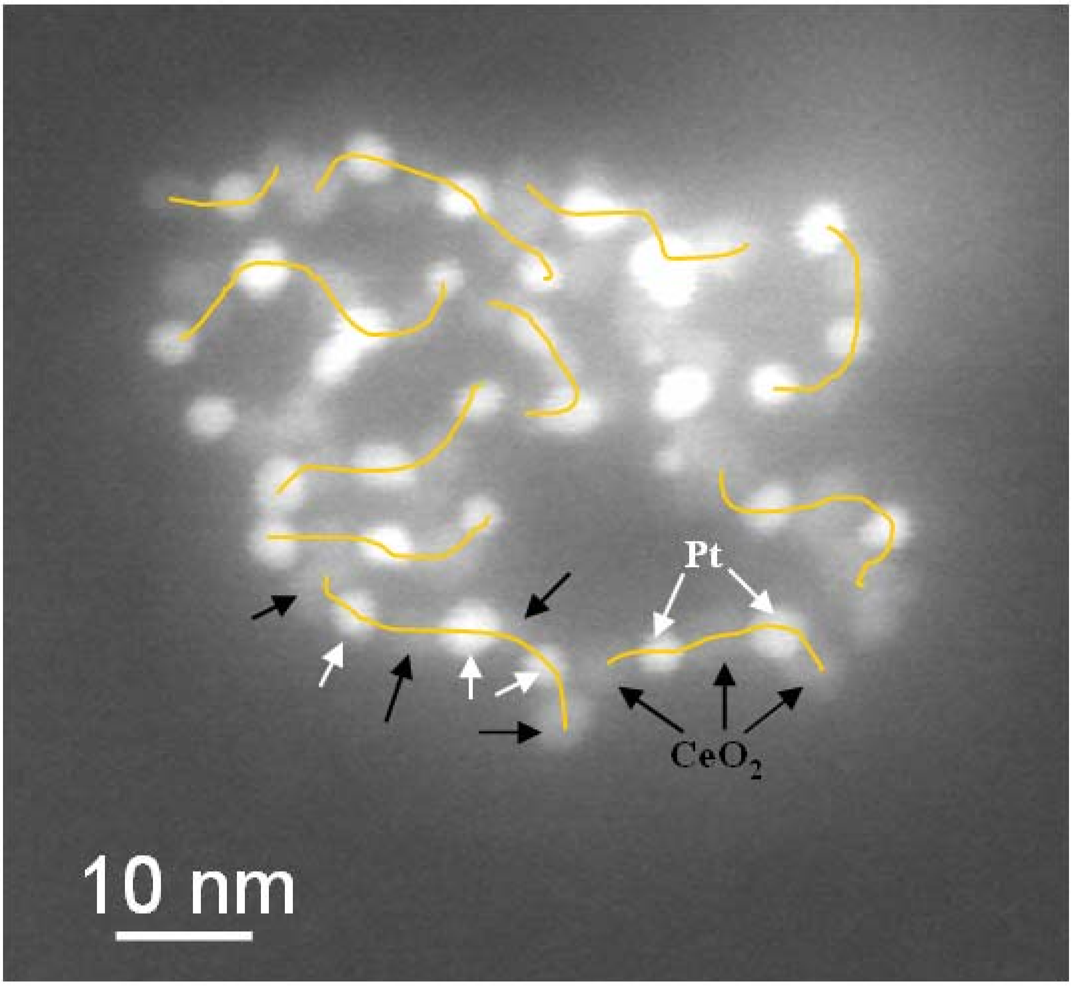

Fig. S5 Scanning TEM image of the Pt-CeO_2 nanonecklace.

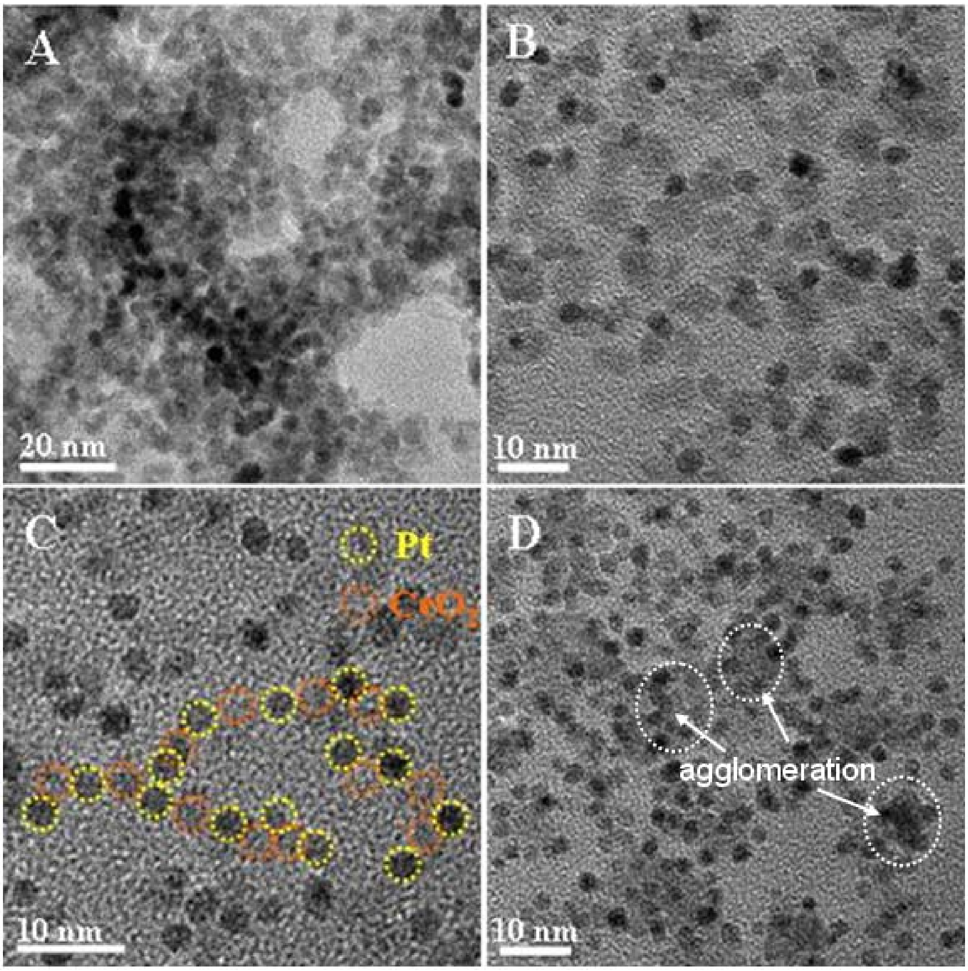

Fig. S6 TEM images of (A) the Pt NPs, (B) the Pt-CeO_2 nanoflower, (C) the Pt-CeO_2 nanonecklace, and (D) the Pt-CeO_2 nanosatellite after 20 catalytic cycles.

Compared with Fig. 1 and Fig. S6, after 20 cycles, the TEM images in Figure S6 indicate that the pure Pt nanoparticles agglomerated as well as the nanosatellite. This should be caused by the lack of surface protection of Pt nanoparticles. However, the structures of the nanonecklace and nanoflower were well maintained, indicating the good protection of CeO_2 components on Pt nanoparticles in the two types of hybrids, and hence they could exhibit rather stable catalytic performance.

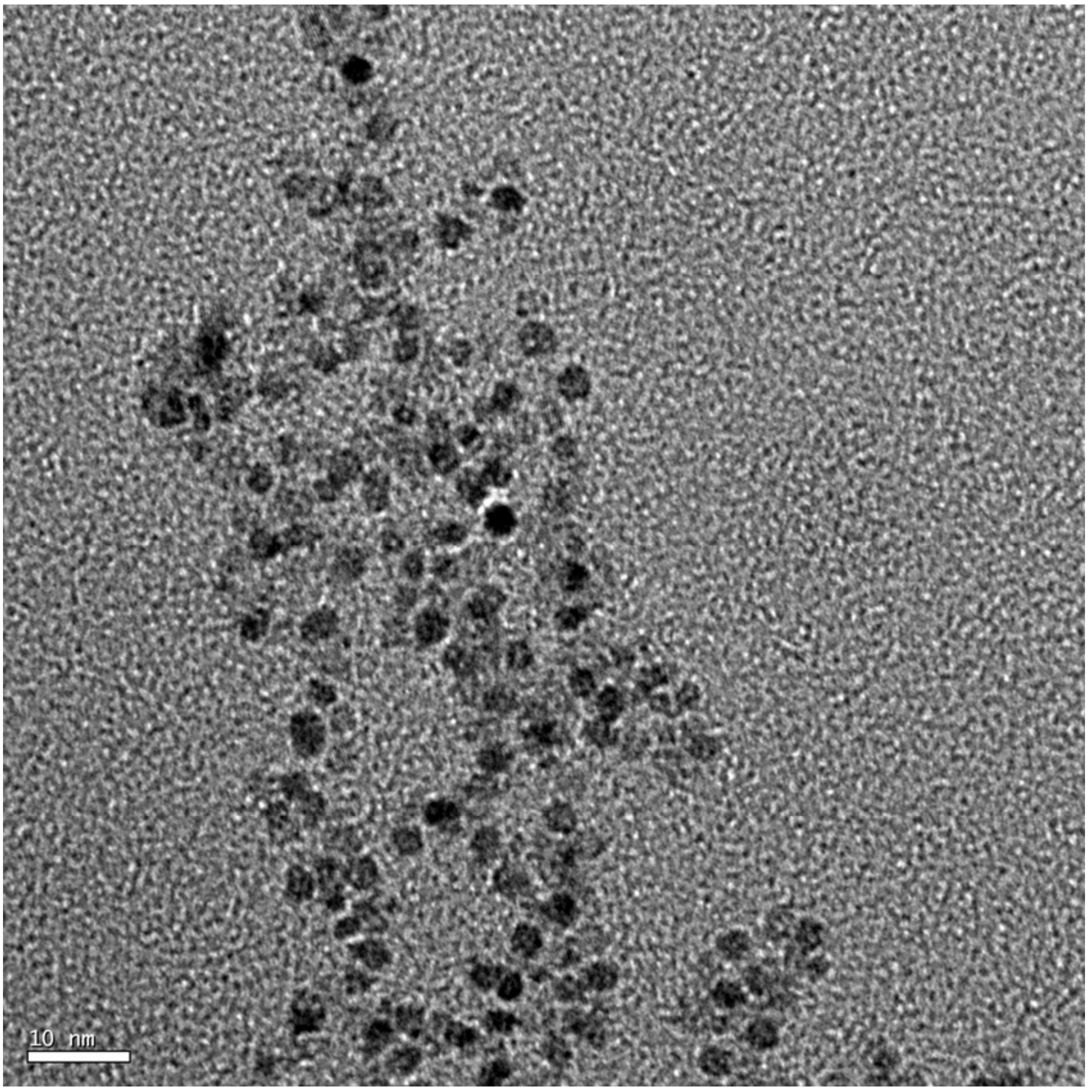

Fig. S7 The products prepared by further decreasing the amount of $Ce(NO_3)_3$ to 0.1 mmol. Obviously, no Pt-CeO_2 nanosatellites but aggregated nanonecklaces were formed.

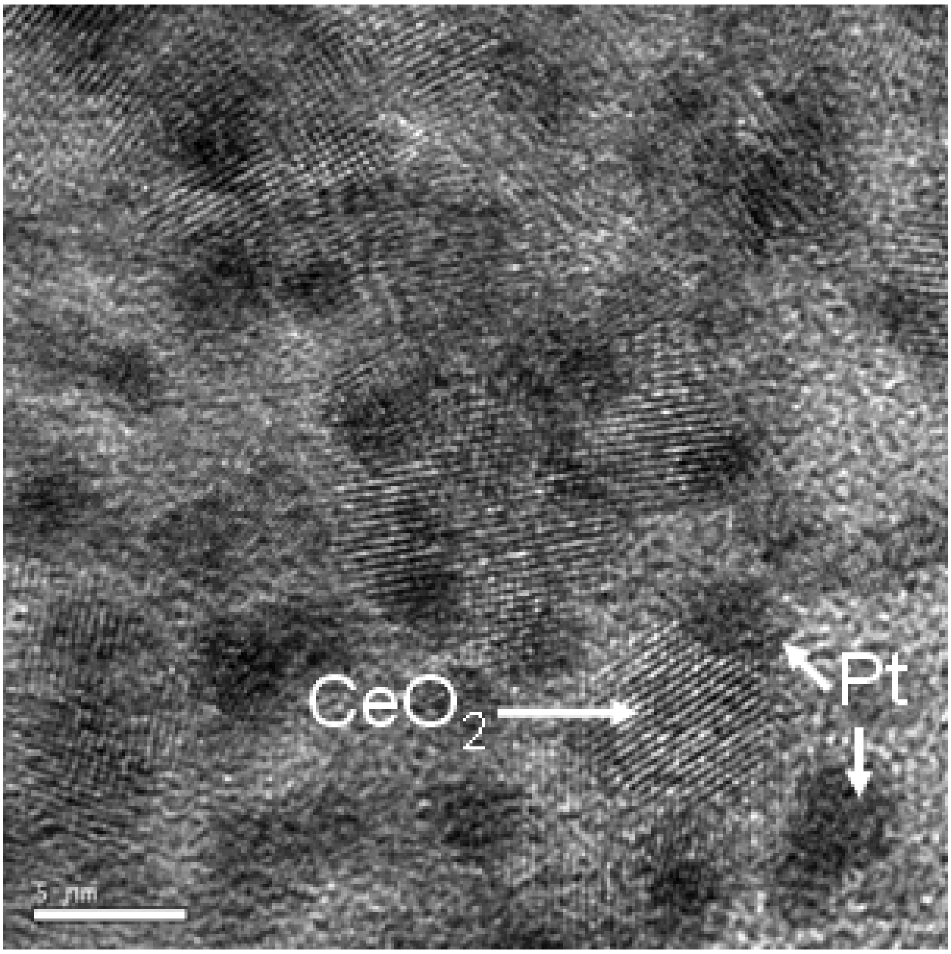

Fig. S8 TEM image of Pt-5.7 nm CeO_2

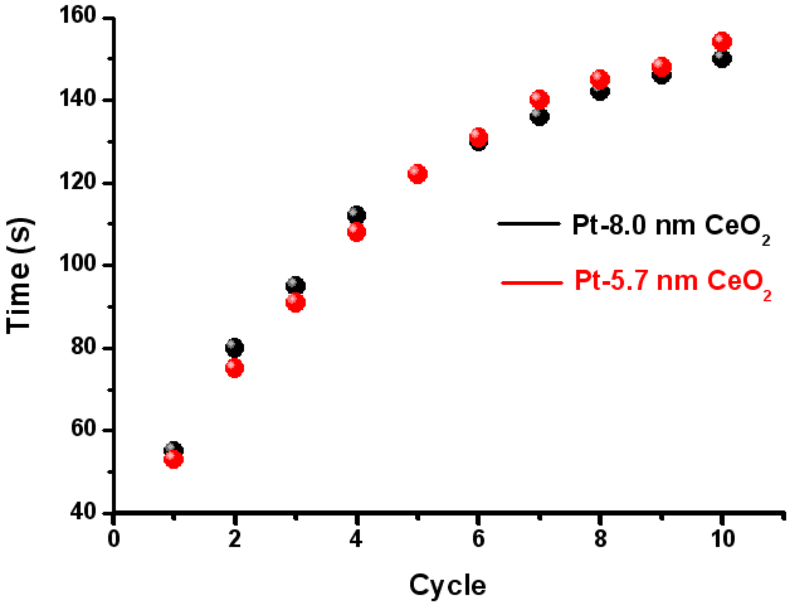

Fig. S9 The reaction time plots of Pt-8.0 nm CeO_2 (black line) and Pt-5.7 nm CeO_2 (red line).

[1] L. Carbone, P. D. Cozzoli, *Nano Today* 2010, **5**, 449.