Supporting information

Experimental Section

Materials.

Zirconium sulfate tetrahydrate, sodium acetate trihydrate, 3-Aminophenol, formaldehyde and styrene were purchased from Alfa Aesar, aceticacid was purchased from Beijing Chemical Works, ammonium tetrachloropalladate(97%) was purchased from Sigma-Aldrich. All materials were of analytical pure, and they were used without further purification.

Preparation of PS@ZrO_2 Core-shell Nanoparticle.

The polystyrene spheres (d=560nm) were synthesized according to the literature[1]. 0.027g $CH_3COONa.3H_2O$, 4ml CH_3COOH were slowly dissolved in 30 mL water to get the buffer solution (pH=2.3), 550 μL (100 mg/mL) the obtained PS spheres solution were added to the 30 mL buffer solution and then 0.02g $Zr(SO_4)_2$ were added. The mixed solution was kept at 50 °C for 5h under vigorously stirring. The obtained product was centrifuged at 10000 rpm for 2 min, the supernatant was removed, and the concentrated particles were washed by water and ethanol 3 times, then were collected at the bottom of the Eppendorf tubes and drying at 80 ℃ for 10h, respectively. The obtained powder was annealed at 500 °C for 2h in air to remove the core and obtain the ZrO_2 hollow spheres. The concentration of $Zr(SO_4)_2$ solution to PS determined the thickness of ZrO_2 coating layer.

Preparation of ZrO_2 Hollow Spheres.

The obtained powder was annealed at 700 °C for 2h in air to remove the core and obtain zirconium oxide hollow spheres.

Preparation of MWCNT@ZrO_2.

0.02g MWCNT, 0.021g $ZrSO_4$ were slowly dissolved in 30mL pH=2.3 buffer solution under mechanical magnetic stirring. Subsequently, the resultant solution was incubated at 50 ℃ for 5h under vigorously stirring. The obtained product was separated from the solution by centrifuging at 8000 rpm for 1min, washing with water and ethanol and drying at 80 ℃ for 10h, respectively.

Preparation of RF@ZrO_2.

0.4g 3-Aminophenol was dissolved in water under mechanical magnetic stirring, 0.4ml formaldehyde was added to the solution. After 5h, the obtained product was centrifuged at 10000 rpm for 2 min, the supernatant was removed, and the concentrated particles were washed by water 3 times to get the RF nanospheres.0.01g RF, 0.021g $Zr(SO_4)_2$ were slowly dissolved in 30 mL pH=2.3 buffer solution under mechanical magnetic stirring. Subsequently, the resultant solution was incubated at 50

℃ for 5h under vigorously stirring. The obtained product was separated from the solution by centrifuging at 8000 rpm for 1min, washing with water and ethanol and drying at 80 ℃ for 10h, respectively.

Preparation of Yolk-shell Structured Pd@ZrO_2 Nanocatalyst.

Pd nanoparticles were loaded on RF spheres according to the literature[2], that is, 0.5ml ammonium tetrachloropalladate, 0.1g 3-Aminophenol, 0.1ml formaldehyde were added to 30ml water. After 5h, the obtained precipitate was centrifuged at 10000 rpm for 2 min, the supernatant was removed, and the concentrated particles were washed by water 3 times, then the products of Pd/RF were collected. 0.1g Pd/RF were dispersed in 30 mL pH=2.3 buffer solutions under ultrasound. 0.06g $Zr(SO_4)_2$ were added. The mixed solution was kept at 50°C for 5h under vigorously stirring. The obtained product was centrifuged at 10000 rpm for 2 min, the supernatant was removed, and the concentrated particles were washed by water 3 times, then were collected at the bottom of the Eppendorf tubes and drying at 80 ℃ for 10h, respectively. The RF cores were removed by calcination at 500 ℃ for 5 h to achieve the target catalyst.

Catalytic tests

We take the samples for CH_4 oxidation in acontinuous–flow microreactor,the internal diameter of which is 6 mm. We mixed the catalyst (~50 mg) and quartz particles (60/80 mesh) to avoid catalytic “hot spots”. The feed gas contains 1 vol% CH_4, 21 vol% O_2 and balance He at a flow rate of 50 cm^3 min-1, corresponding to a space velocity of 60000 $cm^3h^{-1}g_{cat}^{-1}$.

Notes and references

1 Z. Yang, Z. Niu, Y. Lu, Z. Hu and C. C. Han, Angew Chem, 2003, 3.
2 X.-J. Lin, T.-Q. Sun, Y.-G. Sun, C. Zeng, R.-W. Lu and A.-M. Cao, New J. Chem., 2018, 42, 3184–3187.

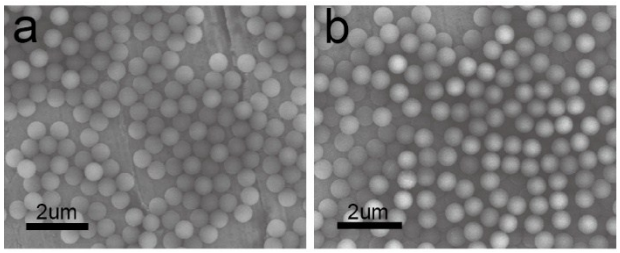

Figure.S1. SEM images of PS before (a) and after (b) zirconium oxide surface coating

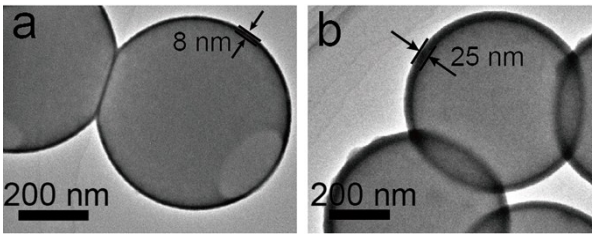

Figure.S2. TEM images of the products (a) 2 h (b) 6 h

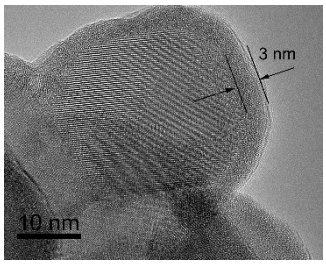

Figure.S3. TEM image of TiO_2@ZrO_2

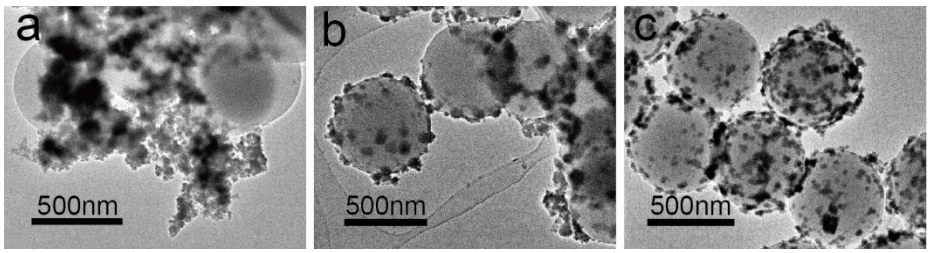

Figure.S4. TEM images of PS@ZrO_2 prepared by using ammonia (a), water (b) and urea (c)

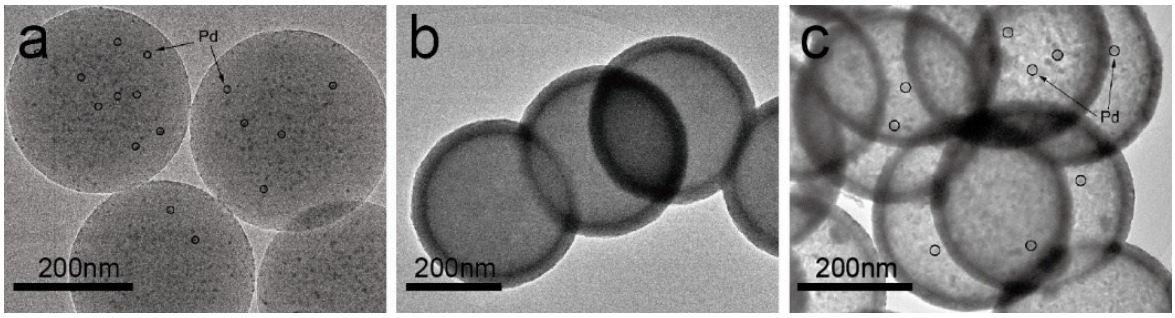

Figure.S5. TEM images of products obtained at each stage during the whole process for preparing yolk-shell structured Pd@ZrO_2 nanocatalyst, (a) RF/Pd after annealing in Ar, (b)RF/Pd@ZrO_2 (c) Pd@ZrO_2

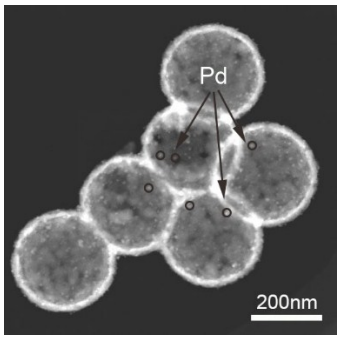

Figure.S6. A DF-STEM image of $Pd@ZrO_2$

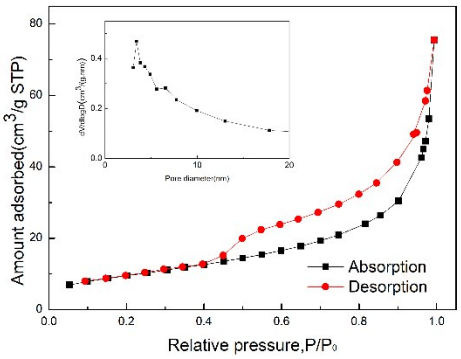

Figure.S7. Nitrogen adsorption-desorption isotherms and pore size distribution of $Pd@ZrO_2$