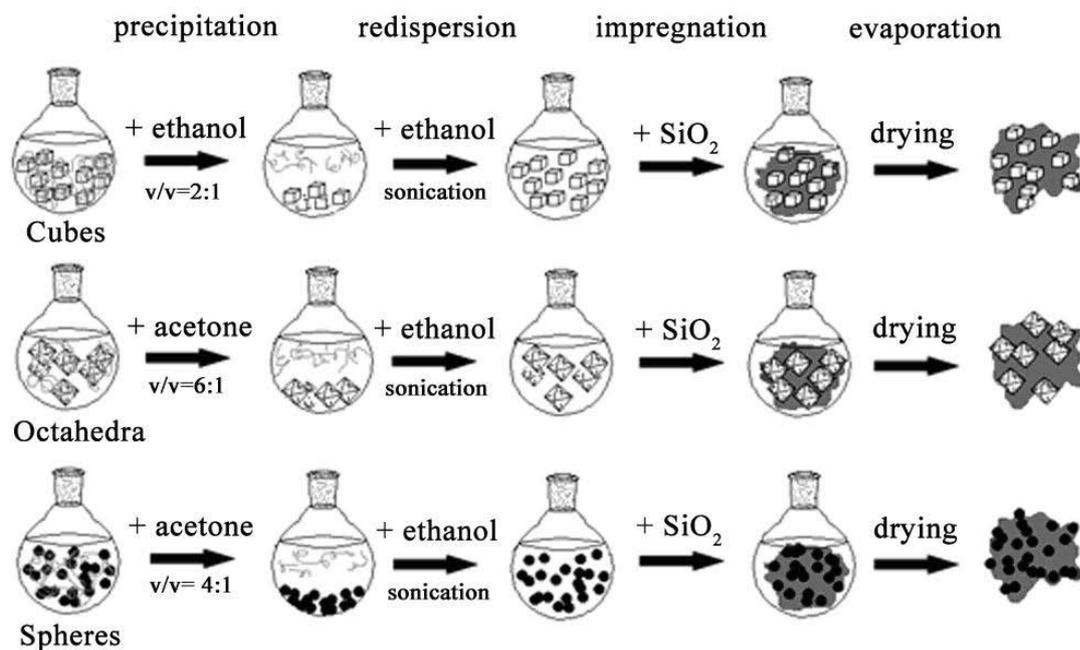


Supplementary Information



Scheme S1 The “deposition-redispersion” strategy used for the preparation of supported Pd/SiO₂ catalysts with clean surface of the metal nanocrystals.

Fig. S1 Size distributions of the cubic (a), octahedral (b) and spherical (c) Pd nanoparticles. Approximately 120 particles were counted for each figure.

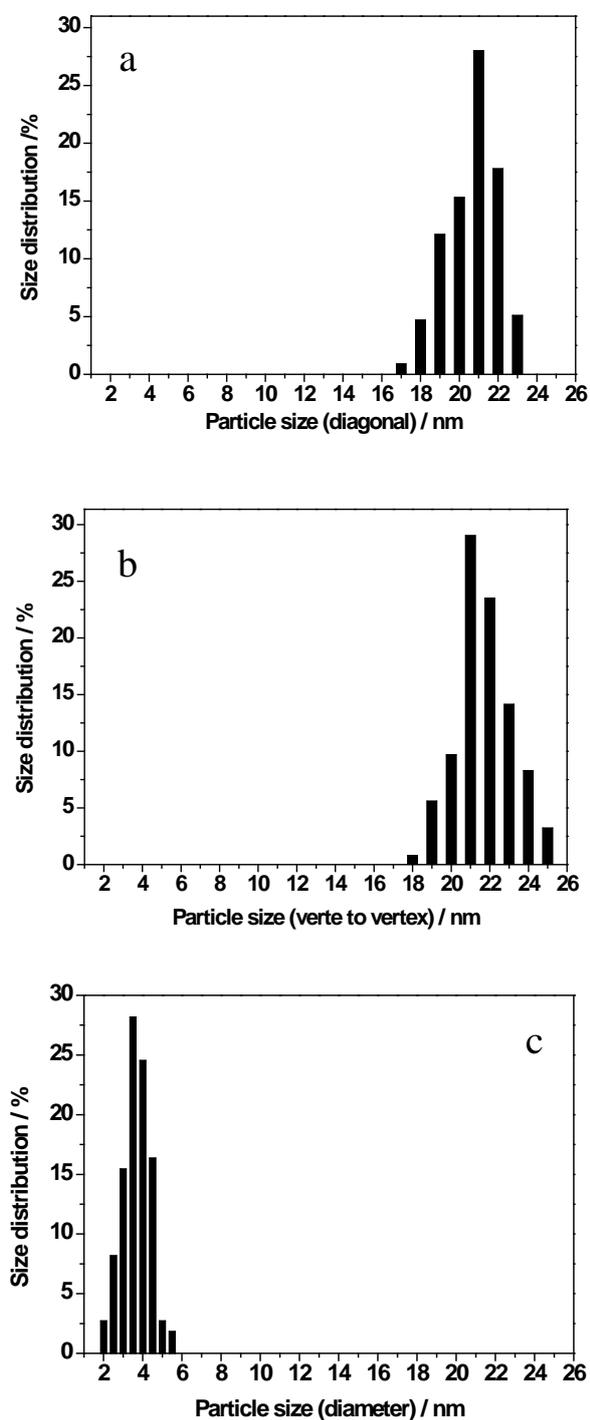


Fig. S2 SAED patterns obtained from a single Pd nanocube (a) and Pd octahedron (b).

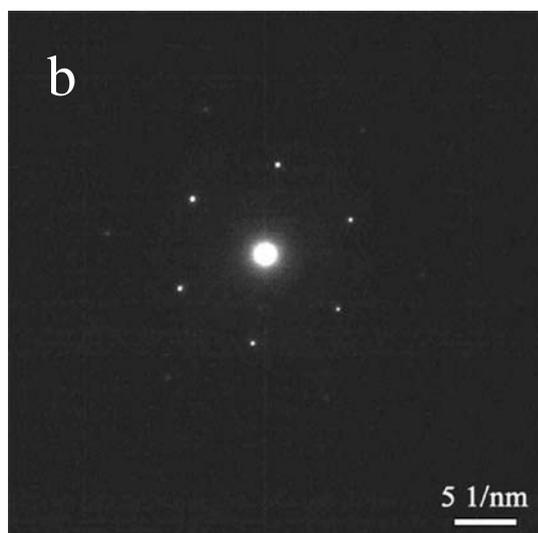
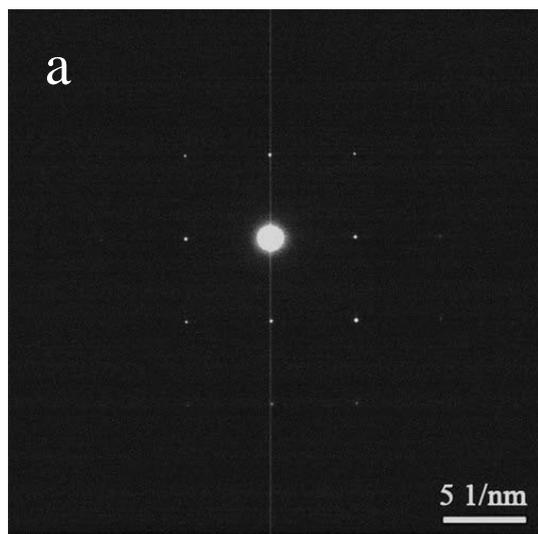


Fig. S3 SEM images of Pd cubes (a, b) and Pd octahedra (c).

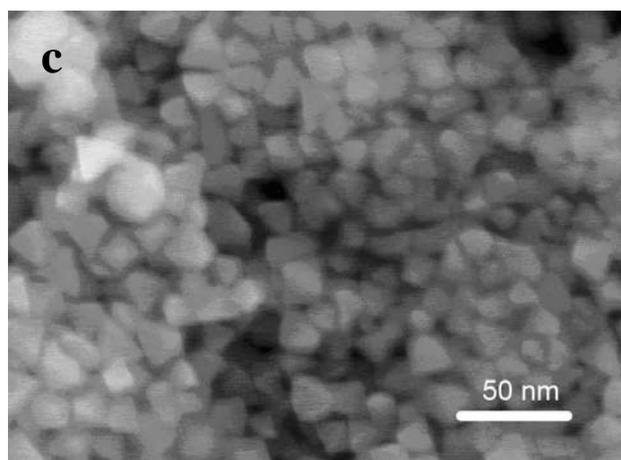
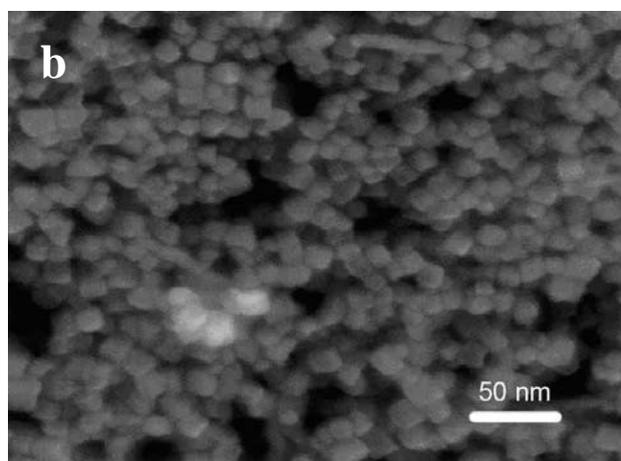
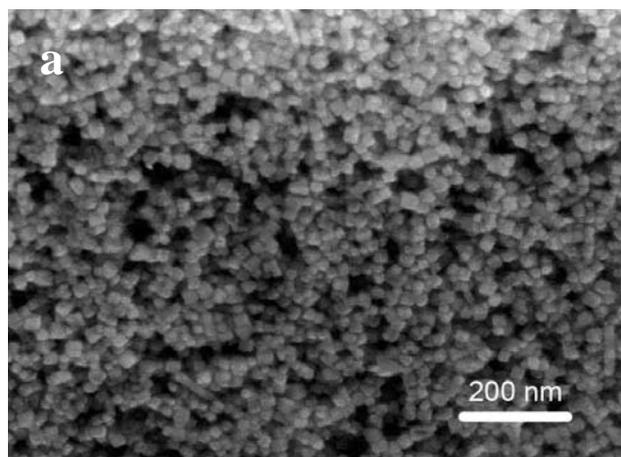


Fig. S4 The Fourier transform infrared spectroscopy (FT-IR) of Pd (octahedron)/SiO₂ at different stages of the supporting procedure. PVP was used as the capping agent here, which should be removed before the catalytic activity evaluation. The three characteristic peaks of PVP at 1436, 1670 and 2930 cm⁻¹ disappeared after the “precipitation-redispersion” method, indicating an effective elimination of PVP.

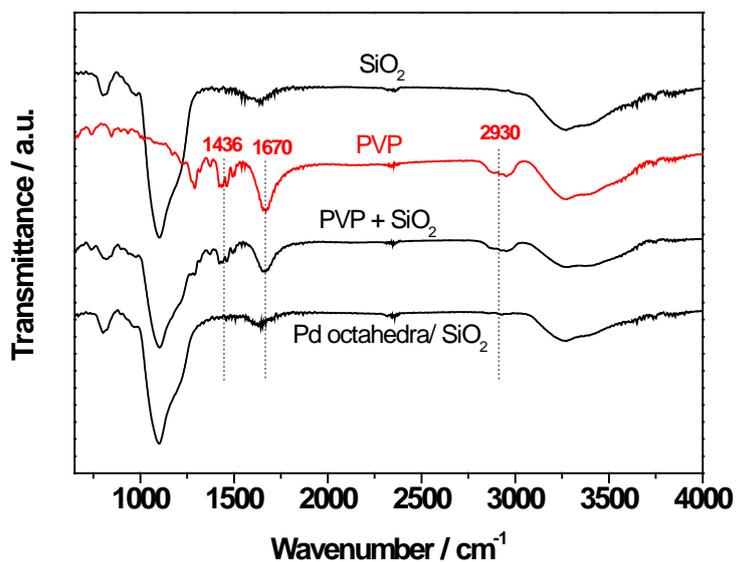


Fig. S5 The corresponding Arrhenius plots for comparison of apparent activation energies for CO oxidation reaction of the different as-synthesized Pd/SiO₂ catalysts.

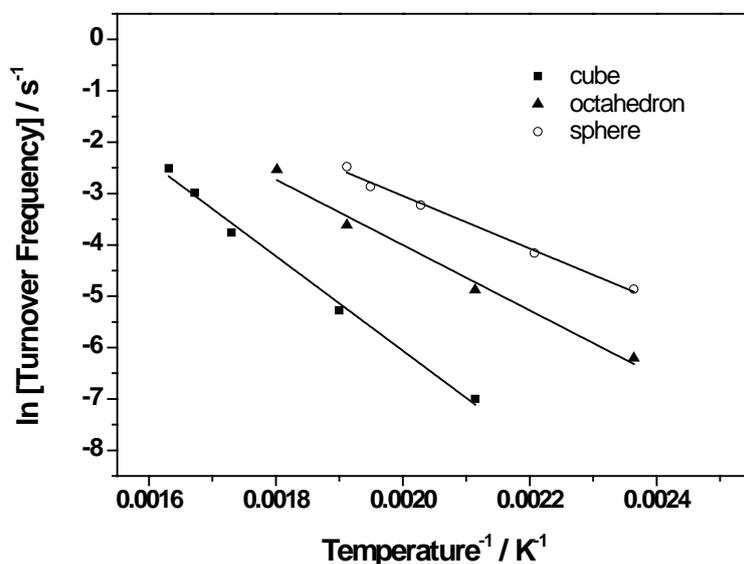


Table S1 Apparent activation energies based on the Arrhenius plots data and related data of supported Pd catalysts.

Pd catalyst ^a	actual loading ^b / wt%	surface atom ratio ^c	dispersion ^d	TOF ^e / s ⁻¹	Ea / kJ mol ⁻¹
cube	2.91	0.15	0.68	0.52	76.5
octahedron	2.94	0.12	0.61	0.69	52.9
sphere	2.89	0.38	0.72	0.19	42.6

^a Loaded on fumed silica. ^b Elemental analyses determined by ICP-AES. ^c The approximate percentage of the surface atoms to the overall bulk atoms. ^d Based on CO chemisorption isotherm. ^e Maximum TOF measured for all the catalysts.

Note: Here the TOF values were calculated as the following equation (actual Pd loading, Pd dispersion and surface atom ratio were all taken into account):

$$\text{TOF} = \frac{F_{\text{gas}} \cdot C_{\text{CO}} \cdot X_{\text{CO}}}{\frac{m_{\text{Pd}}}{M_{\text{Pd}}} \cdot D \cdot S}$$

Where F_{gas} is the total molar flow rate, C_{CO} is the concentration of CO in gas mixture, X_{CO} is the conversion of CO, m_{Pd} is the mass of Pd in the reactor bed, M_{Pd} is the Pd atom weight, D is the Pd dispersion obtained from the CO chemisorption, S is the percentage of surface atoms to the overall bulk atoms (or surface atom ratio), which was calculated based on the shape and size of the Pd nanocrystals in our experiments.

Fig. S6 TEM images of the Pd nanospheres with the average size of 3.9 nm (A, a), 7.5 nm (B, b) and 9.6 nm (C, c).

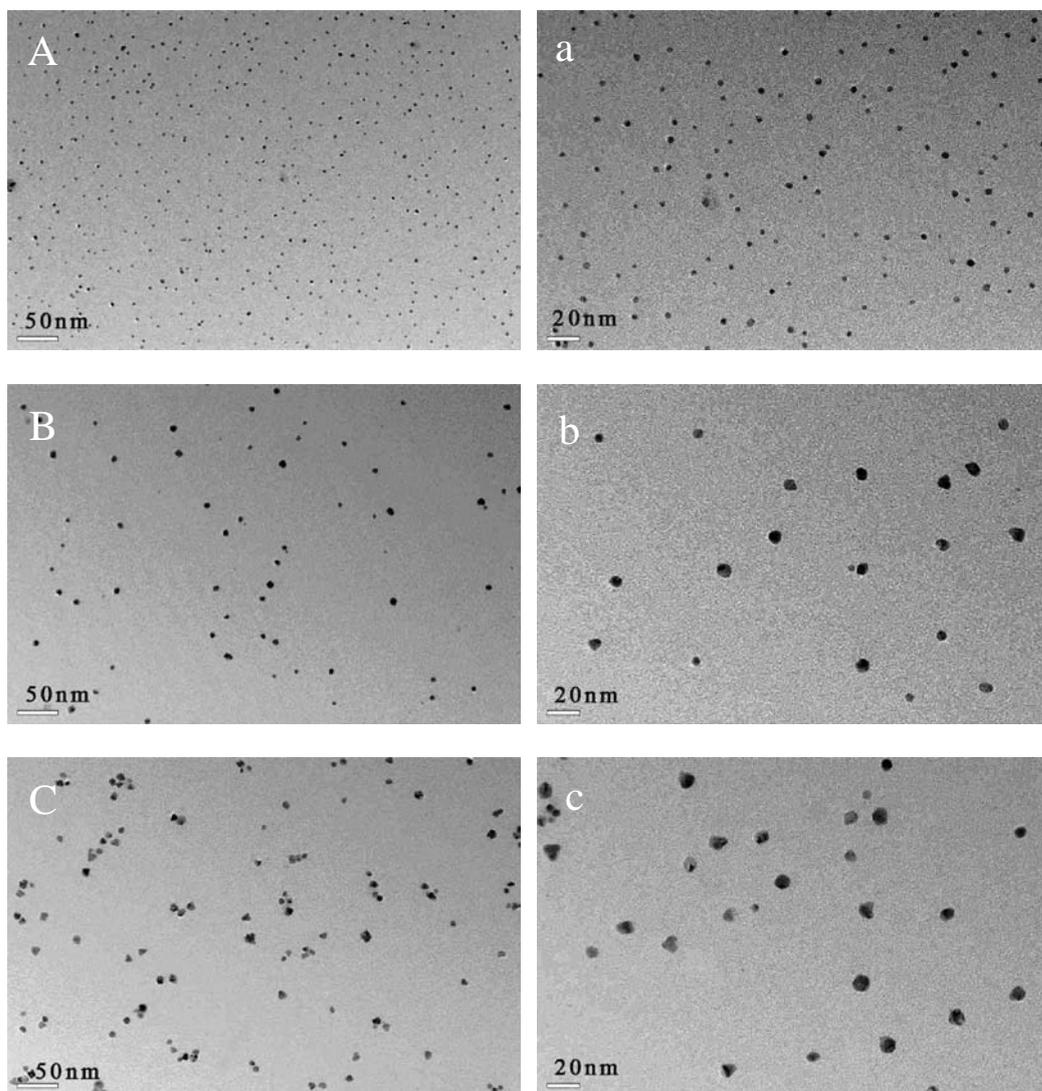


Fig S7 Size distributions of the Pd nanospheres with the size of 3.9 nm (a), 7.5 nm (b), 9.6 (c) nm. Approximately 120 particles were counted for each figure.

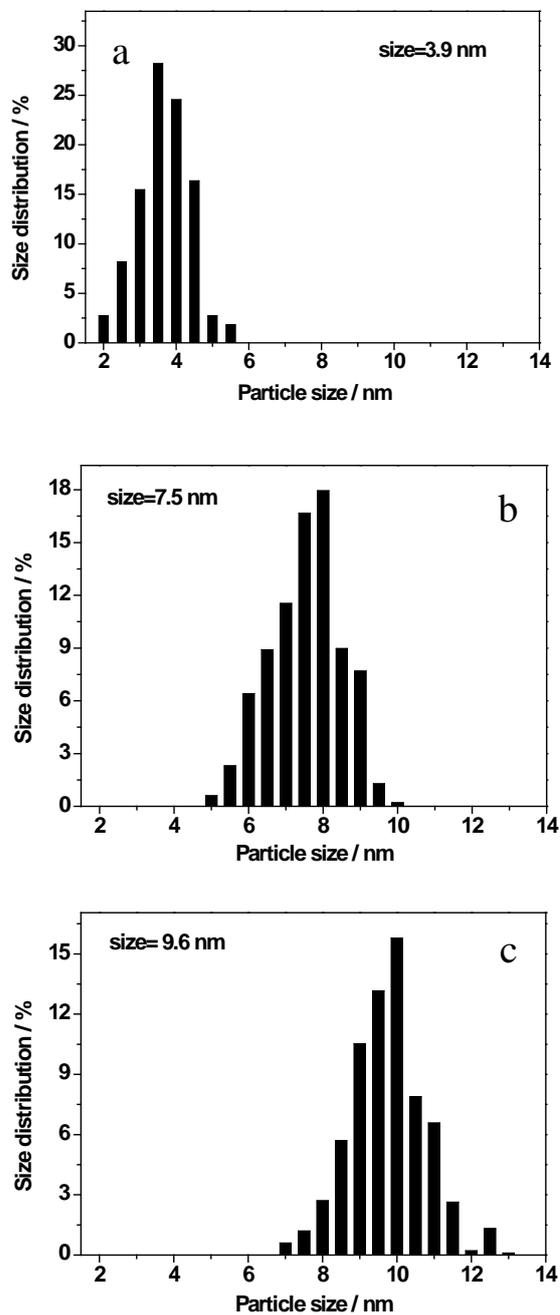


Fig. S8 The CO oxidation activities over the Pd (sphere)/SiO₂ catalysts with the average size of 3.9 nm, 7.5 nm and 9.6 nm. The CO oxidation activity were evaluated in a packed-bed flow reactor using 50 mg of catalyst (40–60 mesh size) in a gas mixture of 1.0 % CO, 1.0 % O₂ in 98 % N₂ at a flow rate of 97.2 mL min⁻¹ and a space velocity of 32.4 mL s⁻¹ g⁻¹.

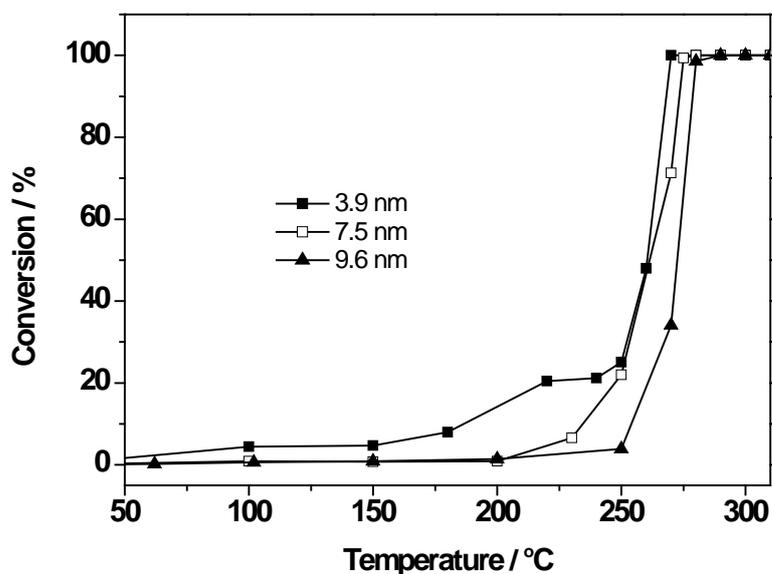


Fig. S9 The DRIFT spectra of CO adsorption on Pd (cube)/SiO₂ under different temperatures.

