

Electronic Supplementary Information

Highly efficient hydrogen peroxide direct synthesis over hierarchical TS-1 encapsulated subnano Pd/PdO hybrid

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Materials and Method

Catalyst preparation

Synthesis of TS-1 zeolite

TS-1 was synthesized via a solvent evaporation-assisted dry gel conversion (DGC) route.^{1, 2} In a typical procedure of TS-1, TEOS (tetraethylorthosilicate), TEOT (tetraethyl titanate), TPAOH (tetrapropylammonium hydroxide solution) and ethanol were first mixed to form a homogeneous solution with a molar ratio of $\text{SiO}_2 : 0.04\text{TiO}_2 : 0.2\text{TPAOH} : 15\text{EtOH}$. The mixture was aged at room temperature for 24 h and then sealed in an autoclave reactor with a little water at the bottom of the autoclave to create steam for hydrothermal synthesis. After crystallization, the solid was collected by centrifugation, washed with water and dried overnight at 110 °C. Finally, the products were calcined at 500 °C for 7 h in air to obtain zeolites with $\text{SiO}_2/\text{TiO}_2$ of 25, denoted as TS-1.

Synthesis of Pd@TS-1 zeolite

The synthesis route for encapsulation of Pd within TS-1 channels was carried out using an in situ hydrothermal crystallization method by adding 3-mercaptopropyl-trimethoxysilane (KH590) to the mixture.¹⁻³ Typically, TPAOH and KH590 were mixed and stirred in an open polypropylene container. After stirring at room temperature for 8 h, a palladium solution ($\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$) was added dropwise into the mixture over 0.5 h with stirring. TEOS, TEOT and ethanol were then added to form a gel with the composition of $\text{SiO}_2 : 0.04\text{TiO}_2 : 0.2\text{TPAOH} : 15\text{EtOH} : x\text{Pd} : 6x\text{KH590}$ (where x indicated the molar amount of Pd metal in the synthesis gel composition). The resultant gel was then aged and crystallized. Finally, the product was collected by centrifugation, washed with deionized water several times, dried overnight at 110 °C and calcined at 500 °C for 7 h; the obtained zeolite with $\text{SiO}_2/\text{TiO}_2$ of 25 was denoted as Pd@TS-1.

Synthesis of Pd@HTS-1 zeolite

The hierarchical Pd@HTS-1 catalyst was also prepared through a dry gel conversion (DGC) route. Compared to Pd@TS-1, HTS (Hexadecyltrimethoxysilane) as template agent was employed to create mesoporous structure from the composition of $\text{SiO}_2 : 0.04\text{TiO}_2 : 0.2\text{TPAOH} : 0.05\text{HTS} : 15\text{EtOH} : x\text{Pd} : 6x\text{KH590}$. Besides, the age, crystallization and calcination process were similar. The final obtained hierarchical zeolite with $\text{SiO}_2/\text{TiO}_2$ of 25 was denoted as Pd@HTS-1.

Catalyst characterization

The total Pd contents of the catalysts was determined by ICP-OES (Optima 8300DV). X-ray diffraction

(XRD) was performed using an X-ray diffractometer (X'Pert Pro) with Cu K α radiation at 30 mA and 40 kV. Fourier transform infrared (FT-IR) spectra were measured on a Nexus FT-IR spectrometer. Ultraviolet-visible diffuse reflectance (UV-vis) spectra from 200 to 600 nm was obtained by a Cary Series UV-Vis-NIR spectrometer. For pyridine adsorption (Py-IR), pyridine vapour was introduced into the cell at room temperature for 1 h; the spectra were then recorded after evacuation at 200°C for 1 h. The specific surface area of the samples was measured using N₂ adsorption-desorption (BET) with a Belsorp Max II instrument and was calculated employing the BET method. NH₃ temperature-programmed desorption (NH₃-TPD) and O₂ temperature-programmed desorption (O₂-TPD) of the catalysts was performed using a Tianjin XQ TP-5076 chemisorption instrument equipped with a thermal conductivity detector (TCD). SEM images were obtained with a Utral55 scanning electron microscope (FE-SEM, 15 kV). The morphology of Pd nanoparticles-encapsulated TS-1 zeolites was studied by transmission electron microscopy (TEM) using a Tecnai G2 F30. The dispersion measurements were performed with Micromeritics Autochem 2910 gas-adsorption equipment using a CO pulse method.

Size-selective hydrogenation test

Currently, the size-selective hydrogenation test was employed by Tuel et al.⁴⁻⁷ for investigating the performance of the encapsulated metals in zeolites. Catalytic activities of the as-calcined Pd@TS-1 and Pd@HTS-1 were evaluated in hydrogenation of a solution of aromatic nitro-compounds such as nitrobenzene and 1-nitronaphthalene. In a typical run, nitrobenzene (0.1 mmol) or 1-nitronaphthalene (0.1 mmol), 0.01 g catalyst, and 10 ml methanol were added to a 75 ml stainless-steel autoclave equipped with a magnetic stirrer. After air in the reactor was purged with nitrogen and then pressurized three times with 0.7 MPa hydrogen, the catalytic hydrogenation of nitrobenzene and 1-nitronaphthalene was performed at 2.0 MPa H₂ and 60 °C for 2 hours under the stirring of 1000 r/min. At the end of the reaction, the solution was filtered and analyzed using a Fuli GC9590 gas chromatography equipped with a flame ionization detector (FID) and a DB-1 capillary column (30 m×0.25 mm×1.0 μ m).

Hydrogen peroxide synthesis and hydrogenation

The catalysts were evaluated for the direct synthesis of hydrogen peroxide in a stainless steel autoclave with a nominal volume of 100 ml and a maximum working pressure of 20 MPa. The autoclave was equipped with a magnetic stirrer (0–2000 rpm) and provision for measurement of temperature and

pressure. For the standard reaction conditions we have employed as J. Hutchings's method⁸, the autoclave was charged with the catalyst (0.02 g), solvent (5.6 g CH₃OH and 2.9 g H₂O), purged three times with 5% H₂/ Air (0.7 MPa) and then filled with 5% H₂/Air and air to give a hydrogen to oxygen ratio of 1:2 at a total pressure of 4.25 MPa. Stirring (1200 rpm) was commenced at ambient temperature (25±2°C), and experiments were carried out for 5, 15, 30, 45 and 60 min, respectively. The H₂O₂ yield was determined by titration of aliquots of the final filtered solution with acidified Ce(SO₄)₂ (ca 0.1 mol·L⁻¹; aladin). The Ce(SO₄)₂ solutions were standardised against FeSO₄·7H₂O using ferroin as an indicator.

H₂O₂ Hydrogenation experiments were carried out as outlined above, but in the absence of O₂ in the gas stream and in the presence of 4 wt% H₂O₂ in the solvent (solution composition: 5.6 g CH₃OH, 1.77 g H₂O, 1.13 g 30 wt% H₂O₂). The decrease in H₂O₂ concentration (determined from measurements taken before and after reaction) is attributed to a combination of H₂O₂ hydrogenation and decomposition.

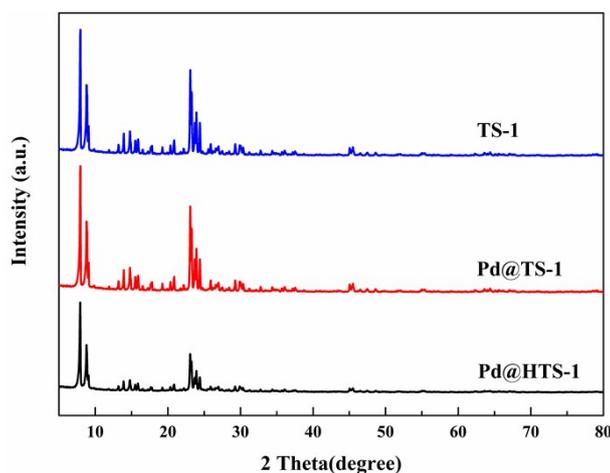


Fig. S1 X-ray diffraction patterns of the synthesized TS-1 and Pd-modified TS-1 catalysts

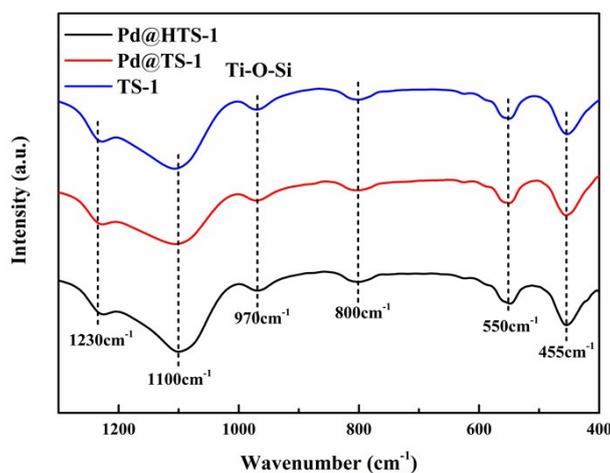


Fig. S2 FT-IR spectra of the synthesized TS-1 and Pd-modified TS-1 catalysts

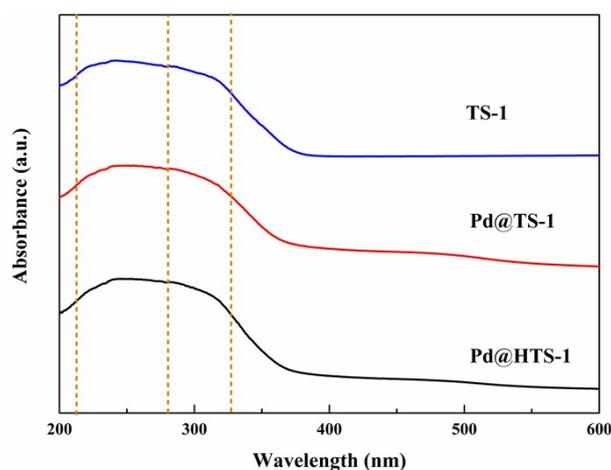


Fig. S3 Diffuse reflectance UV-vis spectra of the synthesized TS-1 and Pd-modified TS-1 catalysts

Table S1 The textural properties of Pd-modified TS-1 catalysts

Samples	Surface area (m ² g ⁻¹)			Pore volume (cm ³ g ⁻¹)	
	BET	Micropore	External	Micropore ^a	Meso+macro
Pd@TS-1	392.3	307.1	85.4	0.15	0.07
Pd@HTS-1	533.1	325.9	207.2	0.14	0.35 ^b

^a Micropore volume was estimated using the t-plot method. ^b The mesopore+macropore volume was calculated from the amount of N₂ adsorbed at P/P₀ = 0.99.

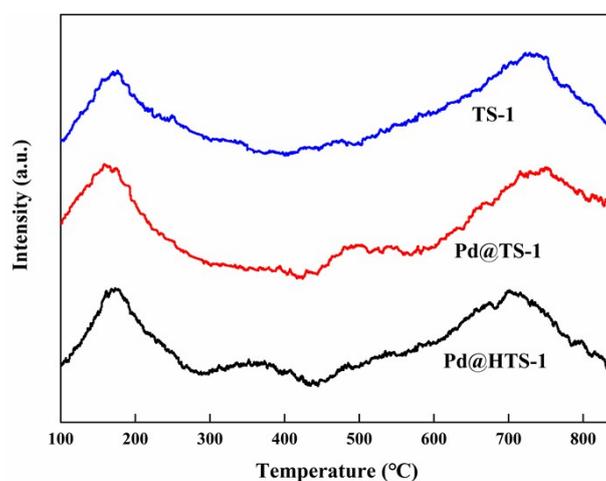


Fig. S4 NH₃-TPD profiles of the synthesized TS-1 and Pd-modified TS-1 catalysts

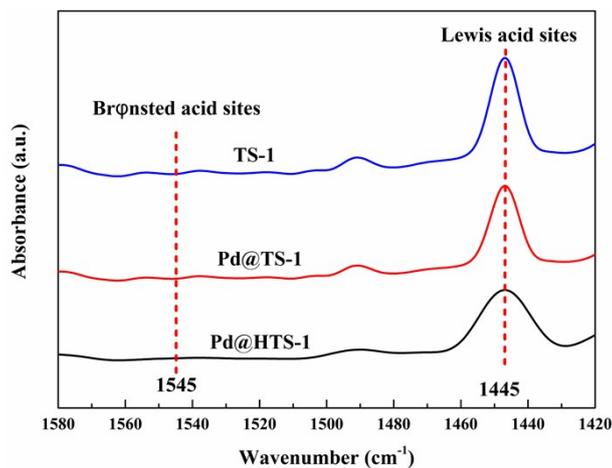


Fig. S5 FT-IR spectra of pyridine adsorption on the synthesized TS-1 and Pd-modified TS-1 catalysts

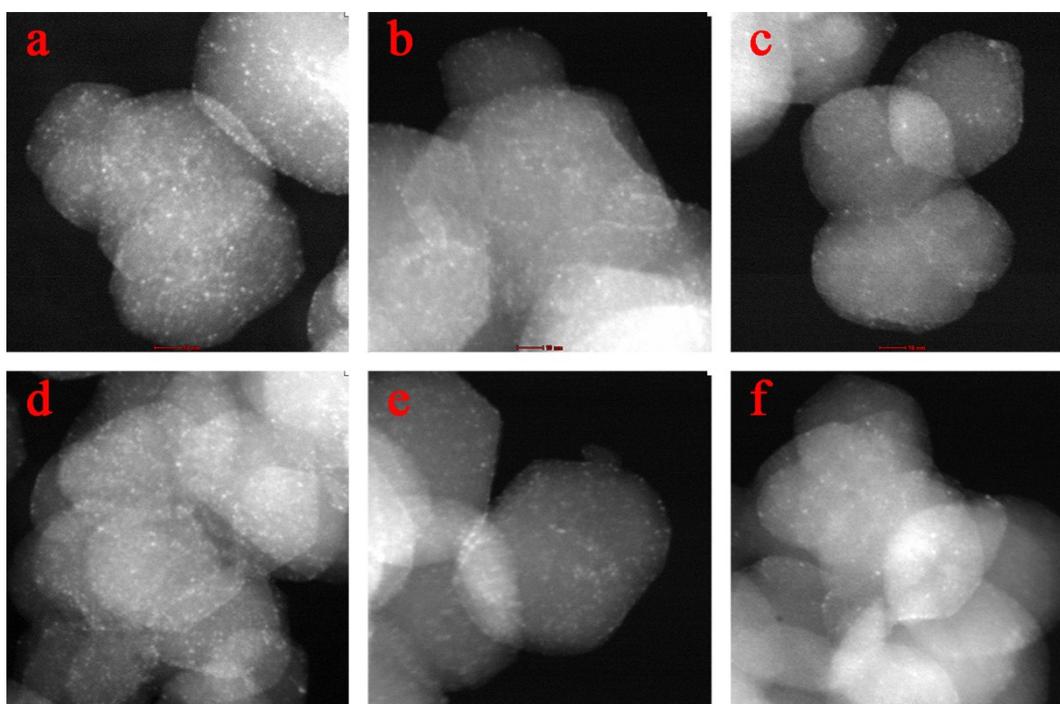


Fig. S6 HRTEM images and metal particle size distributions of the Pd@TS-1 and Pd@HTS-1 before and after high-temperature oxidation-reduction-oxidation treatments. (a Pd@TS-1-O. b Pd@TS-1-OR. c Pd@TS-1-ORO. d Pd@HTS-1-O. e Pd@HTS-1-OR. f Pd@HTS-1-ORO.)

Table S2 Pd dispersion and average Pd nanoparticle size measured by CO-TPD for Pd-modified TS-1 catalysts after reduction in H₂ at 400°C

Sample	Pd loading(wt%)	Pd dispersion(%) ^a	d _{chem} (nm) ^b	d _{TEM} (nm) ^c
Pd@TS-1	0.1	85	1.06	1.62
Pd@HTS-1	0.1	81	1.17	1.69

^a Palladium dispersion estimated from CO chemisorption. ^b Pd nanoparticle diameter estimated from the metal dispersion obtained from CO chemisorption. ^c Surface-area-weighted mean cluster

diameter (d_{TEM}) estimated from TEM analysis, $d_{TEM} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$.

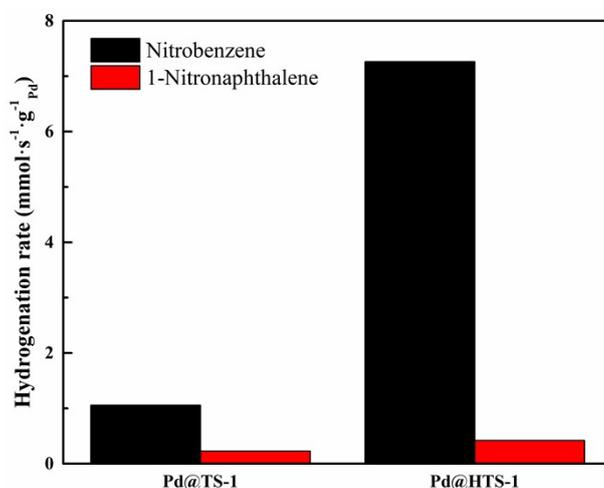


Fig. S7 Hydrogenation rate of a nitrobenzene and 1-nitronaphthalene using two different Pd-modified TS-1 catalysts^a

^a Nitrobenzene (0.1 mmol) or 1-nitronaphthalene (0.1 mmol), 0.01 g catalyst, and 10 ml methanol were added to a 75 ml stainless-steel autoclave equipped with a magnetic stirrer, then 1-nitronaphthalene was performed at 2.0 MPa H₂ and 60 °C for 2 hours under the stirring of 1000 r/min.

Encapsulation selectivities were measured from turnover rates for reactions of small and large reactants, which reflected the restricted access to encapsulated particles by the zeolite aperture size. Therefore, in order to verify the successful encapsulation of Pd particles in TS-1 zeolites, hydrogenation rates of a mixture of nitrobenzene and 1-nitronaphthalene (0.596 and 0.755 nm kinetic minimal cross-sectional diameters^{7, 9}) were used to confirm the predominant presence of Pd particles within TS-1. Nitrobenzene, but not 1-nitronaphthalene, can access active metal sites encapsulated within MFI zeolite voids via diffusion through their interconnected voids and apertures. Then, the TS-1 as a typical microporous catalyst was strongly affected by diffusion property, such as pore volume and diameter. Hydrogenation nitrobenzene and 1-nitronaphthalene was evaluated over Pd@TS-1-OR and Pd@HTS-1-OR (Fig. S6). Compared to the Pd@TS-1-OR, the catalyst with hierarchical structure, the increasing tendency of reaction rate of nitrobenzene and 1-nitronaphthalene were much higher than the Pd@TS-1-OR. For comparison, nitrobenzene can enter into 10-MR windows of TS-1 with a MFI structure (5.1 × 5.5 Å and 5.6 × 5.3 Å)¹⁰ and contact with intracrystalline active sites on encapsulated particles, while 1-nitronaphthalene is bigger leading the diffusion become very difficult and cannot enter the zeolite interior. The minor amounts of 1-nitronaphthalene may be hydrogenated via hydrogen spillover which activated H atoms migrate from hydrogen-rich metal particles to the surface of support.¹¹ This result indicated the successful encapsulation of Pd into the interior of MFI zeolite, which was in accord with its thermal stability. Besides, it was also proved that the introduction of mesopore decreased the diffusion limitation and enhanced the catalytic performance.

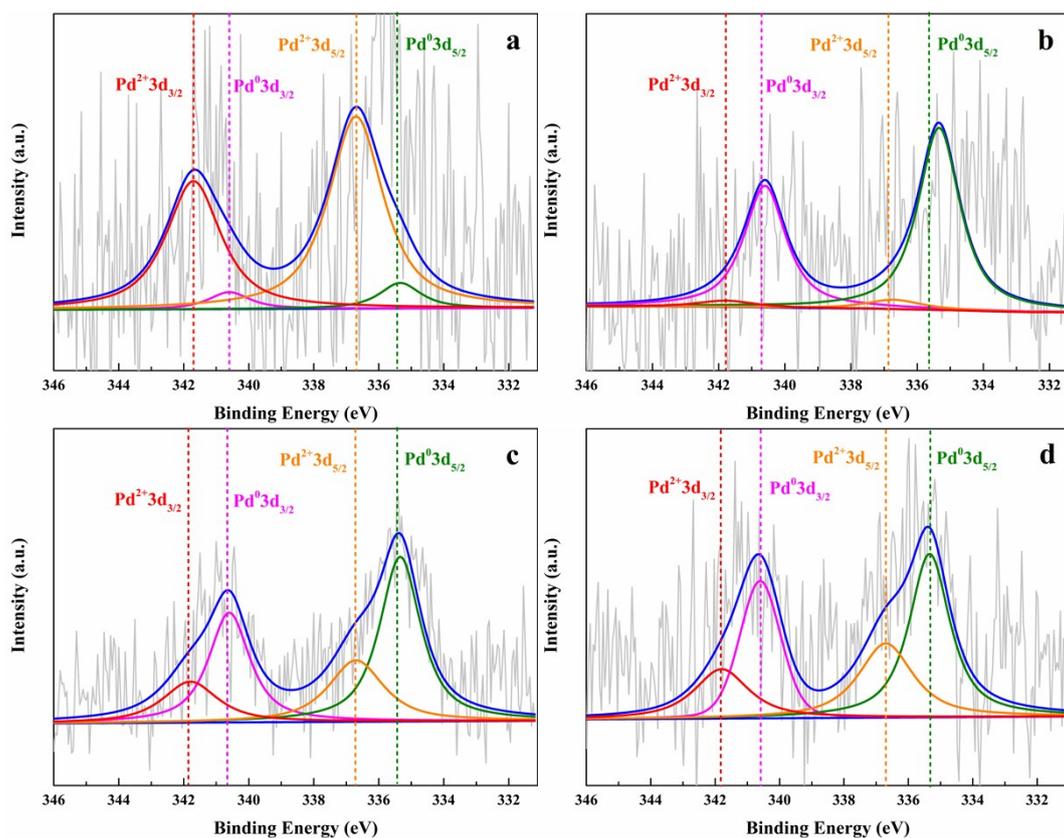


Fig.S8 Pd3d XPS spectra of the Pd-modified TS-1 catalysts after oxidation-reduction-oxidation heat treatment: (a) Pd@TS-1 and (b) Pd@HTS-1 catalysts. (a Pd@TS-1-O. b Pd@TS-1-OR. c Pd@TS-1-ORO. d Pd@HTS-1-ORO.)

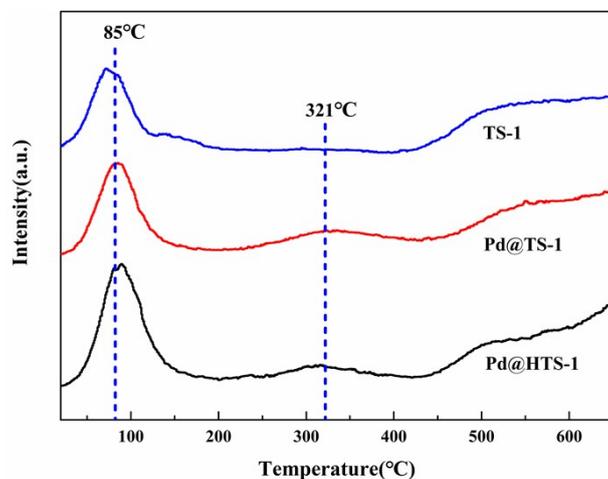


Fig. S9 O₂-TPD profiles of synthesized TS-1 and Pd-modified TS-1 catalysts

Table S3 Direct H₂O₂ synthesis and degradation testing^a

Entry	Catalyst	H ₂ O ₂ production (mmol g _{Pd} ⁻¹ hour ⁻¹)	H ₂ O ₂ degradation (mmol kg _{cat} ⁻¹ hour ⁻¹)	H ₂ O ₂ selectivity (%)
0.1%Pd@TS-1(Si/Ti=25)				
1	500°C, 4 hours, air	850	25.65	31.15
2	+Reduced 400°C, 2 hours	2150	32.14	28.49
3	+500°C, 1hours, air	3210	28.50	53.57
0.1%Pd@HTS-1(Si/Ti=25)				

4	500°C, 4 hours, air	29750	28.90	43.66
5	+Reduced 400°C, 2 hours	34470	31.45	29.80
6	+500°C, 6hours, air	35010	25.50	48.35

^a Catalytic testing results of the 0.1%Pd@TS-1(Si/Ti=25) catalyst after being subjected to various heat treatment regimens. H₂O₂ productivity was determined under the following reaction conditions: H₂/Ar(2.9 MPa) and air (1.35 MPa), 8.5 g solvent (2.9 g H₂O , 5.6 g MeOH), 0.02 g catalyst, RT, 1200 rpm, 30 min. H₂O₂ degradation was calculated from the loss of H₂O₂ using standard reaction conditions: H₂/Ar(2.9Mpa), 8.5 g solvent (5.6 g MeOH,2.22 g H₂O, and 0.68 g 50% H₂O₂), 0.02 g catalyst, RT, 1200 rpm, 30 min. n.d.

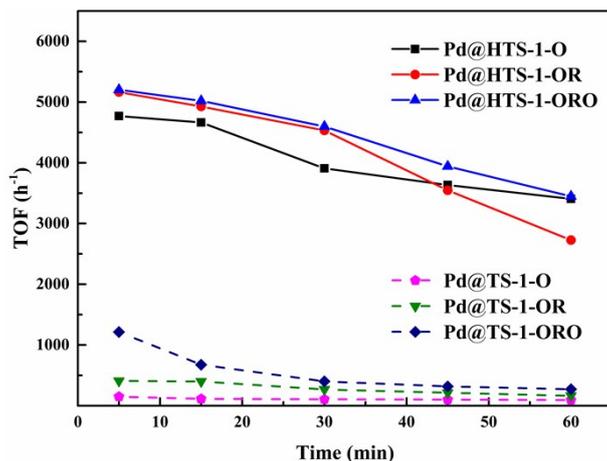


Fig. S10 The TOF of H₂O₂ production with different reaction time over Pd@TS-1 and Pd@HTS-1 catalysts. TON(Turnover number)=mol (H₂O₂)/mol (surface Pd)/h (reaction time)

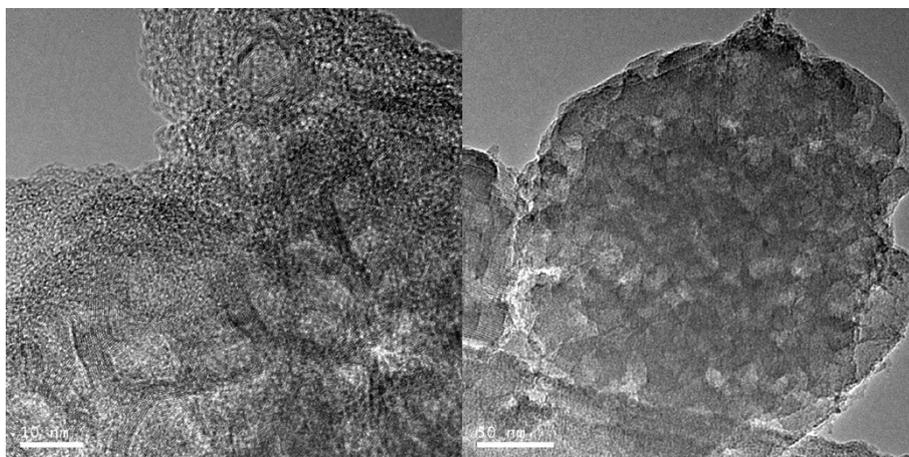


Fig. S11 HRTEM images of the hierarchical Pd@HTS-1



Fig.S12 Physical map of the Pd-modified TS-1 catalysts after calcination: (a) Pd@TS-1 and (b) Pd@HTS-

1 catalysts

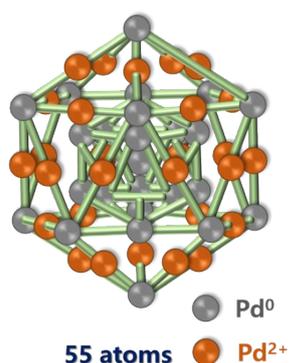


Fig.S13 Schematic illustration for global optimisation of 1.1 nm Pd particles with 55 atoms encapsulated by surface Pd²⁺ layer.

Even with only 55 atoms in this cluster, there are already three shells for this 1.1 nm particle.¹² And there are four shells for 1.6 nm particle with 147 atoms. So it is persuasive that the subnano Pd particles could be encapsulated by surface PdO layer.¹³

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