

Supporting Information

High viscosity to highly dispersed PtPd bimetallic nanocrystals for enhanced catalytic activity and stability

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Author Contributions

J.Y., H.W. and Y.X.X carried out all the experiments. X.Y.Y. conceived the project, provided the idea, and designed and guided the experiments. B.L.S. conceived the project, and supported scientific and technological platform and guidance. Z.Y.H. performed the measurements of TEM. S.C.M. and M.P. provided the electrochemical experiment platform. J.Y. and X.Y.Y. wrote the paper. C.J., G.T. and B.L.S. revised the paper. All the authors discussed results and analyzed the data.

Experimental

Materials synthesis: Mesoporous silica SBA-15 was synthesized according to the published literature¹ and a mass ratio of Pluronic P123/HCl/TEOS/H₂O is 1/1.07/2.09/29.6. Mesoporous silica MCF was synthesized according to the published literature^{2,3} and a mass ratio of Pluronic P123/HCl/1,3,5-trimethylbenzene/TEOS/H₂O is 1/2.2/0.75/2.2/37.5. Mesoporous silica MCM-41 was synthesized according to the published literature⁴ and a mass ratio of CTAB/ammonia/TEOS/H₂O is 1/2.65/4.25/34.5. Mesoporous carbon CMK-3 was synthesized according to the published literature.⁵ To improve the carburization, SBA-15 (1 g) was stirred for 0.5 h in a solution of AlCl₃·6H₂O (1.4 M, 10 mL). The powder was retrieved by filtration and was dried at 353 K in air, and then calcined at 823 K for 4 h in air. CMK-3 was synthesized by using furfuryl alcohol as a carbon source, with a mass ratio of Al-SBA-15/furfuryl alcohol as 1/1.13. In a typical synthesis of PtPd/mesoporous supports, Pt(acac)₂ (0.05 mmol), Pd(acac)₂ (0.05 mmol) and polyvinylpyrrolidone (1 mmol) were added to 1,4-butanediol (20 ml) at room temperature under stirring. Mesoporous supports (200 mg) were added to the solution under sonication for about 15 min until it became homogeneous. After stirring at 323 K for 1 h, the mixture was heated to 488 K under nitrogen atmosphere, and was kept at 488 K for 0.5 h. when cooling to room temperature, the final PtPd/mesoporous supports were obtained after being filtered, washed, and dried. The whole reaction were carried out in solvents using by close reaction system and reflux condensation method. The procedure for the synthesis of PtPd nanoparticles supported on Vulcan XC-72 carbon (denoted as PtPd/C) was similar to that of the PtPd/ mesoporous supports, except that mesoporous supports were substituted with Vulcan XC-72 carbon. The procedure for the synthesis of PtPd nanoparticles was similar to that of the PtPd/ mesoporous supports, except that mesoporous supports were not added. From the inductively coupled plasma-atomic emission spectrometry (ICP-AES) result, the weight percent of the Pt and Pd in the composites are also very near, such as 3.74 wt% and 2.03 wt% for PtPd/MCF, 3.71 wt% and 1.98 wt% for PtPd/SBA-15, 3.73 wt% and 2.02 wt% for PtPd/MCM-41, 3.71 wt% and 2.01 wt% for PtPd/MCF(EG), 3.66 wt% and 1.95 wt% for PtPd/MCF(W), 3.65 wt% and 1.98 wt% for PtPd/CMK-3, and 3.67 wt% and 1.99 wt% for PtPd/C, respectively. The loading number of Pt and Pd in our synthesized PtP/supports is about 0.190 mmol and 0.188 mmol per gram of all the mesostructured supports

Physical characterization: XRD patterns were collected on a Bruker D8 Advance X-ray diffractometer equipped with Cu K α radiation. SEM experiments were performed on an S-4800 electron microscope (HITACHI). Transmission electron microscopy (TEM) images

were collected on a JEOL JEM-2100F microscope, operated at 200 kV in Wuhan University of Technology. HAADF-STEM and EDX were performed on a FEI Titan 80-300 “cubed” microscope fitted with an aberration-corrector for the probe forming lens, and four Bruker Quanta X EDX detectors, operated at 200 kV in the University of Antwerp. The nitrogen adsorption and desorption isotherms were measured by using a Micromeritics ASAP 3020 system. Before the adsorption/desorption measurements, the samples were outgassed for 8 h at 453 K. The BET specific surface area was evaluated from adsorption data in the relative pressure range of 0.1-0.3. The pore size distribution for each sample was calculated from the adsorption isotherm branch using the BJH method. The total pore volume was estimated from the amount adsorbed at $P/P_0 = 0.99$. The amount of catalysts was determined by the inductively coupled plasma atomic emission spectroscopy (Optima 4300DV, Perkin Elmer Ltd., USA).

Hydrogenation of nitrobenzene: In a typical catalytic reaction, catalysts (the total amount of PtPd is 0.1 mg), nitrobenzene (2.0 mmol), and ethanol (10.0 mL) were mixed together and placed into a glass pressure vessel. The vessel was purged with H₂ before the reaction for removing the air from the reaction system. The vessel was pressurized with 1 bar and the pressure was maintained during the reaction. The catalytic products produced at different reaction time were measured by gas chromatograph. All PtPd/silica catalysts were dried under vacuum at 423 K for 10 h before catalytic reaction. For experiments with multiple runs each catalytic reaction was run for 4 h. After each run the catalyst was separated from reaction mixture, washed with water and dried carefully before using in the next run. The same procedure was repeated for other runs.

Electrochemical measurements: A three-electrode cell was used to do the electrochemical measurements. A Ag/AgCl (3 M) electrode was used as a reference electrode and a platinum mesh was used as a counter electrode. The working electrode was a glassy-carbon Rotating Disk Electrode (RDE, diameter: 5 mm, area: 0.196 cm²). The loading amount of metal for the catalysts was 3 μg. CV measurements were performed in 0.1 M HClO₄ solutions under a flow of N₂ at a sweep rate of 50 mV/s. ORR measurements were carried out in 0.1 M HClO₄ solutions under flow of O₂ using the glassy-carbon RDE at a rotation rate of 1600 rpm and a sweep rate of 10 mV/s. The accelerated durability tests were performed at room temperature in O₂-saturated 0.1 M HClO₄ solution by applying cyclic potential sweeps between 0.6 and 1.1 V versus RHE at a sweep rate of 50 mV/s for a given number of cycles.

References

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Supporting Figures:

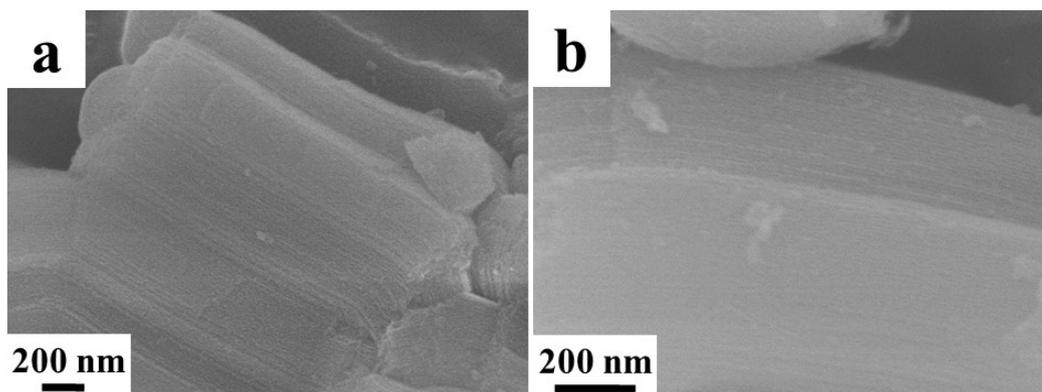


Fig. S1 Representative SEM images of (a) SBA-15 and (b) PtPd/ SBA-15.

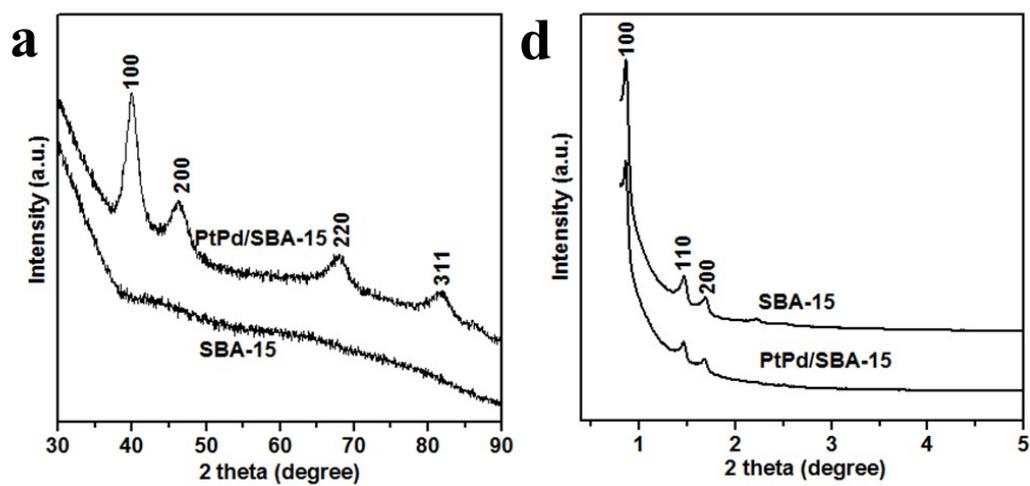


Fig. S2 (a) High-angle and (b) low-angle XRD patterns of SBA-15 and PtPd/SBA-15.

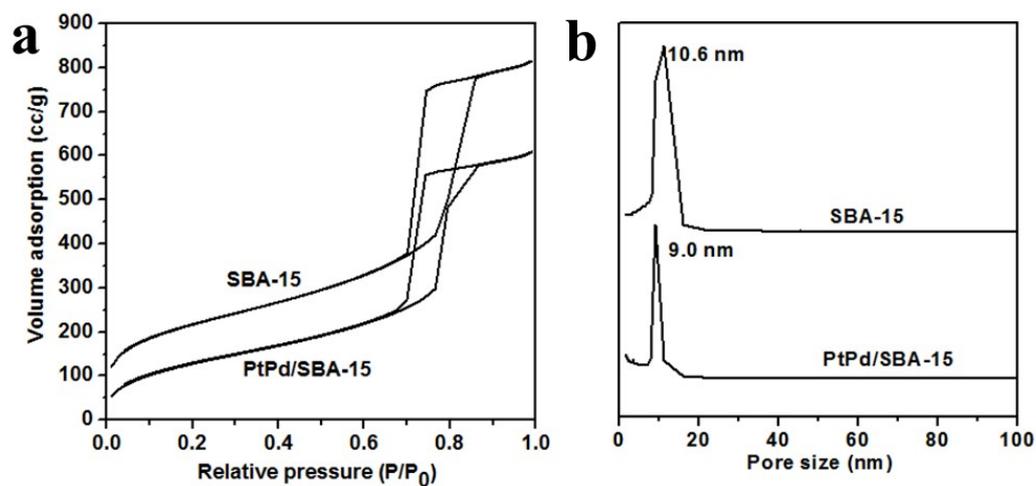


Fig. S3 (a) Nitrogen adsorption-desorption isotherms and (b) corresponding pore size distributions of SBA-15 and PtPd/ SBA-15.

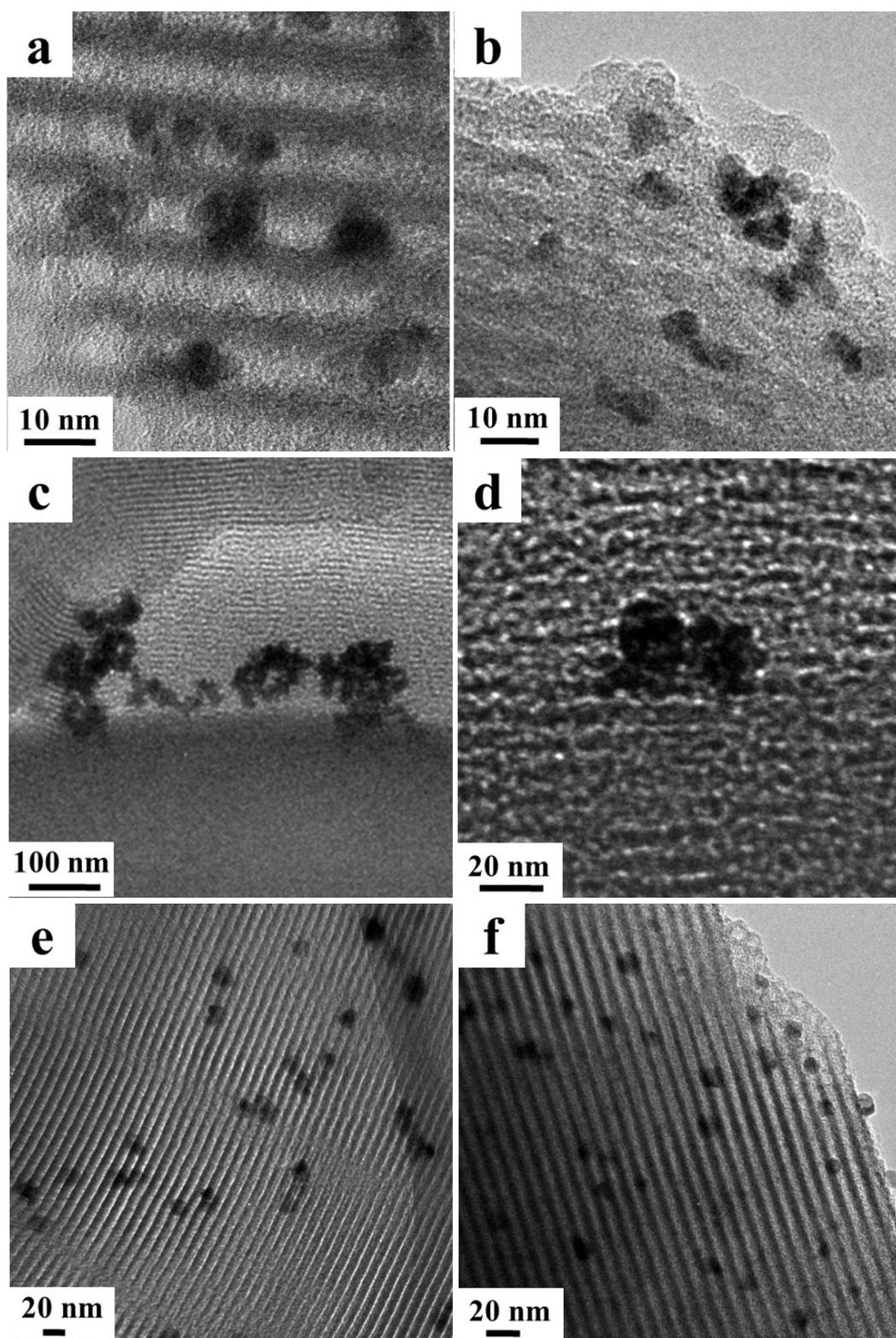


Fig. S4 Representative TEM image of PtPd/SBA-15 synthesized in (a) 1, 4-butanediol, (b) ethylene glycol, (c, d) water, (e) 1,2-propanediol, and (f) 1,5-pentadiol.

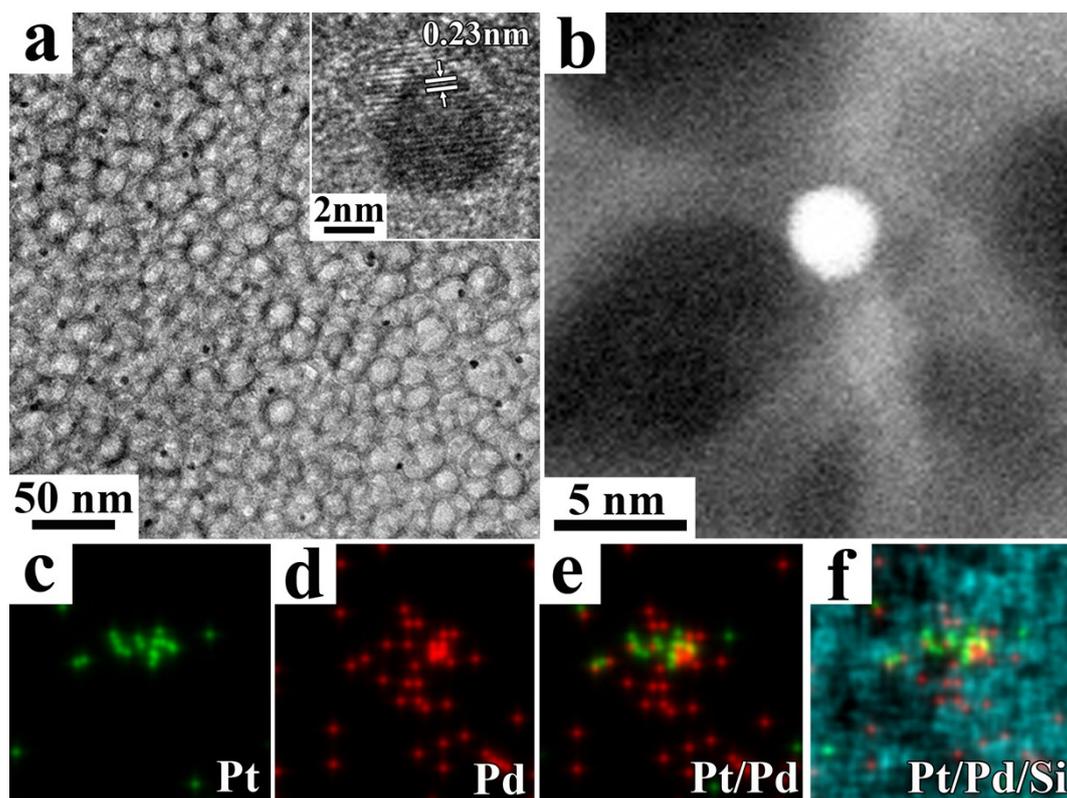


Fig. S5 (a) Representative low-magnification TEM image of PtPd/MCF. Inset shows high-magnification TEM image of an individual PtPd nanocrystal within PtPd/MCF. (b) High magnification HAADF-STEM image of PtPd/MCF, (c–f) corresponding EDX elemental mapping results: (c) Pt (green), (d) Pd (red), (e) Pt and Pd, and (f) Pt, Pd and Si overlaid color mapping.

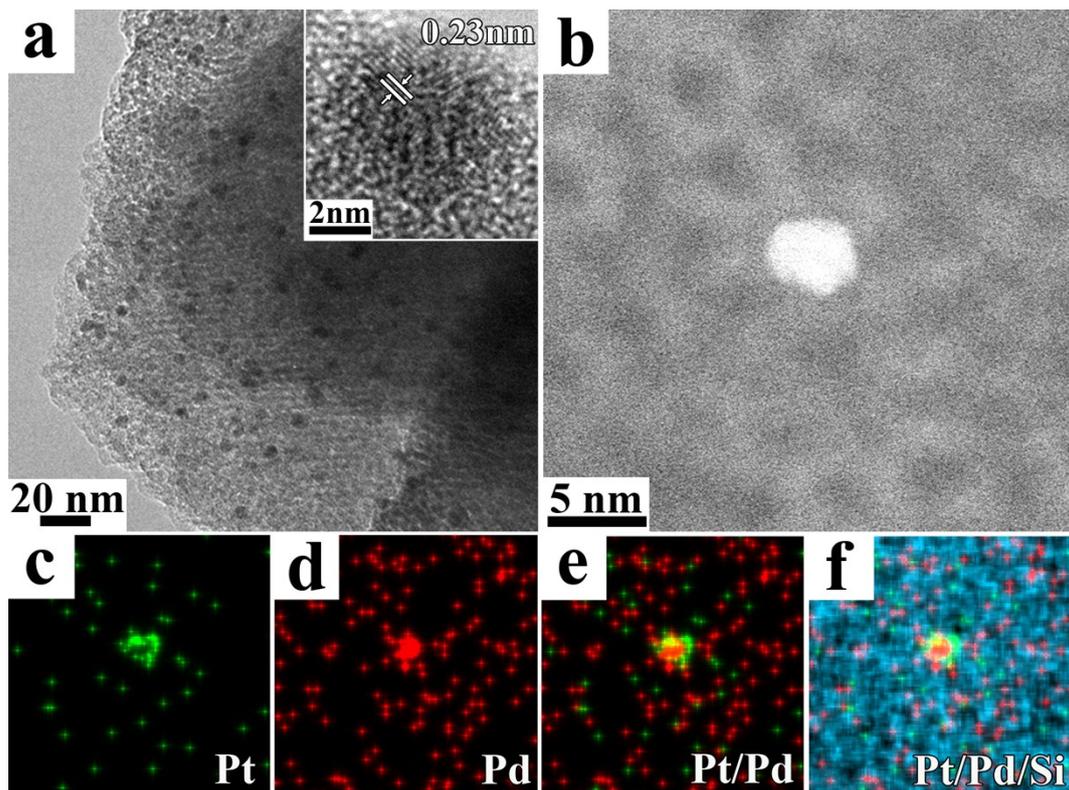


Fig. S6. (a) Representative low-magnification TEM image of PtPd/MCM-41. Inset shows a high-magnification TEM image of an individual PtPd nanocrystal within PtPd/MCM-41. (b) High magnification HAADF-STEM image of PtPd/MCM-41, (c–f) corresponding EDX elemental mapping results: (c) Pt (green), (d) Pd (red), (e) Pt and Pd, and (f) Pt, Pd and Si overlaid color mapping.

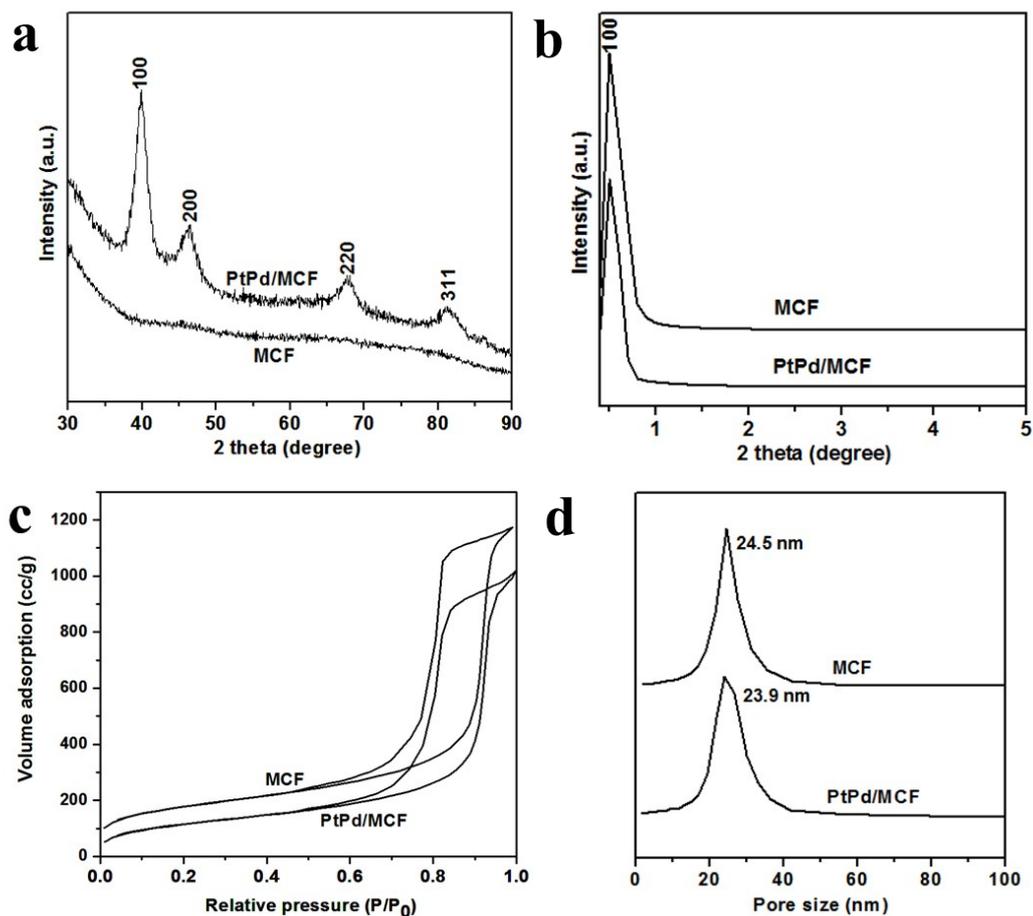


Fig. S7 (a) High-angle and (b) low-angle XRD patterns of MCF and PtPd/MCF. (c) Nitrogen adsorption-desorption isotherms and (d) corresponding pore size distributions of MCF and PtPd/MCF.

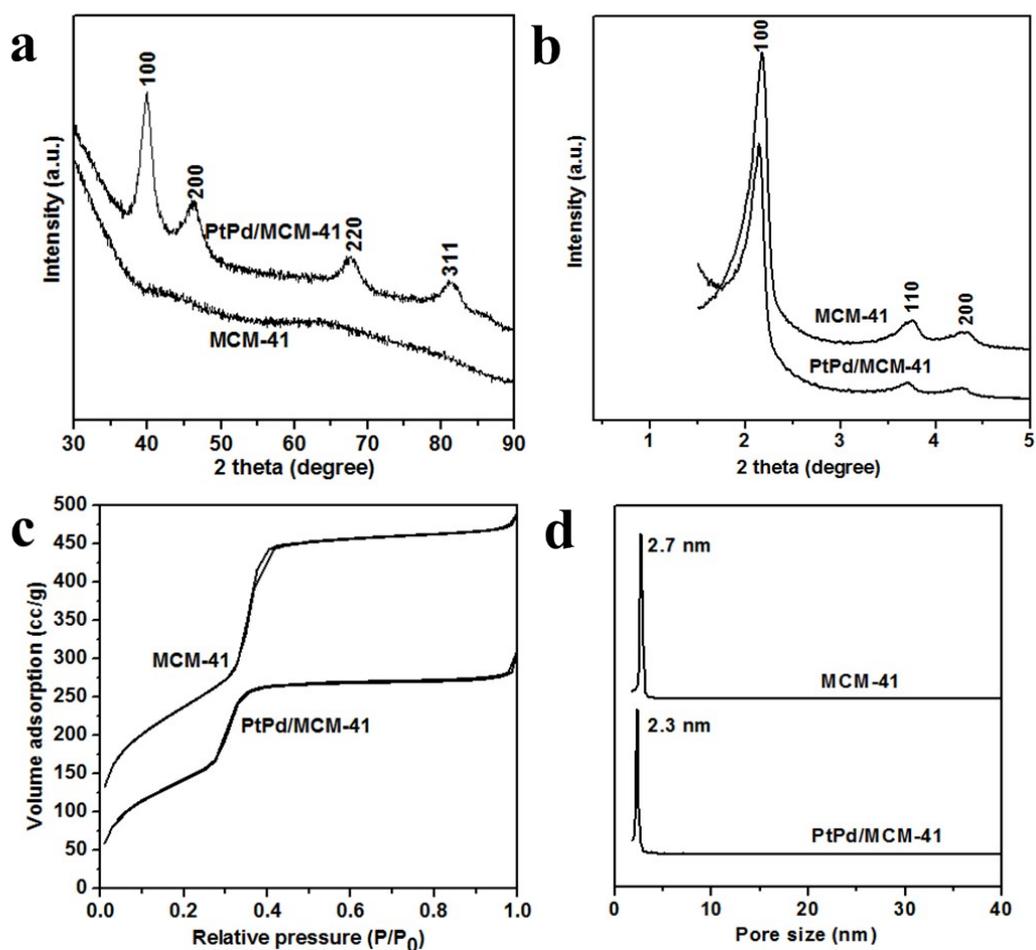


Fig. S8 (a) High-angle and (b) low-angle XRD patterns of MCM-41 and PtPd/MCM-41. (c) Nitrogen adsorption-desorption isotherms and (d) corresponding pore size distributions of MCM-41 and PtPd/MCM-41.

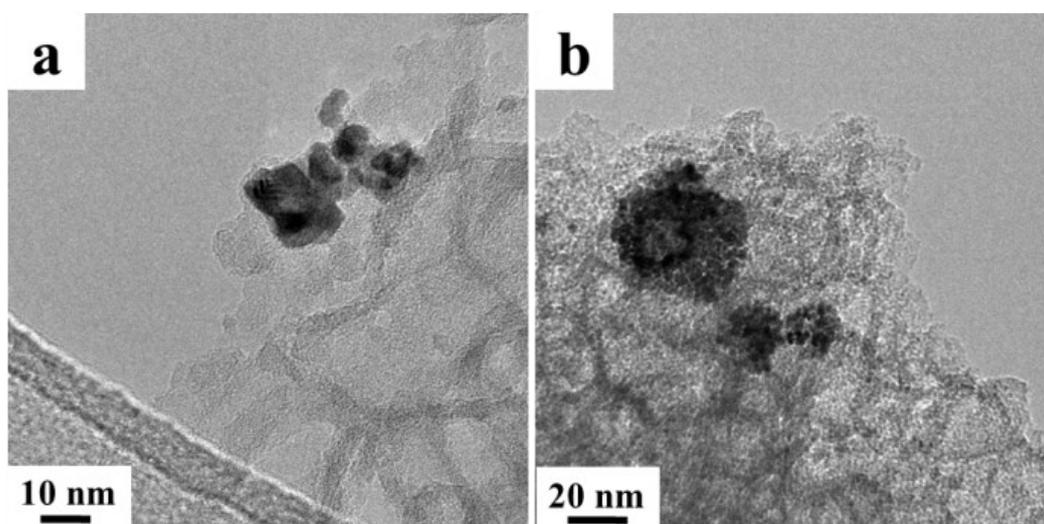


Fig. S9 Representative TEM images of PtPd/MCF synthesized in different solvents: (a) ethylene glycol and (b) water.

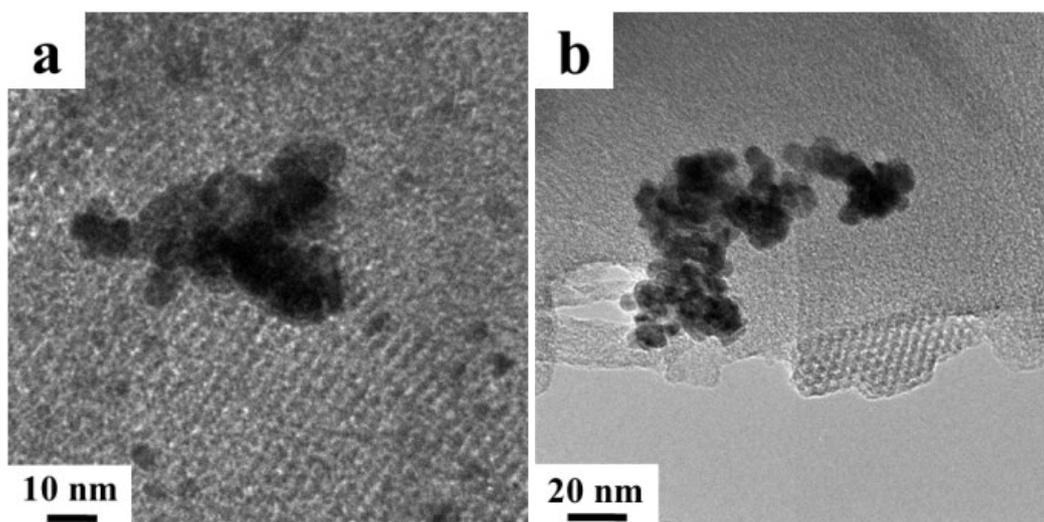


Fig. S10 Representative Representative TEM images of PtPd/MCM-41 synthesized in different solvents: (a) ethylene glycol and (b) water.

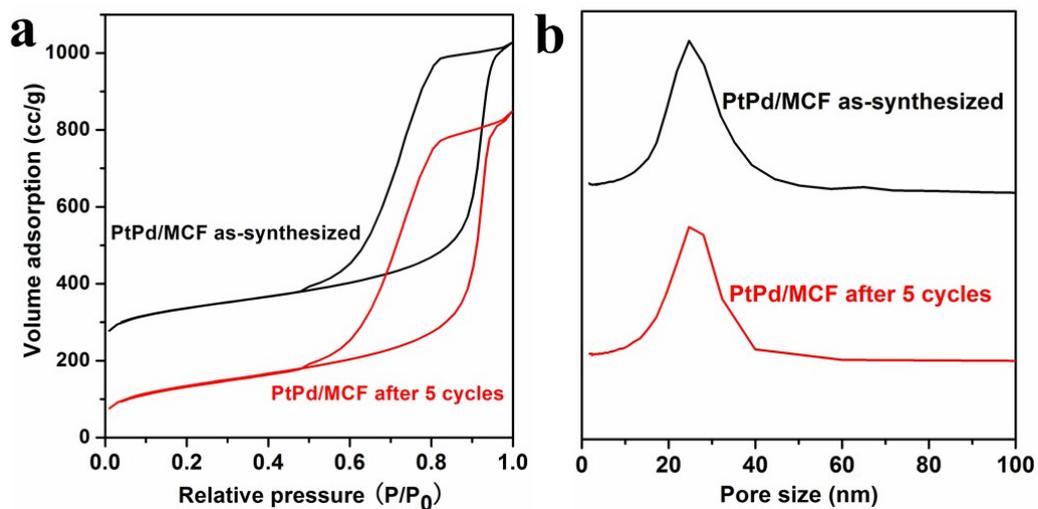


Fig. S11 (a) Nitrogen adsorption-desorption isotherms and (b) corresponding pore size distributions of PtPd/MCF before and after five cycles. The isotherms of PtPd/MCF as-synthesized is offset from 200 cc/g at the beginning for clarity.

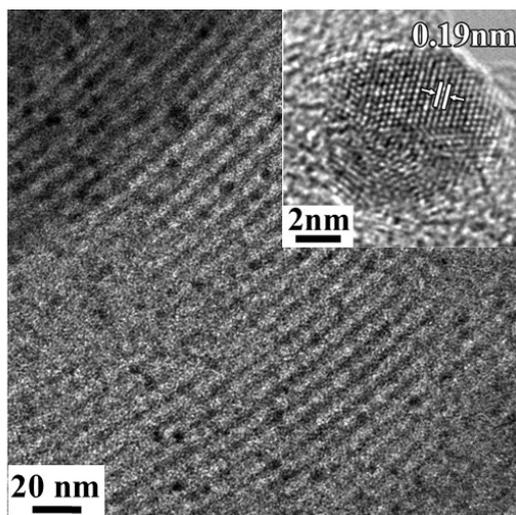


Fig. S12 Representative TEM image of PtPd/CMK-3. Inset shows a high-magnification TEM image of an individual PtPd nanocrystal within PtPd/CMK-3.

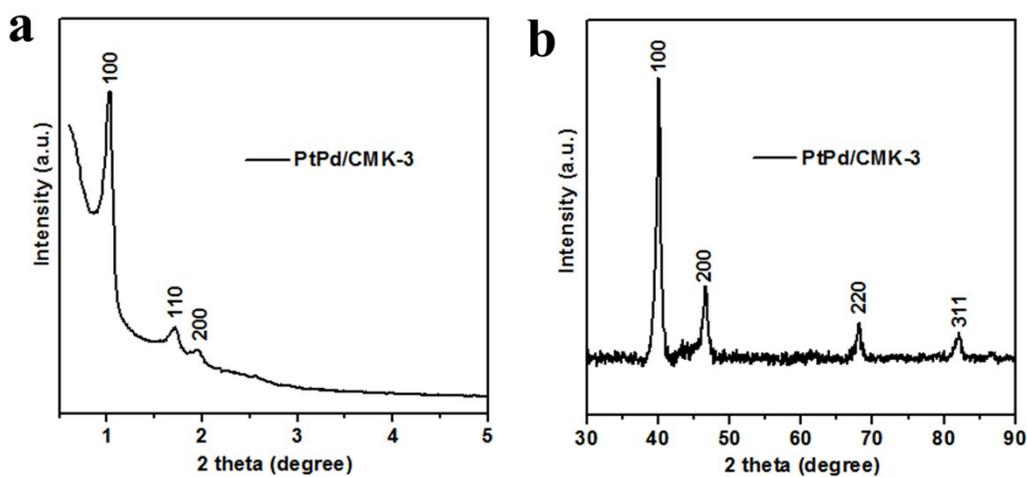


Fig. S13 (a) Low-angle and (b) high-angle XRD patterns of PtPd/CMK-3.

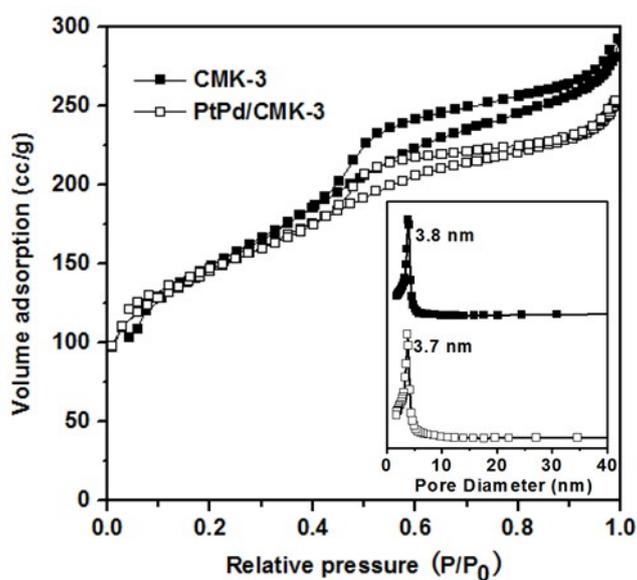


Fig. S14 Nitrogen adsorption-desorption isotherms and corresponding pore size distributions of CMK-3 (■) and PtPd/CMK-3 (□).

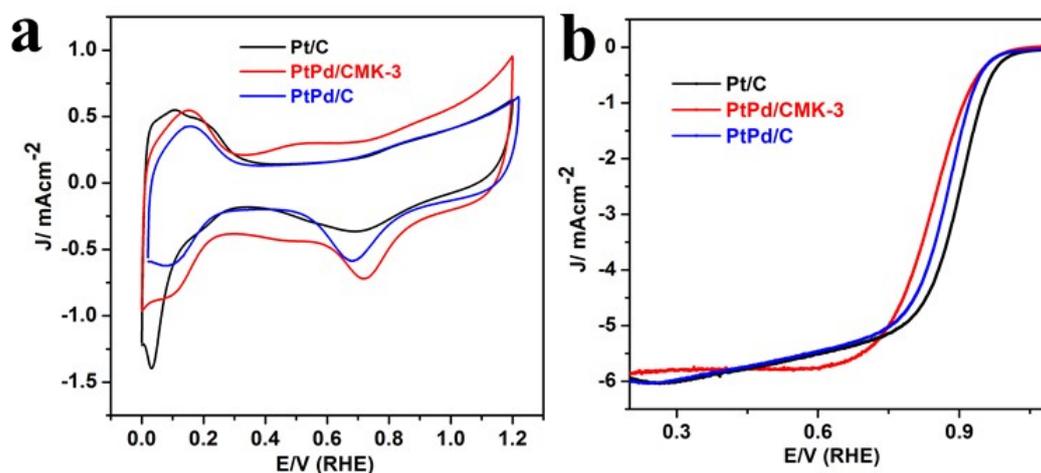


Fig. S15 (a) Cyclic voltammetry (CV) curves, (b) ORR polarization curves of commercial Pt/C, PtPd/CMK-3 and PtPd/C

Table S1 Physical parameters of SBA-15, PtPd/SBA-15, MCF, PtPd/MCF, MCM-41 and PtPd/MCM-41 samples.

Sample	$D_{(100)}$ ^{a)} (nm)	D_S ^{b)} (nm)	Surface Area ^{b)} (m ² /g)	Pore Volume ^{b)} (cm ³ /g)
SBA-15	10.3	10.6	747	1.19
PtPd/SBA-15	10.1	9.0	576	1.01
MCF	17.8	24.5	658	1.98
PtPd/MCF	17.7	23.9	481	1.72
MCM-41	4.1	2.7	847	1.05
PtPd/MCM-41	4.1	2.3	600	0.96

^{a)} Determined from small-angle XRD; ^{b)} Determined from nitrogen sorption.

Table S2 The viscosity values of various solvents at room temperature (20 °C).

Solvents	Theoretical value (mPa.s)	Experimental value ^{a)} (mPa.s)	Experimental value for solvent with PVP ^{b)} (mPa.s)
1,5-pentadiol	N.A.	103.0	108.5
1,4-butanediol	88.8	77.1	92.1
1,2-propanediol	60.5	54.4	57.8
ethylene glycol	22.1	18.9	22.6
water	1.01	0.87	1.11

^{a)} Measured on a NDJ-8S viscometer; ^{b)} The concentrations of PVP in different solvents are the same with the synthesis experimental conditions.

Table S3 Catalytic results of the hydrogenation of nitrobenzene using various catalysts. ^{a)}

Catalyst	Conversion (%)	TOF ^{b)} (mol g ⁻¹ h ⁻¹)
PtPd/MCF	99.6	4.98
PtPd/SBA-15	84.5	4.23
PtPd/MCM-41	76.1	3.81
PtPd/MCF(EG)	56.2	2.81
PtPd/MCF(W)	48.2	2.41
PtPd	14.4	0.72

^{a)} Reaction conditions: nitrobenzene, 2.0 mmol; catalysts, 0.1 mg; solvent, 10.0 mL ethanol; 1 atm hydrogen gas; room temperature; reaction time, 4 h. ^{b)} TOF of the catalyst = (mole of substrate conversion)

Table S4 Physical parameters of PtPd/MCF before and after 5 cycles

Sample	D _S ^{a)} (nm)	Surface Area ^{a)} (m ² /g)	Pore Volume ^{a)} (cm ³ /g)	Pt loading amount ^{b)} (wt%)	Pd loading amount ^{b)} (wt%)
PtPd/MCF as-synthesized	24.6	476	1.72	3.7	2.0
PtPd/MCF after 5 cycles	24.6	473	1.68	3.0	1.6

^{a)} Determined from nitrogen sorption.; ^{b)} Determined from ICP-AES.

Table S5 Specific ECSA and ORR activities at 0.9 V versus RHE for Pt/C, PtPd/C and PtPd/CMK-3 catalysts.

Samples	Specific ECSA (m ² /g)	Mass activity (A/mg)	Specific activity (mA/cm ²)
Pt/C	68.2	0.101	0.144
PtPd/C	55.5	0.261	0.470
PtPd/CMK-3	53.2	0.316	0.594