Electronic Supplementary Information

Pd nanoparticles supported on hierarchically porous carbon derived from assembled nanoparticles of zeolitic imidazolate framework (ZIF-8) for methanol electrooxidation

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Experimental Section

Chemicals and Materials

Methanol (CH_3OH, Tokyo Chemical Industry Co., Ltd., >99.8%), ethanol (C_2H_5OH, Kishida Chem. Co., >99.8%), hydrochloric acid (Wako Pure Chemical Industries, Ltd., 35.0-37.0%), triethylamine (EA, Chameleon reagent), 2-methylimidazole (MeIM, Tokyo Chemical Industry Co., Ltd.), 5% Nafion® Dispersion solution DE 520 CS type (Wako Pure Chemical Industries, Ltd.), Vulcan XC-72R (Carbon, specific surface area = 240 m^2 g^{-1}, Cabot Corp., USA), zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, Wako Pure Chemical Industries, Ltd.), sodium hydroxide (NaOH, Chameleon Reagent, >98%), potassium hydroxide (KOH, Kishida Chem. Co., >85.0%), sodium borohyride (NaBH4, Sigma-Aldrich, 99%), potassium tetrachloropalladate (K_2PdCl_4, Wako Pure Chemical Industries, Ltd., >97%) were used as received. All reagents were commercial and used without further purification. De-ionized water with a resistivity of 18.2 MΩ·cm was obtained by reverse osmosis followed by ion-exchange and filtration (RFD 250NB, Toyo Seisakusho Kaisha, Ltd.).

Synthesis of ZIF-8

A methanolic solution (500 mL) of zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, 7.4350 g) was added into a methanolic solution (500 mL) of 2-methylimidazole (4.1040 g) and triethylamine (9 mL) with ultrasonication for 30 min at room temperature. After that, the turbid solution was centrifuged to give a white solid, which was washed carefully with methanol and then dried at 80 °C for 12 h.

Preparation of ZIF-8-derived carbon (ZC)

The ZIF-8 sample (2.0 g) was transferred into a ceramic boat and placed into a temperature-programmed furnace under flowing Ar for 3 h to exclude air. Subsequently, the sample was heated from room temperature to 800, 900, 1000, or 1100 °C in 1.5 h, and then kept at the temperature for 8 h. After cooled down to room temperature under an argon flow, the resultant black materials were washed several times with a HCl (10 vol % in water) solution to remove the residual ZnO and/or Zn species, then washed with de-ionized water and dried at 80 °C for 12 h to afford ZIF-8-derived carbon (denoted as ZC-800, ZC-900, ZC-1000, and ZC-1100) (over 0.4 g). The product yield of ZCs is over 20%.

Syntheses of Pd/ZC and Pd/XC-72R catalysts

The Pd catalyst supported by ZC or XC-72R was synthesized by a facile sodium hydroxide-assisted reduction method reported recenty.[1] Generally, 50 mg of ZC or XC-72R carbon powder dispersed in 1.25 mL of water was mixed with an aqueous solution of K_2PdCl_4 (0.30 M, 0.15 mL) and subsequently the aqueous suspension was further homogenized under ultrasonication for 30 min. Then 10 mg of $NaBH_4$ dissolved in 0.25 mL of 2.0 M NaOH solution was added into the above obtained suspension with vigorous shaking. In order to fully deposit the metallic nanoparticles onto the support, the mixture was shaken for another half an hour. Finally, the desired catalyst Pd/ZC or Pd/XC-72R was collected by centrifuging and washed with de-ionized water for several times and then dried under vacuum at 80 °C.

Instrumentation

Powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku UItima IV X-ray diffractometer with Cu Kα source (40 kV, 40 mA, λ= 0.154 nm). The surface area measurements were performed with N_2 adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp-max) after dehydration under vacuum at 150 °C for 12 h. The pore volume was calculated by a single point method at $P/P_0 = 0.99$. Scanning electron microscopic (SEM) analyses were carried with a Hitachi S-5000 field emission scanning electron microscope. Transmission electron microscope (TEM, TECNAI G^2 F20) equipped with energy dispersed X-ray detector (EDX) was applied for the detailed microstructure and composition information for the prepared samples. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg Kα source (1253.6 eV) operating at 10 kV and 10 mA. Raman spectra were recorded on a Jobin-Yavon T64000 Raman system at room temperature at an excitation wavelength of 532 nm.

Electrode preparation and electrochemical performance test

Electrochemical properties of the catalysts were measured on a Solartron electrochemical workstation (SI1287) using a conventional three-electrode system with a catalyst modified glassy carbon (GC, Φ = 3 mm) working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). Before the surface coating, the GC electrode was polished with 0.5 and 0.05 μm alumina suspensions, followed by washing ultrasonically with HNO_3-H_2O (1:1, v/v ratio) solution, ethanol and deionizer water sequentially. 15 mg of carbon-supported Pd catalyst, 0.8 mL of H_2O, 0.2 mL of ethanol and 24 μL of Nafion solution (5 wt%) were mixed under ultrasonication for 1 h. Then 3 μL of the homogeneously mixed catalyst ink was dropped on the surface of the GC electrode by using a micropipette and dried at room temperature for 4 h. The Pd loading on the electrode was controlled at 0.054 mg cm^{-2}. Before measurement, the electrolyte (1 M KOH or 1 M KOH + 1 M CH_3OH solution) was first de-aerated with highly pure N_2 for half an hour. All electrochemical measurements were performed at ambient temperature (~25 °C). The electrochemical impedance spectroscopy (EIS) was performed in 1 M KOH + 1 M CH_3OH solution at a constant potential of -0.4 V in the frequency range between 100 kHz and 20 mHz on the same Solartron electrochemical workstation (SI1287) with the Solartron impedance/gain-phase analyzer (SI1260).

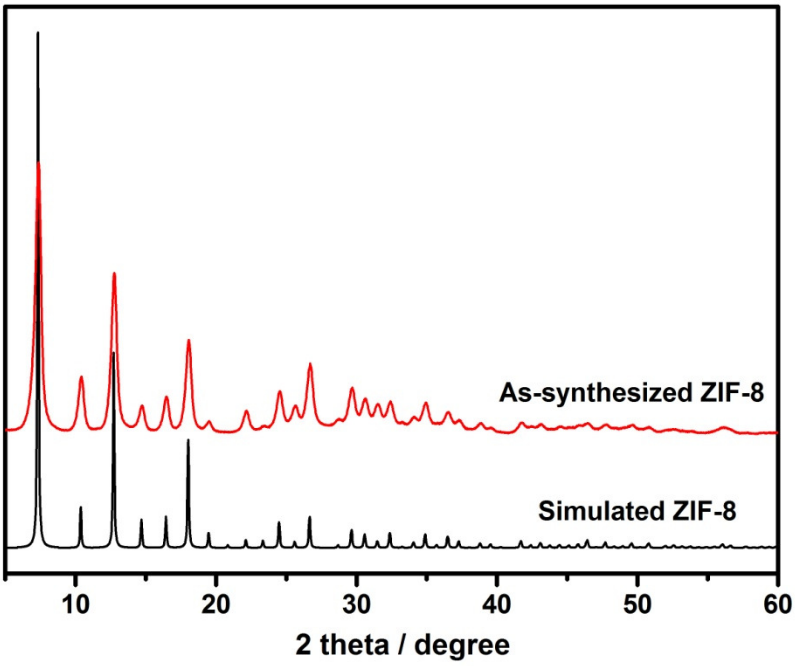

Fig. S1 Powder XRD patterns of ZIF-8.

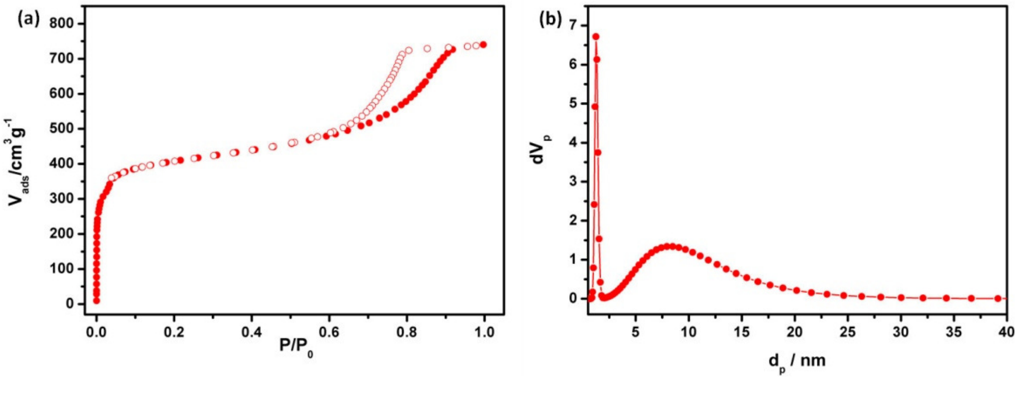

Fig. S2 (a) N_2 sorption isotherms at 77 K (Filled and open symbols represent adsorption and desorption branches, respectively), and (b) the corresponding NL-DFT pore size distribution of the assembled nanoparticles of ZIF-8.

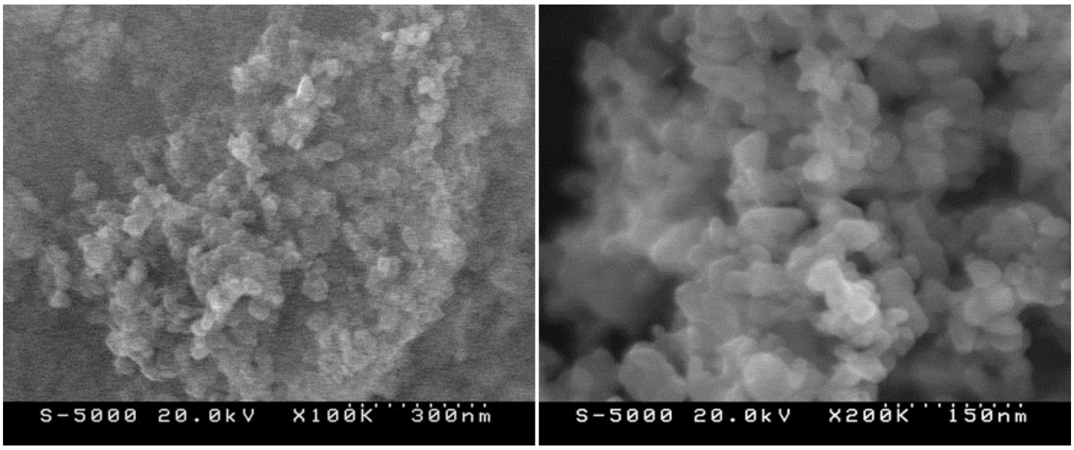

Fig. S3 The SEM images of the assembled nanoparticles of ZIF-8.

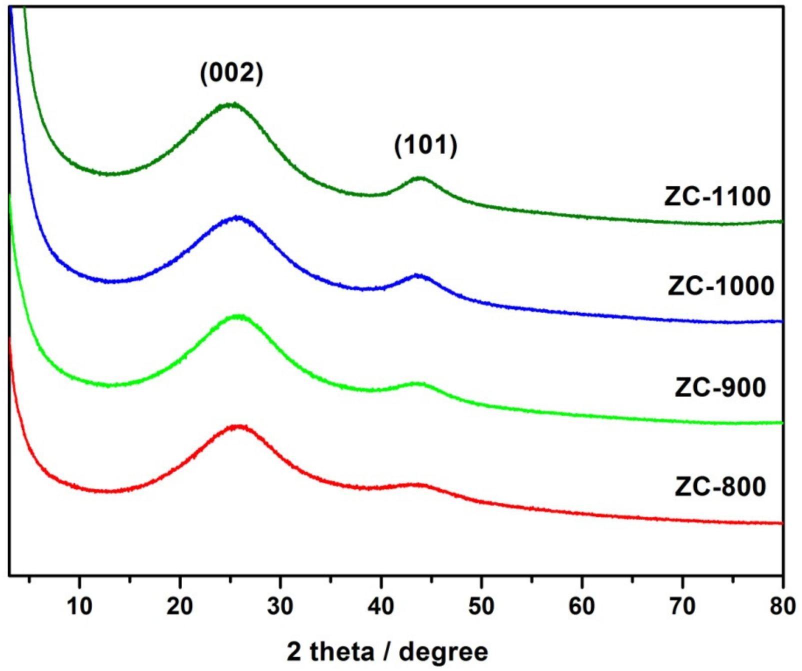

Fig. S4 Powder XRD patterns of carbon materials prepared by carbonization of assembled nanoparticles of ZIF-8 at various temperatures.

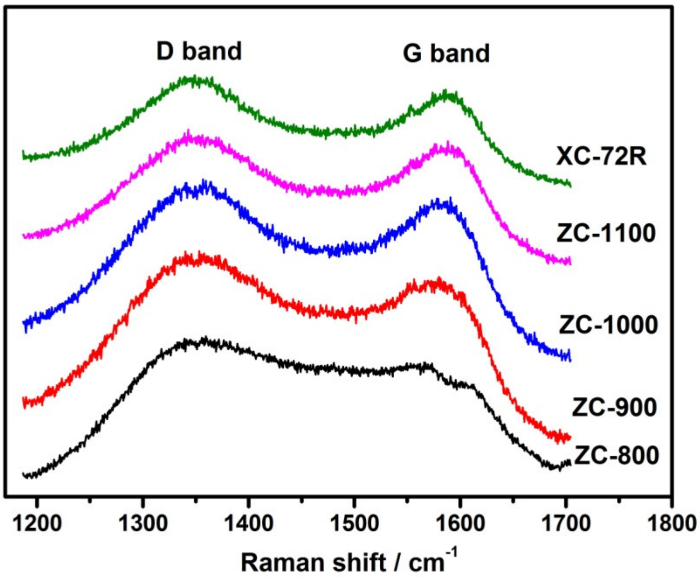

Fig. S5 Raman spectra of carbon materials prepared by carbonization of assembled nanoparticles of ZIF-8 at various temperatures and carbon black Vulcan XC-72R.

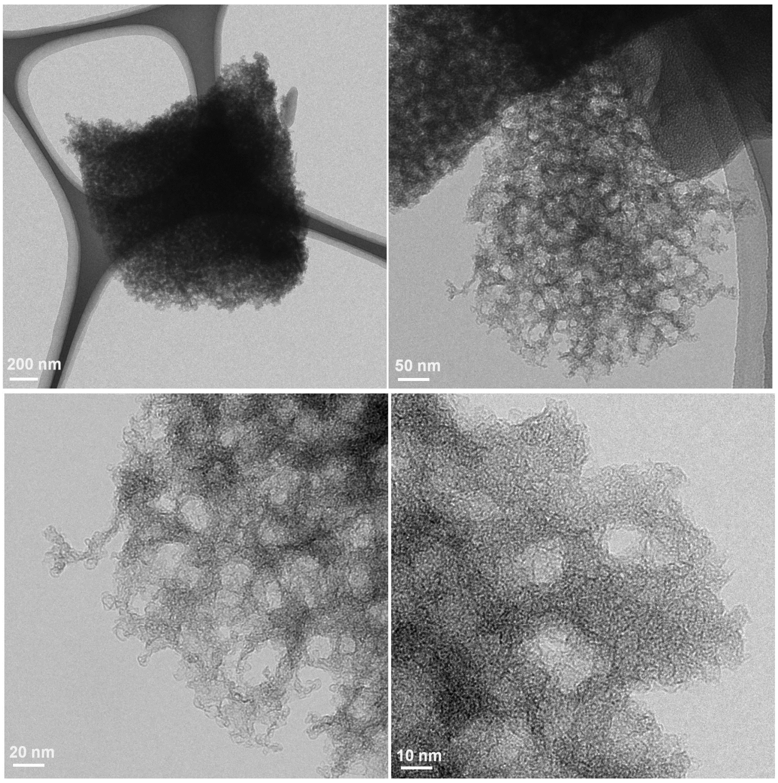

Fig. S6 TEM images of ZC-1000 at different magnifications.

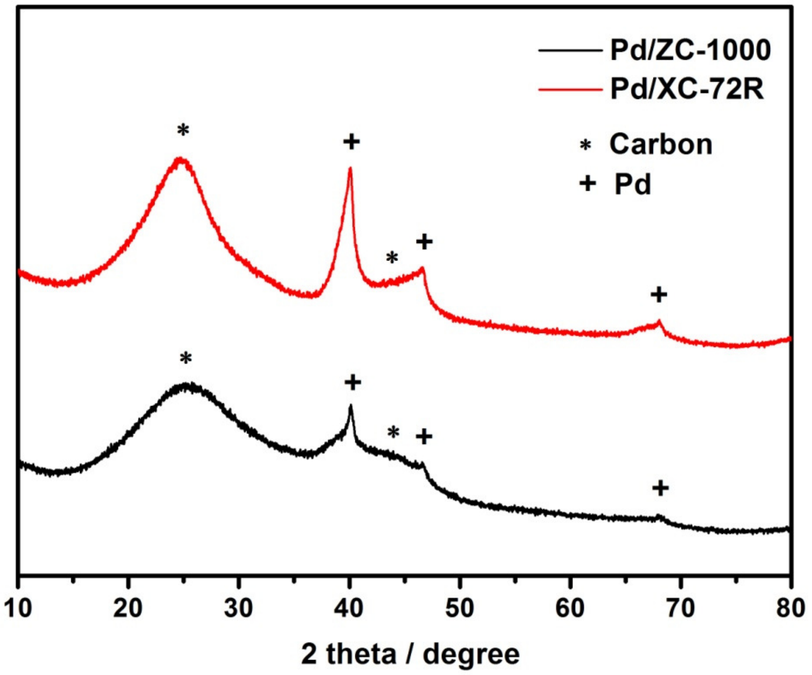

Fig. S7 Powder XRD patterns of Pd/ZC-1000 and Pd/XC-72R..

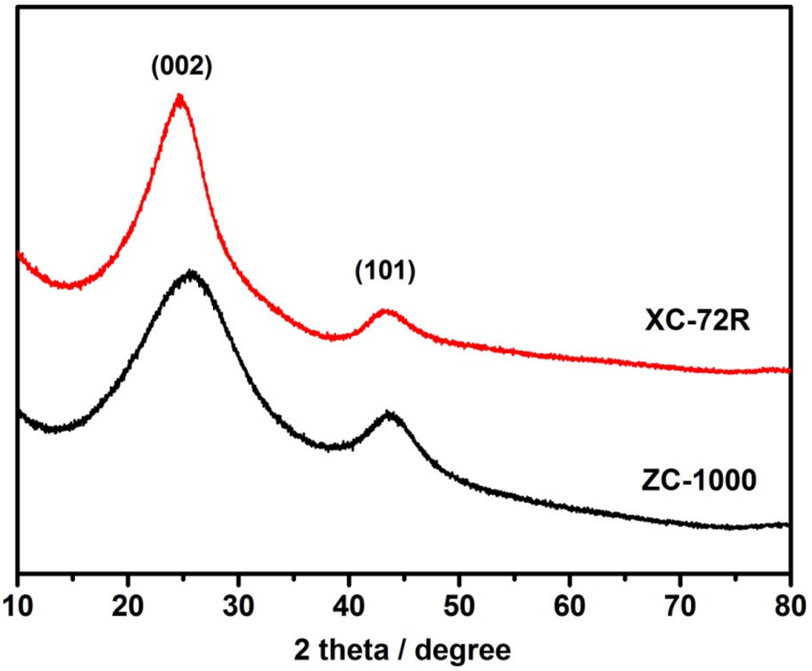

Fig. S8 Powder XRD patterns of ZC-1000 and XC-72R.

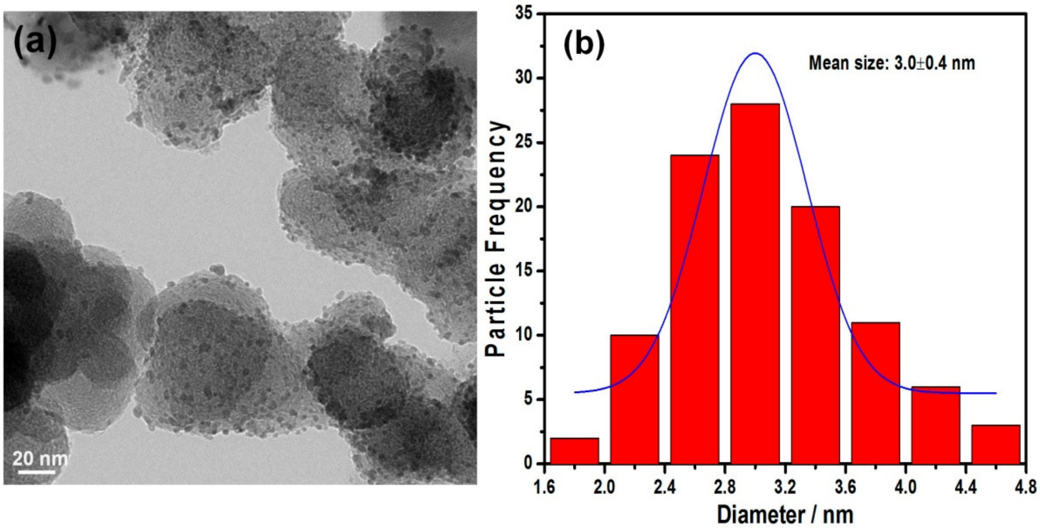

Fig. S9 (a) TEM image and (b) the corresponding particle size distribution histogram of Pd/XC-72R.

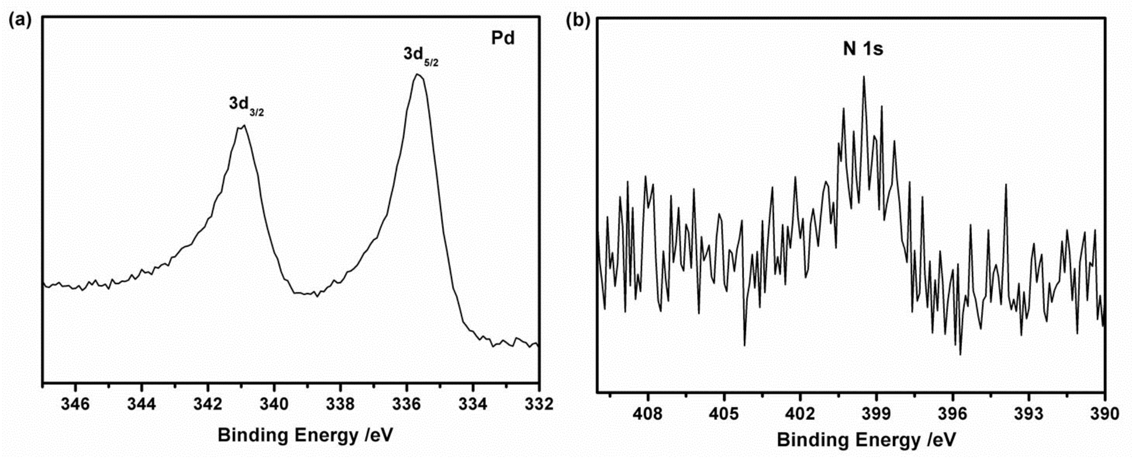

Fig. S10 XPS spectra for Pd/ZC-1000 at (a) Pd $3d_{3/2}$ and $3d_{5/2}$ and (b) N 1s levels.

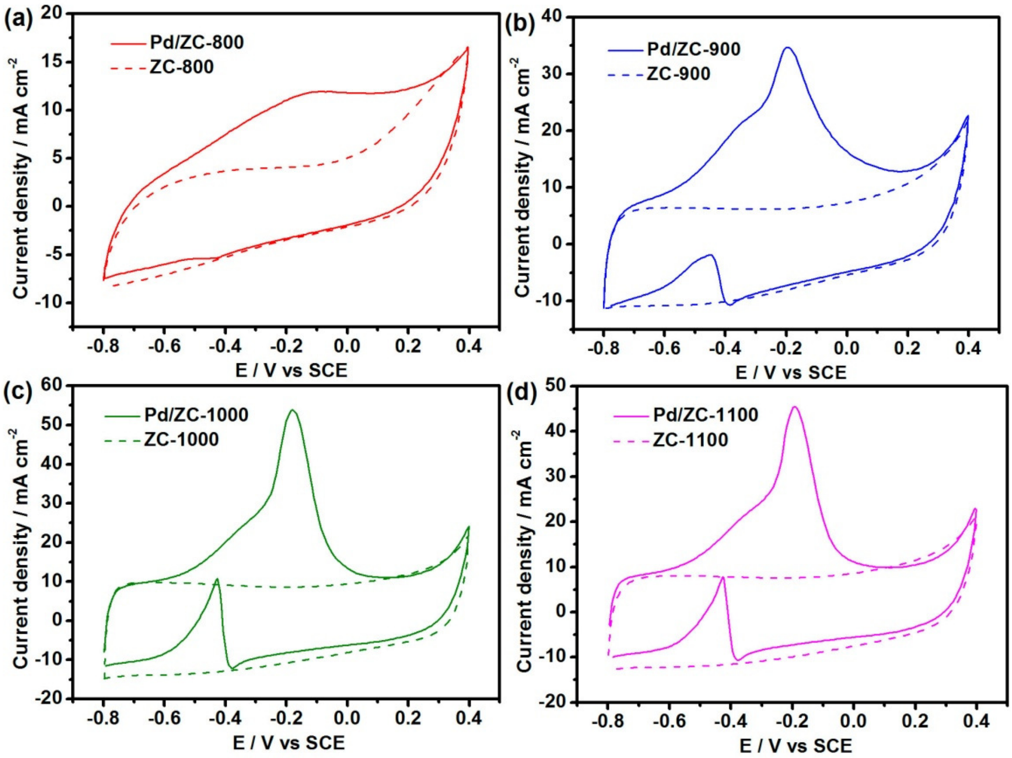

Fig. S11 Cyclic voltammograms of Pd/ZC and ZC electrodes in 1 M KOH solution containing 1 M CH_3OH with sweep rate of 50 mV s^{-1} at room temperature. Pd loading: 0.054 mg cm^{-2}.

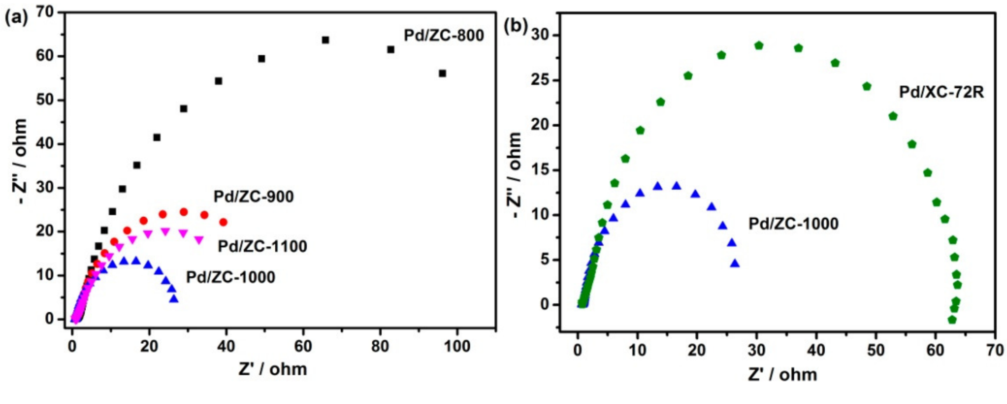

Fig. S12 The Nyquist plot of (a) Pd/ZC electrodes and (b) Pd/XC-72R and Pd/ZC-1000 electrodes in 1 M KOH containing 1 M CH_3OH at -0.4 V.

Table S1 Summary of the surface areas and pore volume distributions for the carbons

Sample	Specific surface area[a] (m^2 g^{-1})	Total pore volume[b] (cm^3 g^{-1})	Mesopore volume[c] (cm^3 g^{-1})	Micropore volume[d] (cm^3 g^{-1})
ZC-1100	1029	0.851	0.487	0.364
ZC-1000	1105	0.952	0.583	0.369
ZC-900	1020	0.871	0.531	0.340
ZC-800	914	0.726	0.376	0.350
XC-72R	240	0.278	0.226	0.052

[a] Calculated from the BET surface area analysis.

[b] Calculated by a single point method at $P/P_0 = 0.99$.

[c] Calculated using a t-plot method.

[d] Calculated by subtracting the total pore volume with the mesopore volumes.

Table S2 The forward anodic peak current density in CVs (specific activity I_f and mass activity j_f), and the current density at the time of 3000 s in chronoamperometry (I_s) for the methanol electrooxidation over different catalysts

Catalysts	Specific activity I_f (mA cm^{-2})	Mass activity j_f (mA mg^{-1})	I_s (mA cm^{-2})
Pd/ZC-1100	37.86	701.1	2.09
Pd/ZC-1000	45.20	837.0	4.36
Pd/ZC-900	28.42	526.3	1.75
Pd/ZC-800	7.64	141.5	1.28
Pd/XC-72R	9.20	170.4	0.13

Table S3 The forward anodic peak current density (specific activity I_f and mass activity j_f) in CVs of the Pd catalyst supported on different carbon materials for methanol electrooxidation in alkaline media

Catalyst electrodes	Solutions	Scan rate ($mV\ s^{-1}$)	I_f ($mA\ cm^{-2}$)	j_f ($mA\ mg^{-1}$)	Ref.
Pd/CMS[a]/CRE[b]	1.0 M MeOH + 1.0 M KOH	5	50	500	2a
Pd/graphite block	1.0 M MeOH + 0.5 M NaOH	50	40	80	2b
Pd/PVP-graphene/GCE[c]	0.5 M MeOH + 1.0 M NaOH	100	1.08	8.0	2c
Pd/CNTs[d]/GCE	0.5 M MeOH + 1.0 M KOH	50	34.1	274.5	2d
Pd/VrGO[e]/GCE	1.0 M MeOH + 1.0 M KOH	50	—	620.1	2e
Pd/ZC-1000/GCE	1.0 M MeOH + 1.0 M KOH	50	45.20	837.0	This work
Pd/XC-72R/GCE	1.0 M MeOH + 1.0 M KOH	50	9.20	170.4	This work

[a] carbon microspheres.

[b] carbon rod electrode.

[c] glassy carbon electrode.

[d] carbon naotubes.

[e] vertically oriented reduced graphene oxide.

References

1 Q.-L. Zhu, N. Tsumoria and Q. Xu, *Chem. Sci.*, 2014, **5**, 195.

2 (a) C. Xu, Y.-L. Liu and D.-S.Yuan, *Int. J. Electrochem. Sci.*, 2007, **2**, 674; (b) S. S. Mahapatra and J. Datta, *Int. J. Electrochem.*, 2011, **2011**, 1; (c) Y.-T. Zhang, H.-H. Shu, G. Chang, K. Ji, M. Oyama, X. Liu and Y.-B. He, *Electrochimica Acta*, 2013, **109**, 570; (d) F.-C. Zhu, G.-S. Ma, Z.-C. Bai, R. Q. Hang, B. Tang, Z.-H. Zhang and X.-G. Wang, *J. Power Sources*, 2013, **242**, 610; (e) L.-M. Yang, Y.-H. Tang, S.-L. Luo, C.-B. Liu, H.-J. Song and D.-F. Yan, *ChemSusChem*, 2014, **7**, 2907.