Highly efficient Pd@CN catalysts with quasi-ordered mesopores synthesized from recycled mother liquid of ZIFs

Liu Yang,[a] Zhengyan Qu,[a] Yanhua Shao,[a] Jiuxuan Zhang*,[a] Hong Jiang,[a] Rizhi Chen[a]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing, Jiangsu, P.R. China, 211816

*Corresponding author. jiuxuanz@njtech.edu.cn

Number of pages: 20

Number of Supporting Figures: 13

Number of Supporting Tables: 4

Chemicals

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.99%) and 2-methylimidazole (2-MeIm 99%) were purchased from Sigma-Aldrich. Palladium acetate ($Pd(OAc)_2$, Pd > 47%) was purchased from Sin-platinum Metals Co., Ltd., China. Methanol (MeOH, HPLC pure) and acetone (C_3H_6O, AR) were purchased from Yonghua Chemical Co., Ltd., China. Nitric acid (AR) was purchased from Shanghai Lingfeng Chemical Regent Co., Ltd., China. Phenol (C_6H_5OH, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals were used without further purification.

Characterization

Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT-2000 X-ray diffractometer and Cu-Kα radiation (40 kV, 40 mA) at a scanning rate of 20°/min. A Jobin Yvon HR Evo Raman spectrometer was used to collect Raman spectra. A Hitachi S-4800 instrument was used to obtain field-emission scanning electron microscopy (FESEM) images. A FEI Tecnai G2 F30S-Twin transmission electron microscope was used to obtain high-resolution transmission electron microscopy (HRTEM) images, high-angle annular dark-field scanning TEM (HAADF-STEM) images, and elemental mappings. A Micromeritics ASAP 2020 instrument was used for nitrogen adsorption−desorption experiments, and the pore size distribution curves were obtained by the Barret-Joyner-Halenda method (BJH). A Thermo ESCALAB 250Xi instrument (equipped with a monochromatized Al-Kα radiation, hv =1486.6 eV) was used for X-ray photoelectron spectroscopy (XPS) measurements. The peak devolution was carried out in XPSPEAK, and the C 1s peak (284.6 eV) was used to calibrate the binding energies. Inductively coupled plasma emission spectroscopy (ICP-AES, Optima 2000DV) was used to determine the

metal content. Thermogravimetric analysis (TGA) was conducted on a TG analyzer (NETZSCH STA449 F3) under nitrogen atmosphere from ambient temperature to 800 °C with a heating rate of 10 °C/min. CO_2-temperature programmed desorption (CO_2-TPD, BELCAT-A) was used to determine the basic strength and basicity of the samples. Elemental analysis was studied on a CHN elemental analyzer (Vario EL cube).
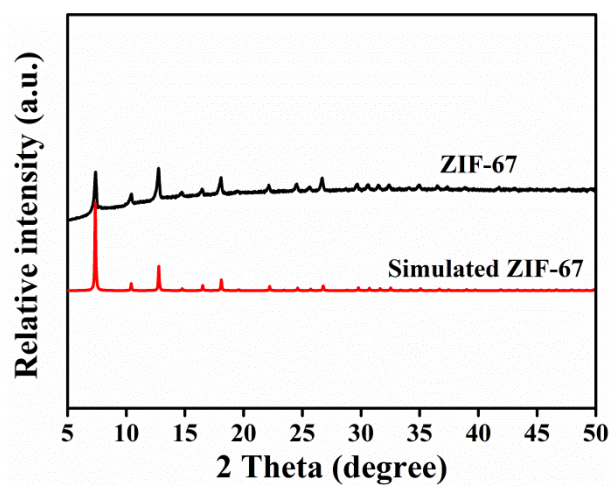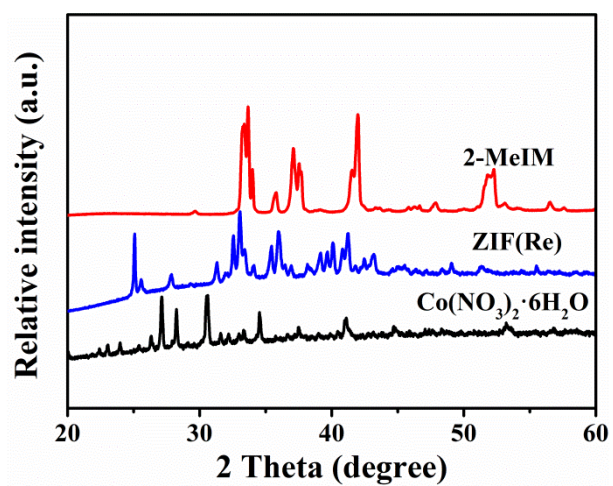
Fig. S1 XRD pattern of ZIF-67

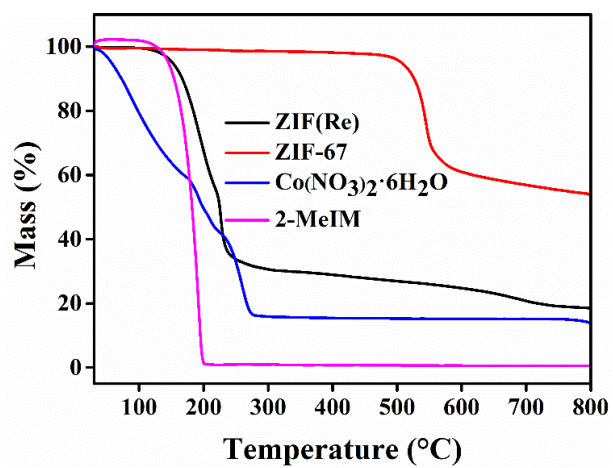**Fig. S2** XRD patterns of ZIF(Re) and precursors

Fig. S3 TG curves of raw materials, ZIF-67, and ZIF (Re)
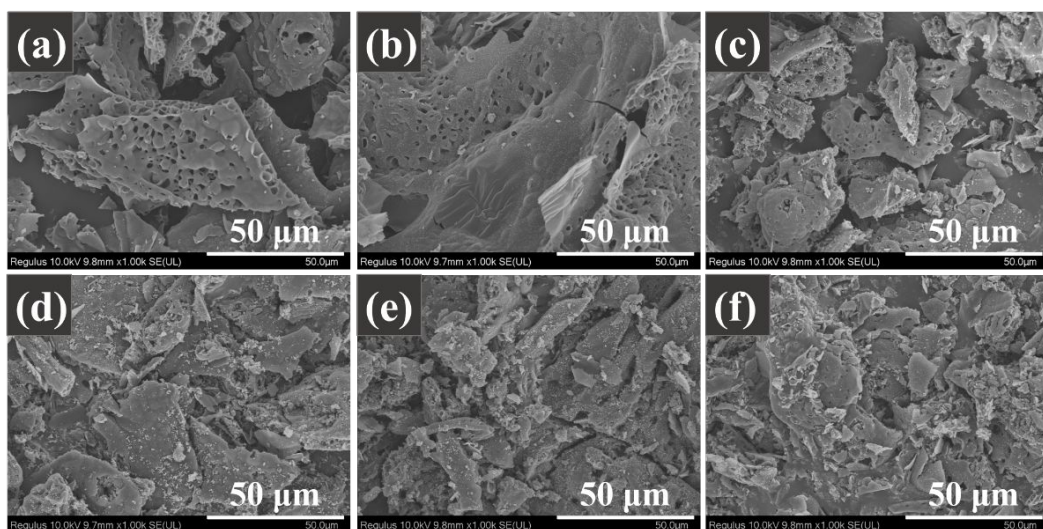
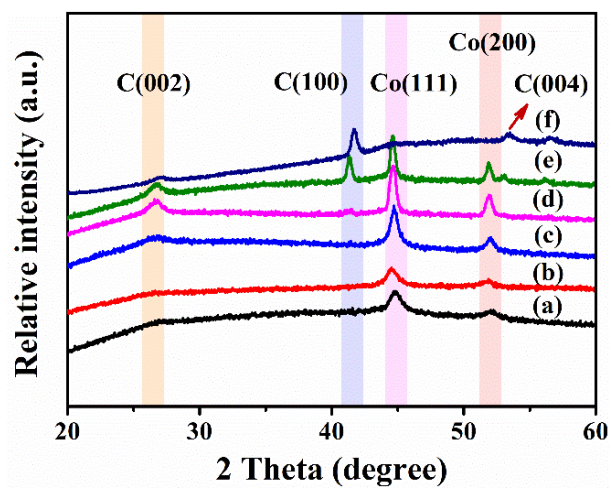**Fig. S4** FESEM images of Co@CN-T (a= 550, b= 600, c= 700, d= 800, e= 900, f= 1000 ^{o}C)

Fig. S5 XRD patterns of Co@CN-T (a= 550, b= 600, c= 700, d= 800, e= 900, f= 1000 °C)
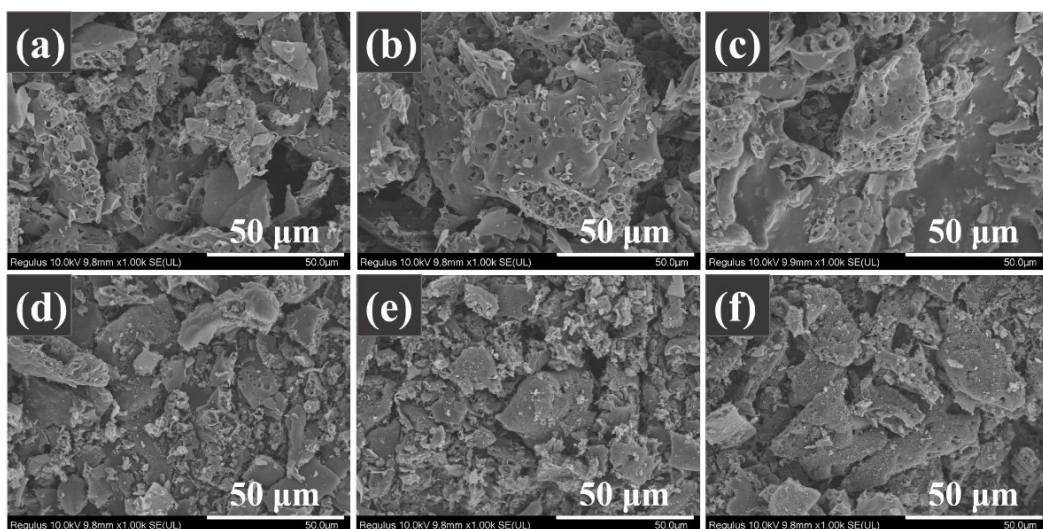
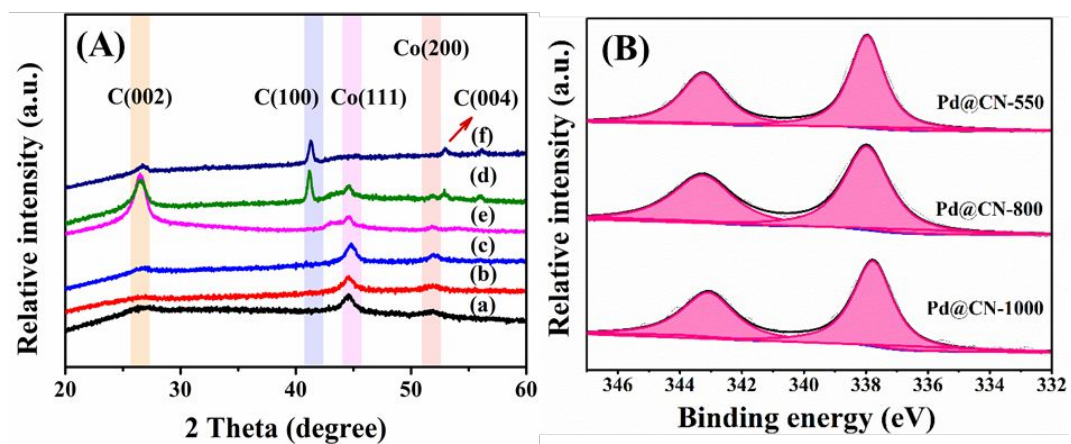**Fig. S6** FESEM images of Pd@CN-T (a= 550, b= 600, c= 700, d= 800, e= 900, f= 1000 ^{o}C)

Fig. S7 XRD patterns of Pd@CN-T (a= 550, b= 600, c= 700, d= 800, e= 900, f= 1000 °C) (A) and
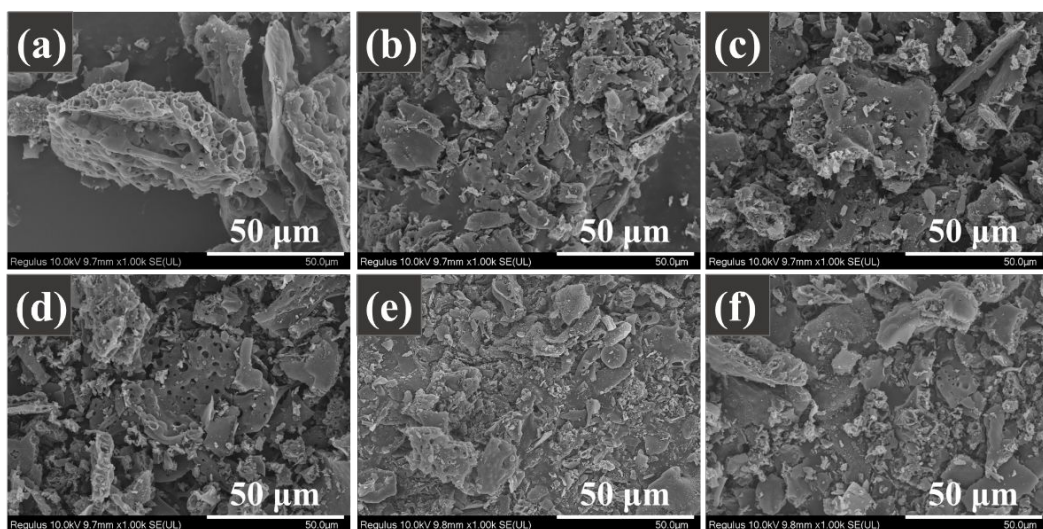
Pd 3d spectra of Pd@CN (B)

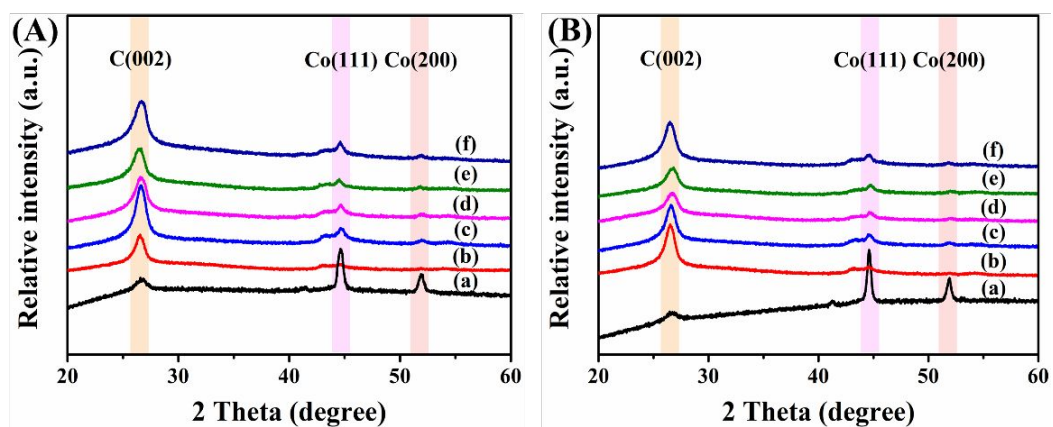**Fig. S8** FESEM images of Pd@CN-800-t (a= 0, b= 30, c= 60, d= 90, e= 120, f= 180 min)

Fig. S9 XRD patterns of CN-800-t (A) and Pd@CN-800-t (B)

(a= 0, b= 15, c= 30, d= 60, e= 120, f= 180 min)
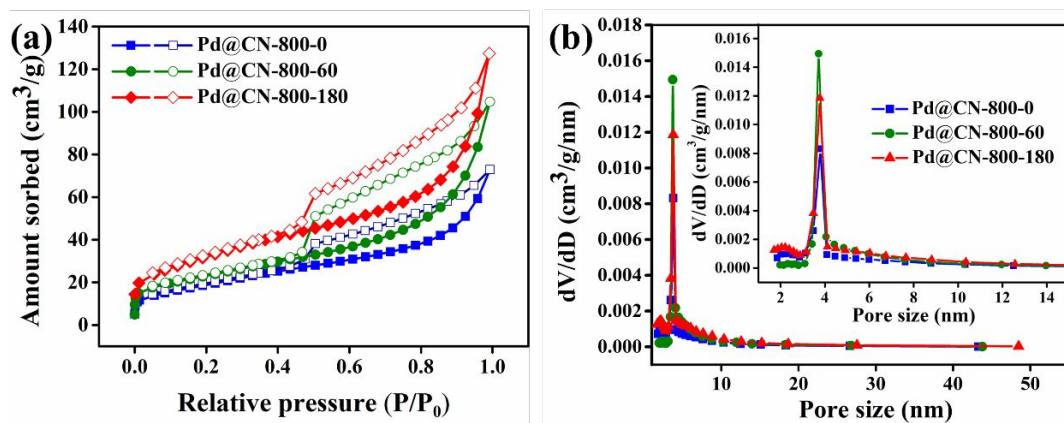
Fig. S10 Nitrogen adsorption-desorption isotherms (a) and pore size distribution curves (b) of
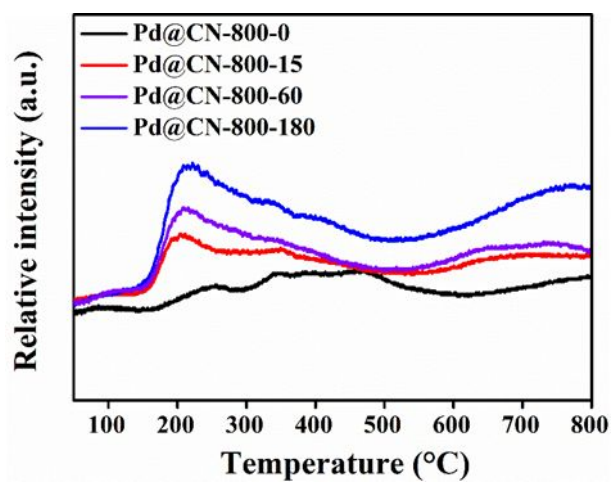
Pd@CN-800

Fig. S11 CO$_2$-TPD spectra of Pd@CN-800
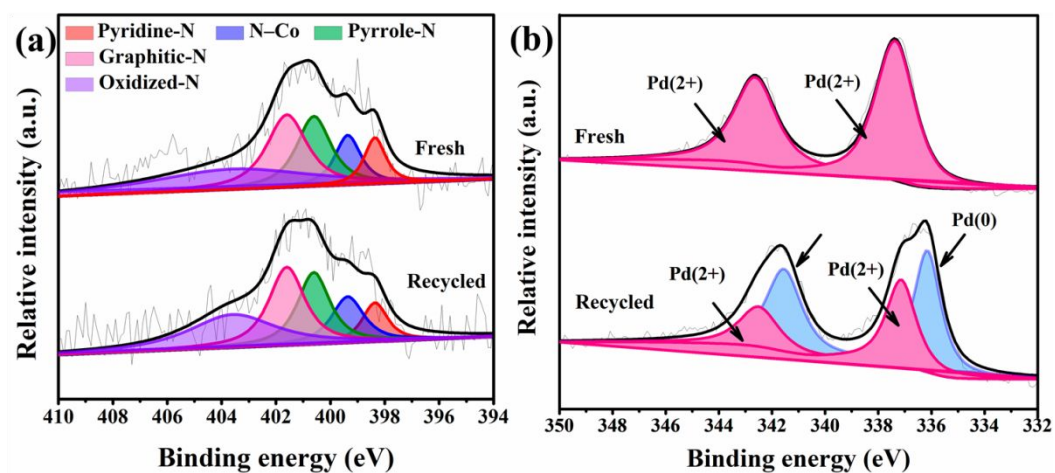
Fig. S12 N 1s spectra (a) and Pd 3d spectra (b) of fresh and recovered Pd@CN-800-60
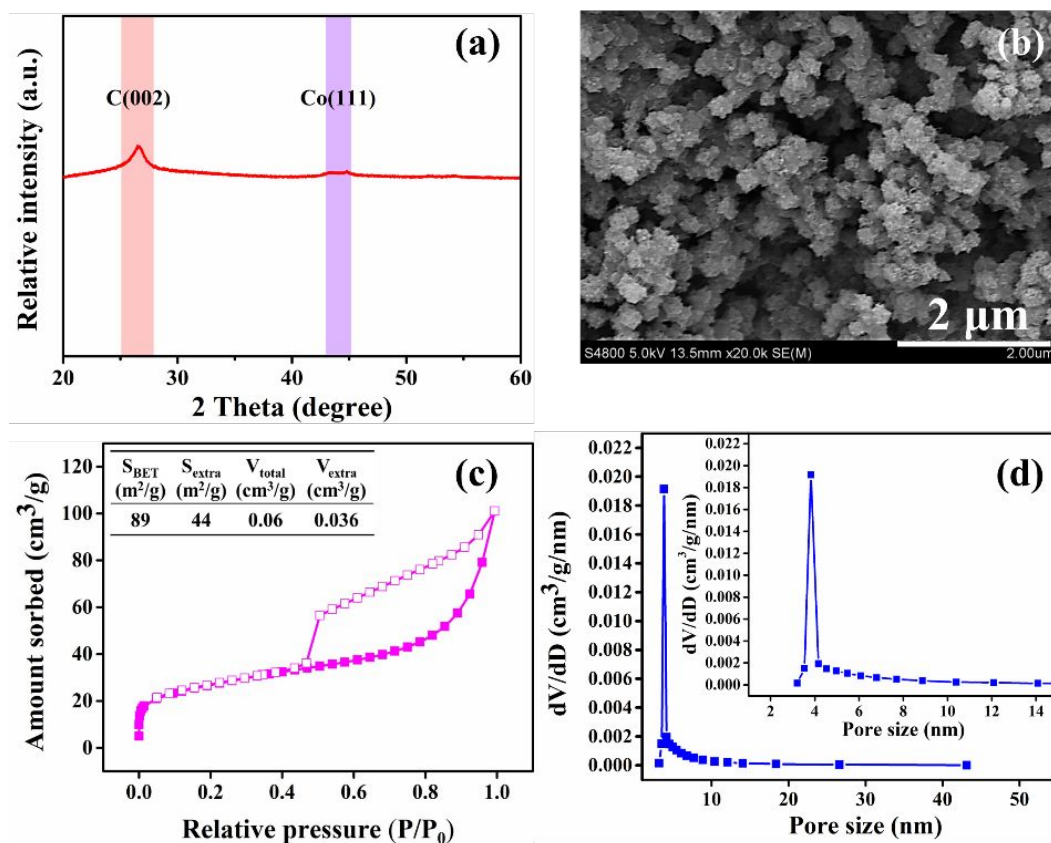
Fig. S13 XRD pattern (a), FESEM image (b), N$_2$ sorption isotherms (c), pore size distribution curve (d) of Pd@CN(67)-800-60

Table S1 Productivity of ZIFs and the corresponding derived carbon materials after different
stages

Samples	Crystallization (g)	Carbonization (g)	Pickling (g)	Pd loading (g)
ZIF(Re)	9.04	1.74	1.56	1.50
ZIF-67	1.20	0.74	0.46	0.44

Table S2 Contents of elements in ZIFs and CN-800

Samples	C (wt. %)[a]	N (wt. %)[a]	H (wt. %)[a]	Co (wt. %)[b]
ZIF-67	43.1	25.4	5.0	27.9
ZIF(Re)-1	46.2	31.0	5.0	5.0
ZIF(Re)-2	46.2	31.0	6.1	5.0
ZIF(Re)-3	46.2	30.9	6.4	5.1
CN(67)-800	90.8	1.1	2.3	0.10
CN(Re)-800	91.0	1.0	3.2	0.08

[a] measured by a CHN elemental analyzer, [b] measured by ICP

Table S3 Surface areas and total pore volumes of Co@CN-800, CN-800 and Pd@CN-800

Samples	S_{BET} (m^2/g)	S_{extra} (m^2/g)	S_{extra} /S_{BET}	V_{total} (cm^3/g)	V_{extra} (cm^3/g)	V_{extra} /V_{total}
ZIF(Re)	5	1	0.20	0.004	0.002	0.50
Co@CN-800	116	56	0.48	0.16	0.12	0.75
CN-800	175	62	0.35	0.19	0.13	0.68
Pd@CN-800-0	58	50	0.86	0.11	0.10	0.91
Pd@CN-800-60	74	63	0.85	0.16	0.15	0.94
Pd@CN-800-180	107	75	0.70	0.20	0.18	0.89

$$S_{extra}= S_{BET}- S_{mic} \tag{1}$$

$$V_{extra}= V_{total}- V_{mic} \tag{2}$$

Table S4 Contents of elements in Pd@CN-800

Samples	C (wt. %)[a]	N (wt. %)[a]	H (wt. %)[a]	Pd (wt. %)[b]	Co (wt. %)[b]
Pd@CN-800-0	70.62	1.13	2.36	0.96	23.8
Pd@CN-800-15	92.88	0.86	2.09	1.52	0.57
Pd@CN-800-30	90.10	1.31	2.08	1.94	0.18
Pd@CN-800-60	87.70	1.67	1.92	2.13	0.20
Pd@CN-800-120	88.54	1.70	2.24	2.06	0.23
Pd@CN-800-180	89.49	1.44	1.76	1.97	0.22

[a] measured by a CHN elemental analyzer, [b] measured by ICP