

Supporting Information

Metallo-supramolecular polymers engineered porous carbon frameworks encapsulated stable ultra-small nanoparticles: a general approach to construct highly dispersed catalysts

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1. General information of characterization

The materials morphology was observed by the JEOL SU-8010 scanning electron microscopy (SEM) and JEM-2100F high resolution transmission electron microscopy (HR-TEM). The scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) are accessories of the HR-TEM apparatus. Fourier transform infrared (FT-IR) spectra were obtained by a Bruker IFS28 spectrometer in the region of 4000–500 cm^{-1} . The solid-state nuclear magnetic resonance (NMR) instrument was JEOL JNMECZ600R. The X-ray diffraction (XRD) experiments were recorded on a Rigaku corporation Smart-Lab, diffractometer using Cu K α radiation ($\lambda = 0.1541 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI Quantera SXM spectrometer, ULVAC-PHI, and the binding energy determination was based on the C 1s at 284.8 eV with an experimental error of $\pm 0.2 \text{ eV}$. Nitrogen adsorption/desorption measurements were conducted with a Tristar II 3020 volumetric adsorption analyzer at $-196 \text{ }^{\circ}\text{C}$. Thermogravimetric analysis (TGA) was carried with a STA449F3 instrument under air atmosphere. Raman spectra were recorded with a Horiba HR-800 spectrometer equipped with a charge coupled device detector cooled by liquid nitrogen. The inductively coupled plasma mass spectrometry (ICP-MS) is PerkinElmer ELAN DRC-e. The AFM was Cypher S (Asylum Research). The detailed reaction procedure was further detected by the UV-visible spectrophotometer (UV-6100 double-beam spectrophotometer). This reaction system was also applied to the hydrogenation of varieties of nitroaromatics with different functional groups. All reactions were monitored by TLC (petroleum ether/ethyl acetate), HPLC (Waters, Kromasil 5mm C18 column) and detected by GC-MS (Bruker 450GC-320MS).

2. Materials characterization

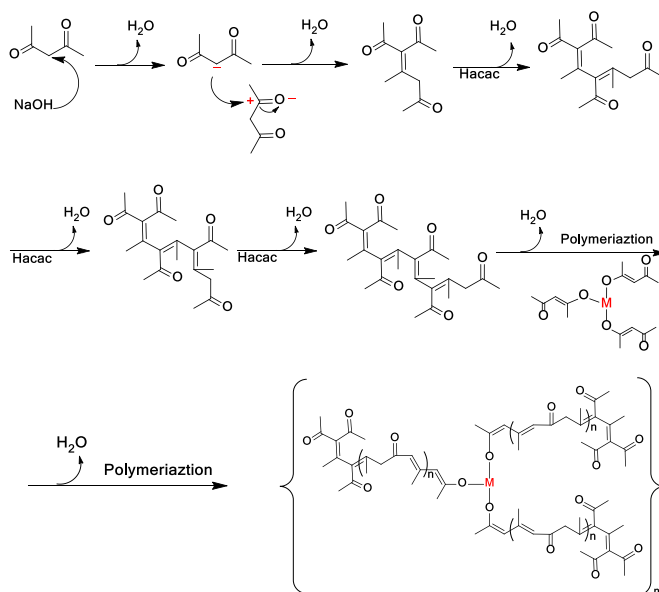


Figure S1. Pathway for the fabrication of metallo-supramolecular polymers.

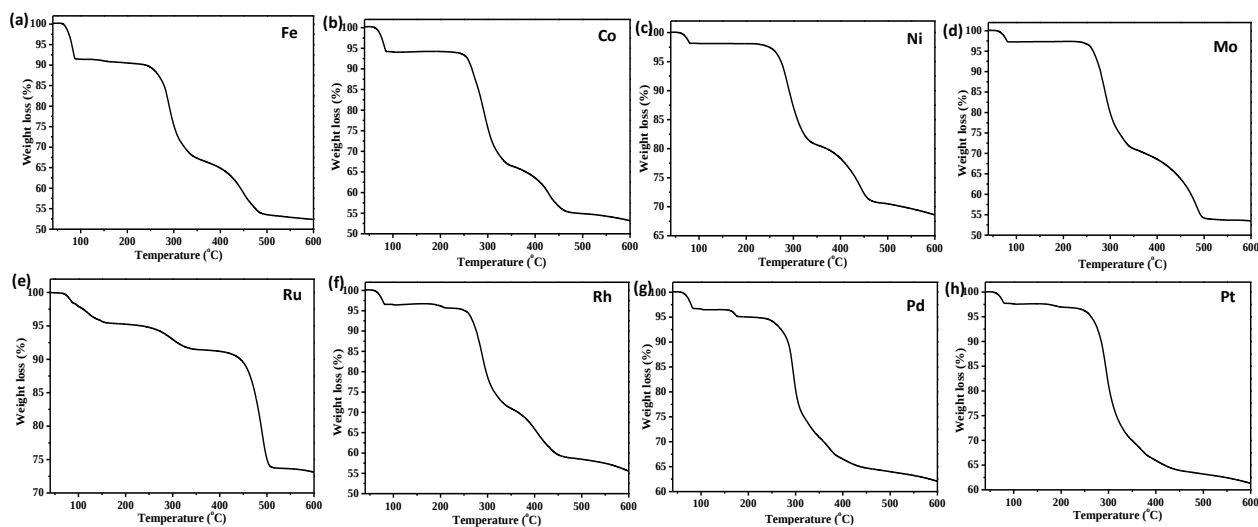


Figure S2. TGA curves of the metallo-supramolecular polymer precursor: (a) Fe, (b) Co, (c) Ni, (d) Mo, (e) Ru, (f) Rh, (g) Pd, (h) Pt.

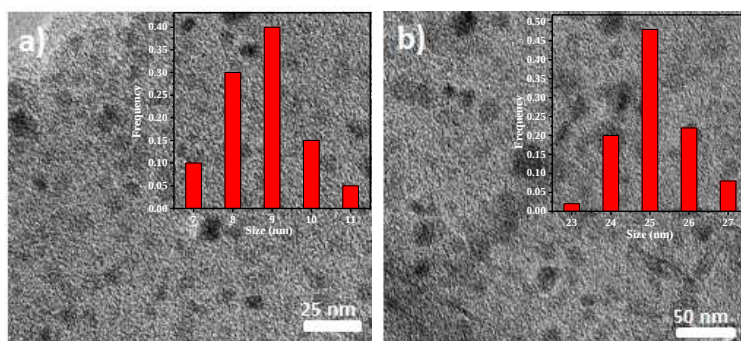


Figure S3. HR-TEM images of Pd@PCF that the polymer precursors annealed at (a) 600 °C and (b)800 °C.

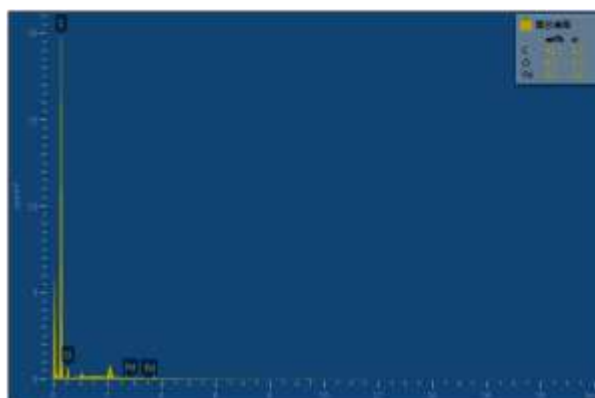


Figure S4. EDS spectrum of Pd@PCF.

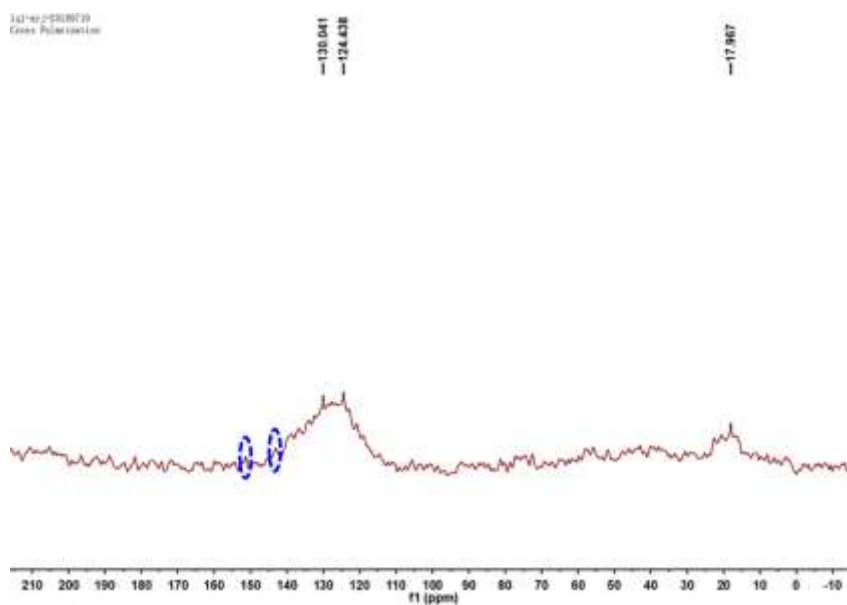


Figure S5. (a) The solid-state ^{13}C NMR of Pd@PCF.

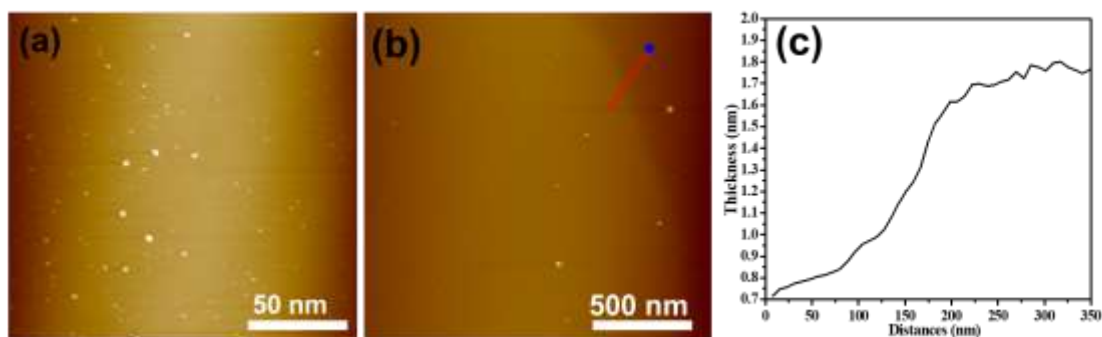


Figure S6. (a) AFM images of the Pd@PCF nanocatalysts, (b-c) the thickness of the PCF.

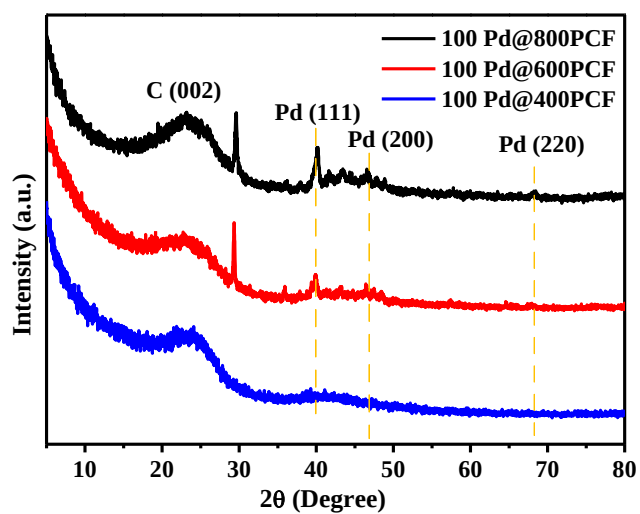


Figure S7. The XRD pattern of Pd@PCF annealed at different temperature.

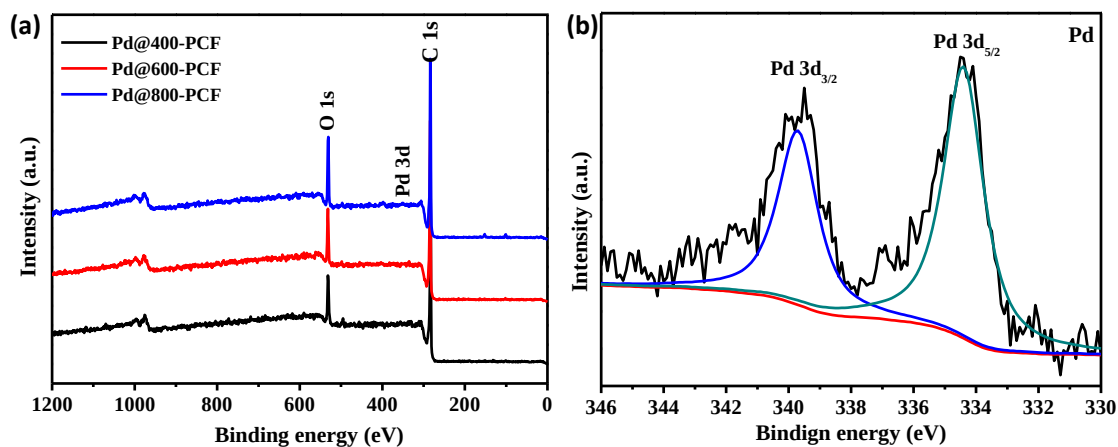


Figure S8. (a) XPS survey spectrum of the Pd@PCF obtained from different temperature; (b) XPS spectrum of the Pd 3d region of Pd@PCF.

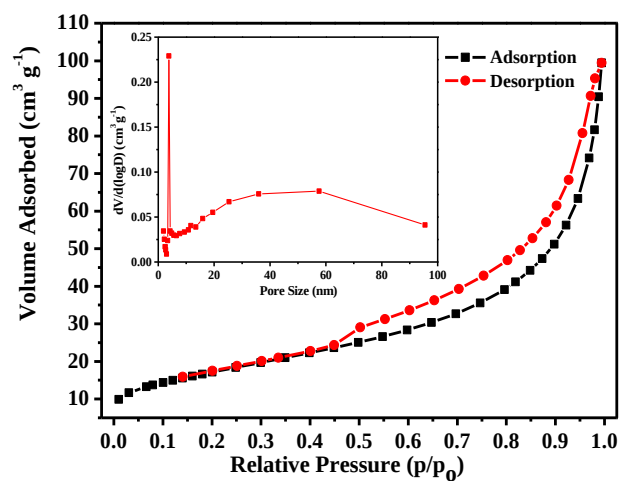


Figure S9. Nitrogen adsorption/desorption isotherms of the Pd@PCF nanocatalysts.

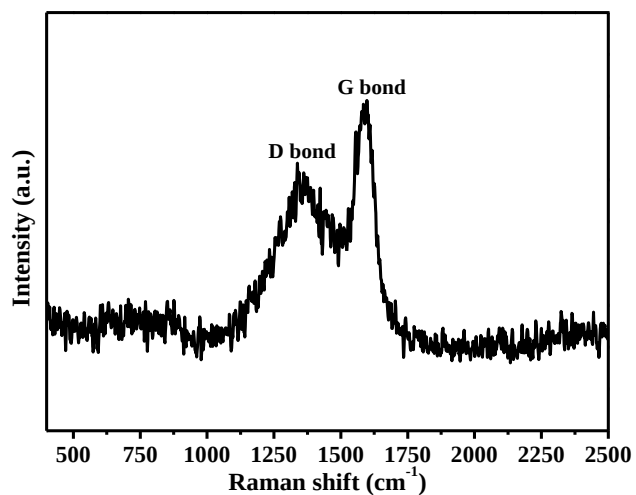


Figure S10. Raman spectra of the Pd@PCF nanocatalysts.

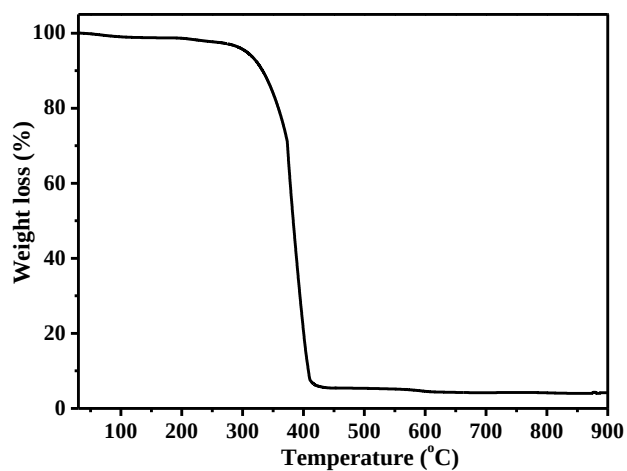


Figure S11. TGA curves of the Pd@PCF nanocatalysts (air atmosphere).

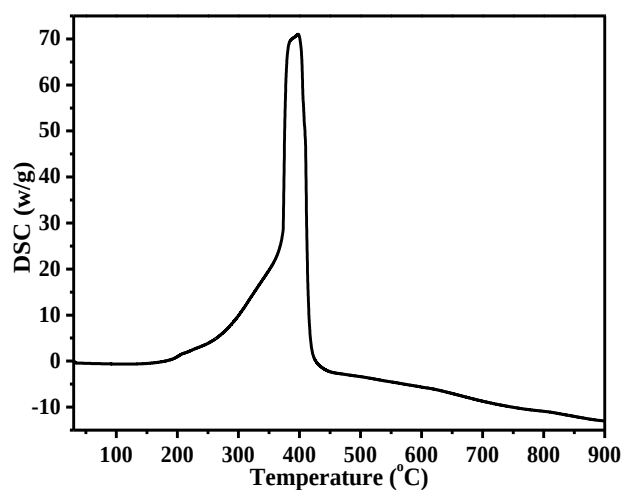


Figure S12. DSC curves of the Pd@PCF nanocatalysts (air atmosphere)

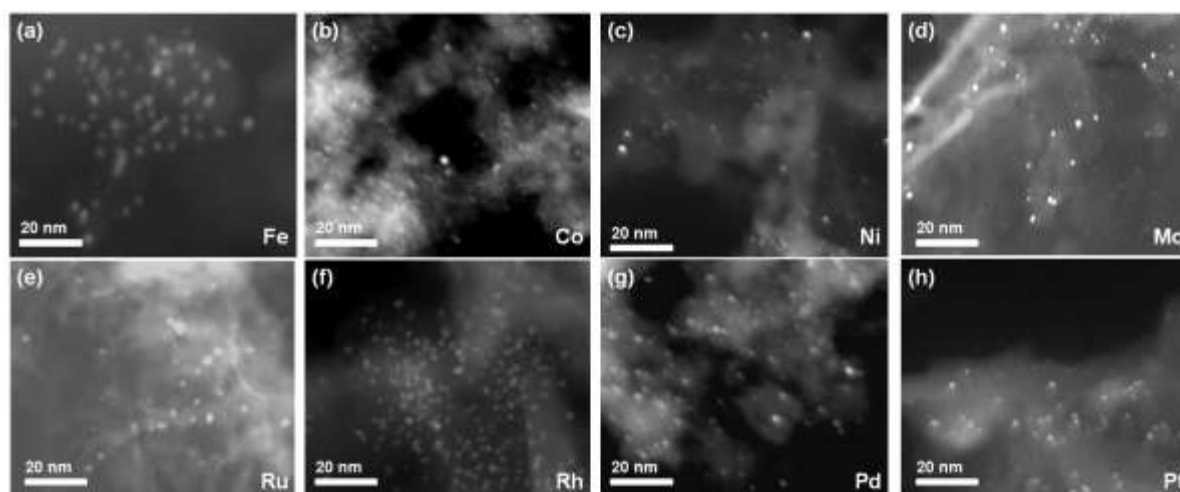


Figure S13. STEM images of M@PCF: (a) Fe, (b) Co, (c) Ni, (d) Mo, (e) Ru, (f) Rh, (g) Pd, (h) Pt

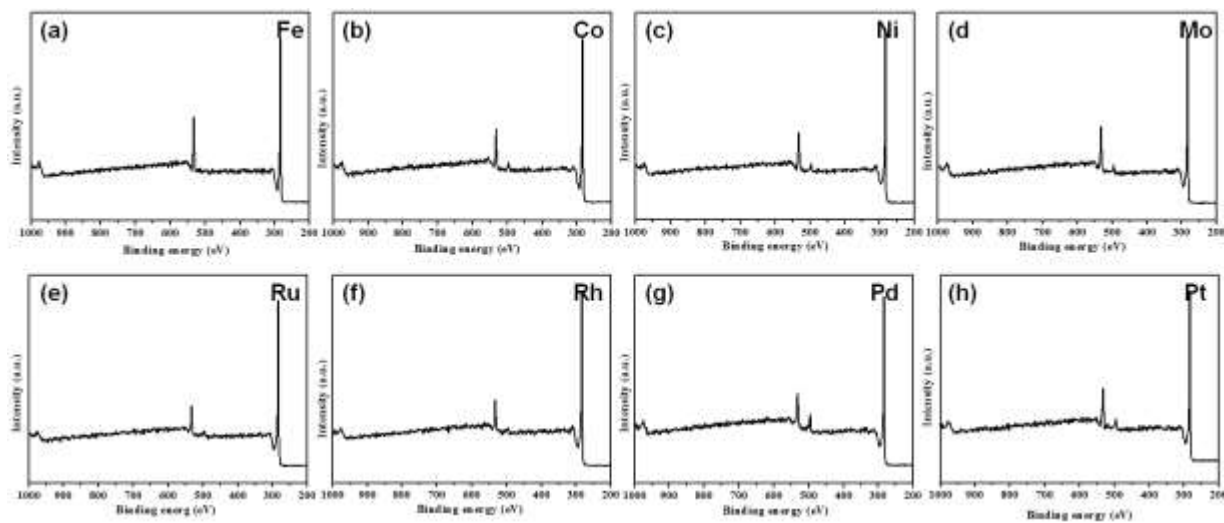


Figure S14. XPS survey spectroscopy of M@PCF: (a) Fe, (b) Co, (c) Ni, (d) Mo, (e) Ru, (f) Rh, (g) Pd, (h) Pt



Figure S15. TEM image of ultra-small Pd nanoparticles as Prasad reported.

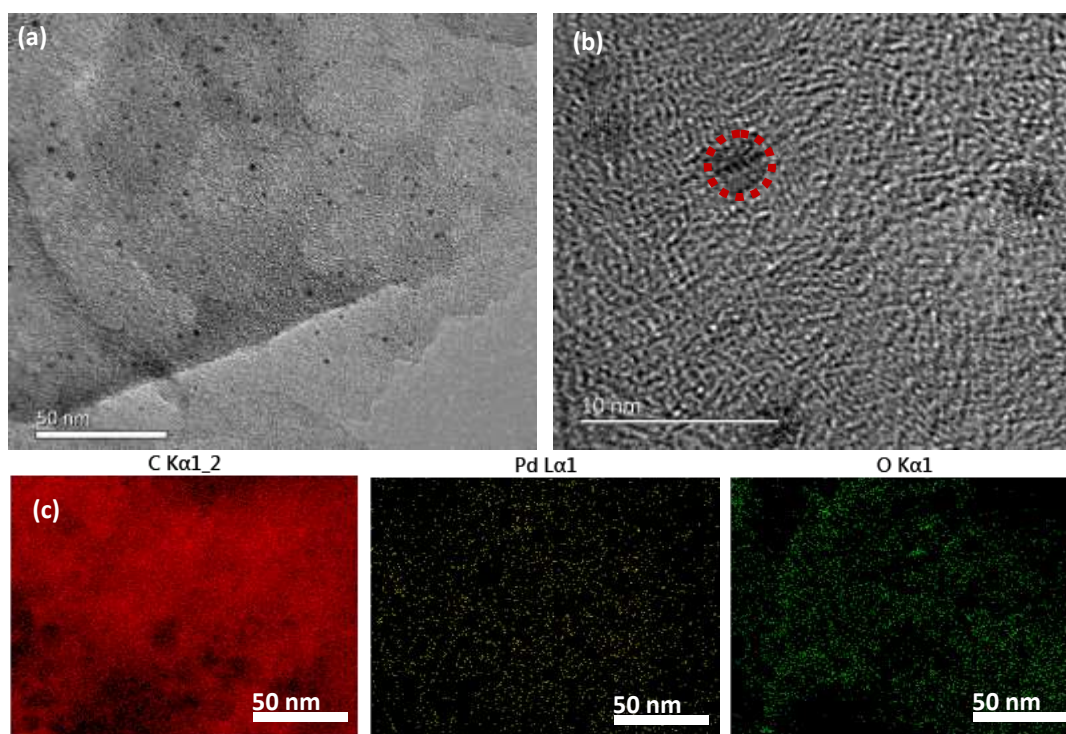


Figure S16. (a-b) HRTEM, (c) EDS images of Pd@PCF after used for 10 cycles.

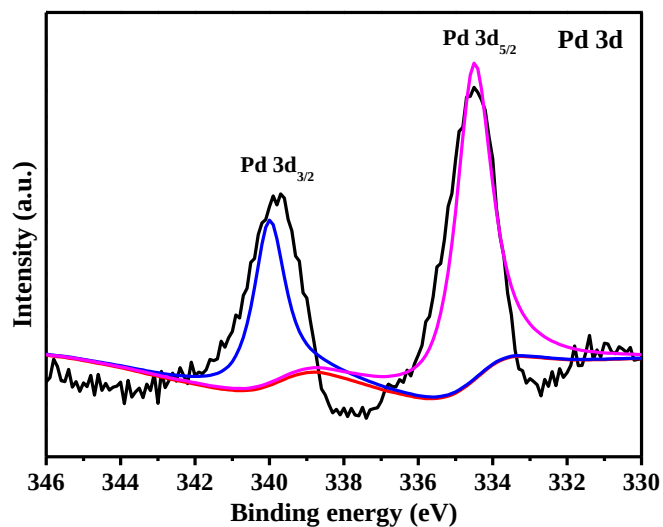


Figure S17. XPS spectrum of the Pd 3d region of the reused Pd@PCF.

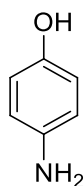
3. Comparison of catalyst activity

Table S1. Comparison of the ability of various noble metal-based catalysts for catalyzing hydrogenation of nitroarenes.

Entry	Catalyst	Reactant	Time (min)	Conv. (%)	TOF (h ⁻¹)	Ref.
1	Pd NP/CNT	4-nitrophenol	7	>99	1080	1
2	Pd@CPP-F	nitrobenzene	60	>99	228	2
3	Pd ₅ NC/PN-CeO ₂	4-nitrophenol	120	>99	10900	3
4	Pd/CNT _{EG}	4-chloronitrobenzene	120	>99	7440	4
5	Pd@Beta	4-chloronitrobenzene	120	>99	1520	5
6	Pd/Gd(OH) ₃	4-nitrophenol	1	>99	2176	6
7	Pd/MCB-EG	nitrate	150	>99	366	7
8	GO@AC/Pd	4-nitrophenol	1.65	>99	36120	8
9	Pd/TiO ₂	4-nitrophenol	5	90	560	9
10	Pt/FeOx	3-nitrostyrene	50	>99	1500	10
11	PtNPs@COF	4-nitrophenol	8	>99	17	11
12	RhNPs/SBA-NH ₂	4-nitrophenol	10	>99	3059	12
13	RhNPs	4-nitrophenol	7	>99	4373	13
14	Ru/CNTs-ht	4-chloronitrobenzene	240	>99	694	14
15	Ru Complex	4-nitrophenol	1200	>99	0.5	15
16	Fe ₃ O ₄ /C@Au	4-nitrophenol	3.3	>99	1044	16
17	Au/NPG	3-nitrostyrene	720	85	0.35	117
18	AgNCs	4-nitrophenol	120	>99	67	18
19	Pd@PCF-400	4-nitrophenol	4	>99	11400	This work

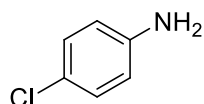
4. GC-MS Data of Anilines:

4-Aminophenol (Table 2, entry 1):



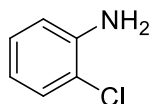
GC-MS: m/z (%) 109 (100) $[M]^+$, 80 (50), 52 (14).^[19]

4-Chlorobenzenamine (Table 2, entry 2):



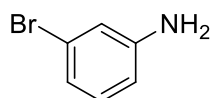
GC-MS: m/z (%) 127 (100) $[M]^+$, 92 (13), 65 (21).^[20]

2-Chloroaniline (Table 2, entry 3):



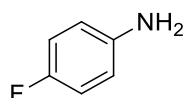
GC-MS: m/z (%) 127 (100) $[M]^+$, 92 (14), 65 (17).^[21]

3-Bromoanilines (Table 2, entry 4)



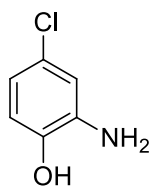
GC-MS: m/z (%) 173 (100) $[M]^+$, 92 (91), 65 (85).^[21]

4-Fluoroaniline (Table 2, entry 5)



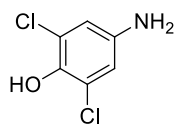
GC-MS: m/z (%) 111 (100) $[M]^+$, 84 (43), 57 (11).^[21]

2-Hydroxy-5-chloro-aniline (Table 2, entry 6):



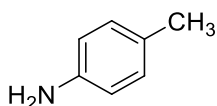
GC-MS: m/z (%) 143 (100) $[M]^+$, 114 (14), 80 (31), 51 (10).^[22]

2,6-Dichloro-4-aminophenol (Table 2, entry 7):



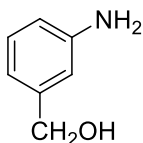
GC-MS: m/z (%) 177 (100) $[M]^+$, 113 (87), 78 (60), 52 (16).^[22]

4-Toluidine (Table 2, entry 8):



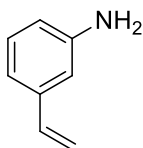
GC-MS: m/z (%) 106 (100) $[M]^+$, 77 (12). Physical and spectral data were consistent with those previously reported.^[23]

(3-Aminophenyl)-methanol (Table 2, entry 9):



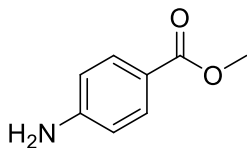
GC-MS: m/z (%) 123 (100) $[M]^+$, 94 (74), 77 (30), 65 (13), 39 (8).^[24]

3-Aminostyrene (Table 2, entry 10):



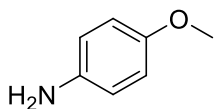
GC-MS: m/z (%) 119 (100) $[M]^+$, 91 (28), 89 (5), 65 (13).^[25]

Methyl 4-aminobenzoate (Table 2, entry 11):



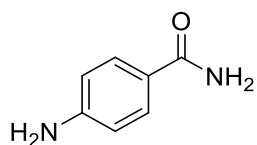
GC-MS: m/z (%) 151 (54) $[M]^+$, 120 (100), 92 (26), 65 (20).^[26]

4-Methoxyaniline (Table 2, entry 12):



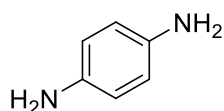
GC-MS: m/z (%) 108 (100) $[M]^+$, 80 (36), 53 (14).^[26]

4-Aminobenzamide (Table 2, entry 13):



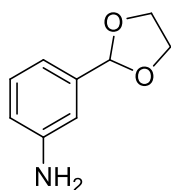
GC-MS: *m/z* (%) 136 (73) [M]⁺, 120 (100), 92 (34), 65 (27), 39 (8).^[23]

1,4-Benzenediamine (Table 2, entry 14):



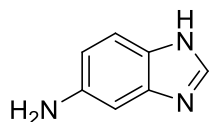
GC-MS: *m/z* (%) 108 (100) [M]⁺, 80 (33), 53 (10).^[22]

5-(Aminophenyl)-1,3-dioxolane (Table 2, entry 15):



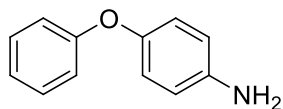
GC-MS: *m/z* (%) 165 (99) [M]⁺, 120 (52), 93 (100), 65 (26).^[23]

6-Amino-1H-benzimidazole (Table 2, entry 16):



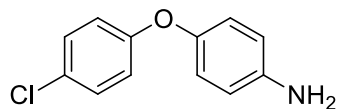
GC-MS: *m/z* (%) 133 (100) [M]⁺, 106 (15), 78 (8), 52 (12).^[21]

4-Aminodiphenyl ether (Table 2, entry 17):



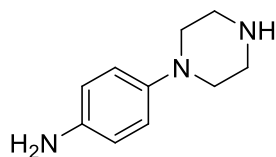
GC-MS: *m/z* (%) 185 (100) [M]⁺, 156 (17), 108 (74), 80 (25), 51 (13).^[27]

4-(4-Chlorophenoxy)benzenamine (Table 2, entry 18):



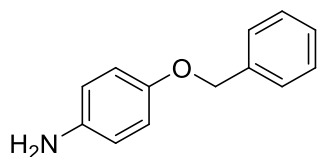
GC-MS: *m/z* (%) 219 (72) [M]⁺, 156 (13), 108 (100), 80 (30).^[24]

1-(4-Aminophenyl)piperazine (Table 2, entry 19):



GC-MS: m/z (%) 177 (51) $[M]^+$, 135 (100), 120 (30), 92 (10) 65 (11).^[27]

4-(Benzyloxy)benzenamine (Table 2, entry 20):



GC-MS: m/z (%) 199 (15) $[M]^+$, 108 (100), 91 (29), 80 (14), 53 (5).^[28]

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Faraday Discuss. **2018**, DOI: 10.1039/c7fd00216e.

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