PdO Nanoparticles Enhancing the Catalytic Activity of Pd/Carbon Nanotubes for 4-Nitrophenol Reduction

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1. Materials

All chemicals were used as received without further purification: Palladium (Ⅱ) nitrate dihydrate, Potassium tetrachloropalladate, (Sinopharm Chemical Reagent Beijing Co., Ltd). Palladinum (Ⅱ) acetate, Palladium dichloride, 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4), (Tokyo Chemical Co., Ltd). Ethanol, methylene chloride (CH_2Cl_2), Acetone, acetic ether, tetrahydrofuran, toluene, N,N-Dimethylformamide (DMF), (Beijing chemical works).

2. Experimental setup

Figure S1 shows the experimental setup of the gas-liquid interfacial plasma. The glow discharge plasma was generated between the top flat stainless steel (SUS) and bottom ionic liquid electrode by using a DC power source (KIKUSUI PMC500-0.1A). Argon gas was introduced and used as the plasma-forming gas. The chamber was a stainless steel with inner diameter of 70 mm and four glass windows, and the gap between electrodes is 4mm.

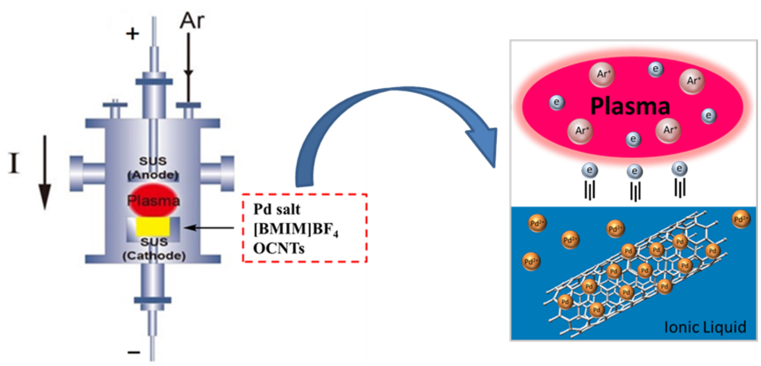

Figure S1. A schematic illustration of plasma system.

3. The TEM images of Pd-1, Pd-2, Pd-3, Pd-4

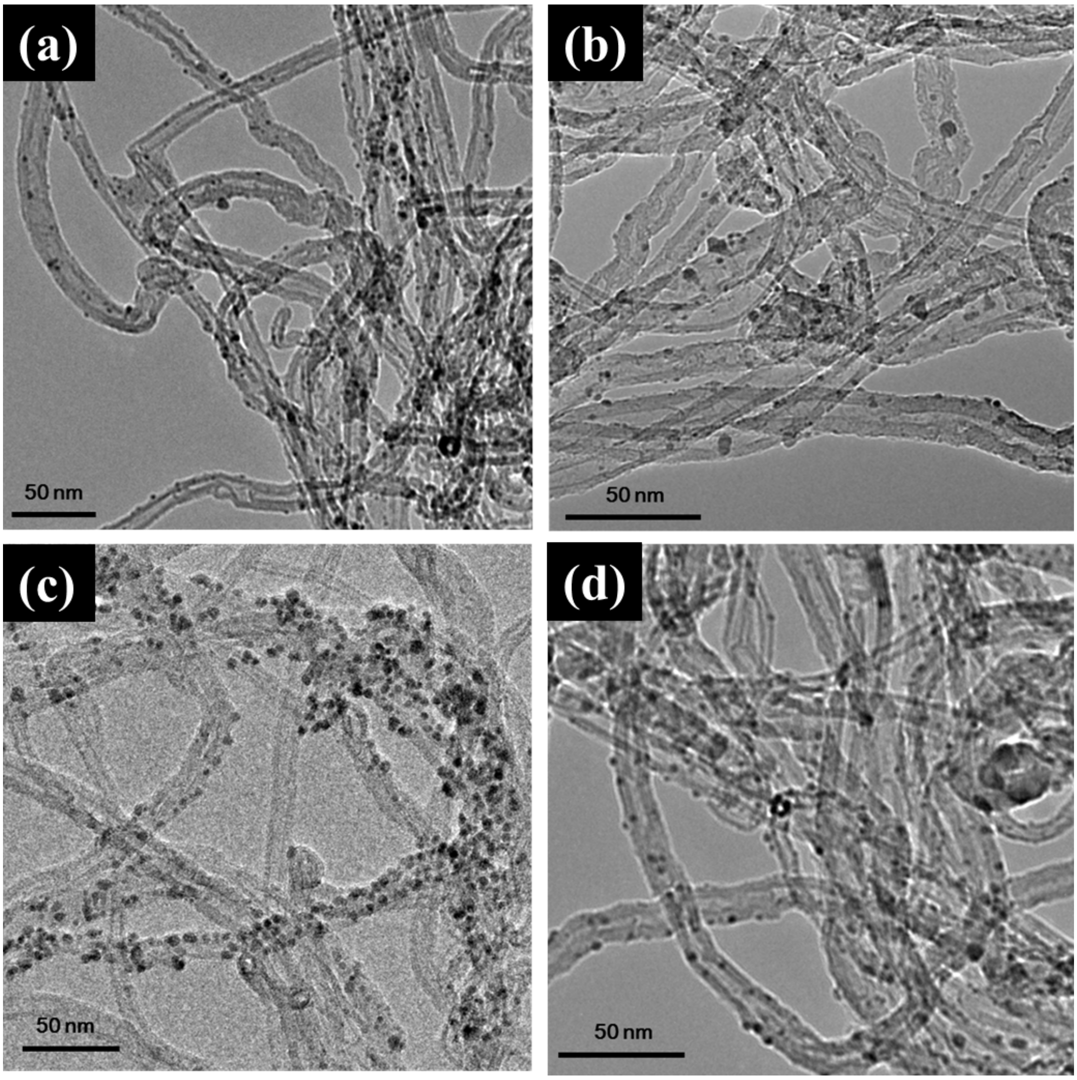

Figure S2. TEM images of Pd-1 (a), Pd-2 (b), Pd-3 (c), Pd-4 (d).

4. The size distribution of Pd nanoparticles decorated on the surface of OCNTs

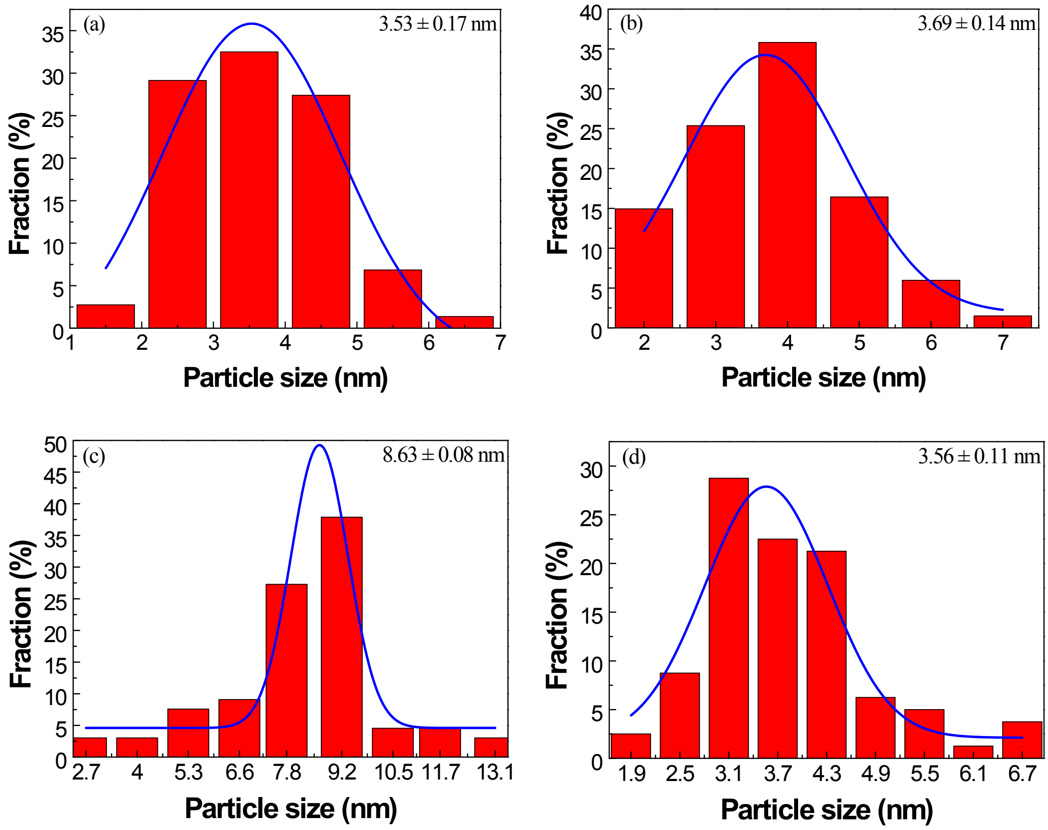

Figure S3. Particle size distribution of Pd-1 (a), Pd-2 (b), Pd-3 (c), Pd-4 (d) from the TEM images in Fig. S2.

5. The TEM images of Pd-5

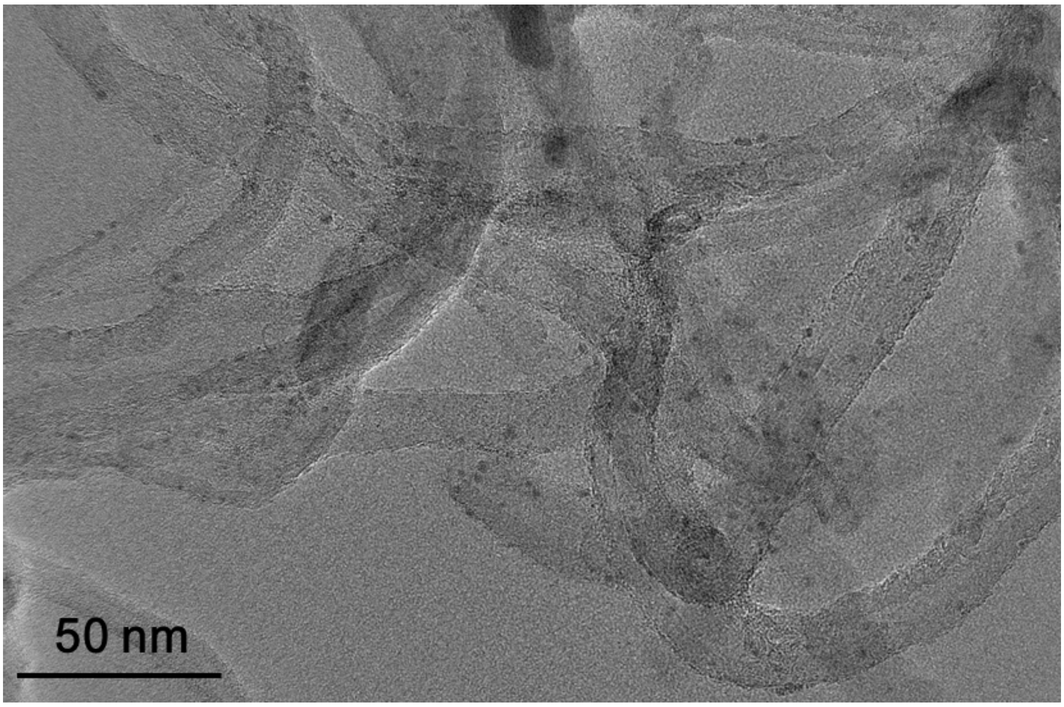

Figure S4. TEM images of Pd-5.

6. The characterization results of Pd-5.

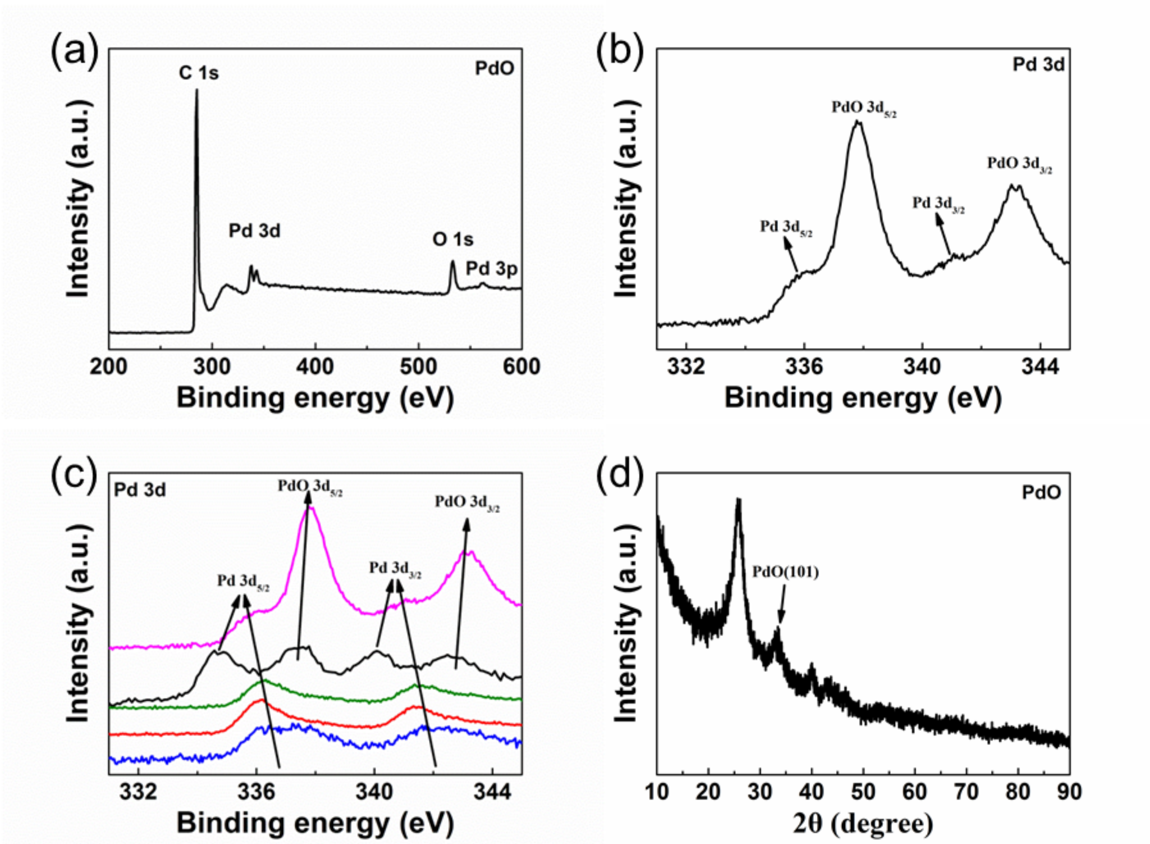

Figure S5. XPS spectra of Pd-5 (a), (b); (c) the enlarged XPS spectra of Pd3d of Pd-5 (magenta), Pd-1 (black curve), Pd-2 (olive curve), Pd-3 (red curve) and Pd-4 (blue curve); (d) The XRD patterns of Pd-5.

7. High-resolution XPS spectra of C1s of Pd-1

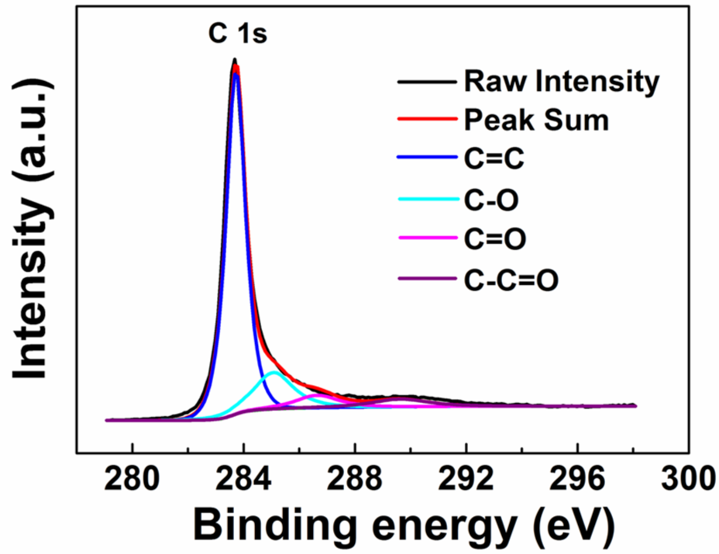

Figure S6. High-resolution XPS spectra of C1s of Pd-1.

8. UV-vis spectra of Pd-n catalysts for 4-NP reduction reaction

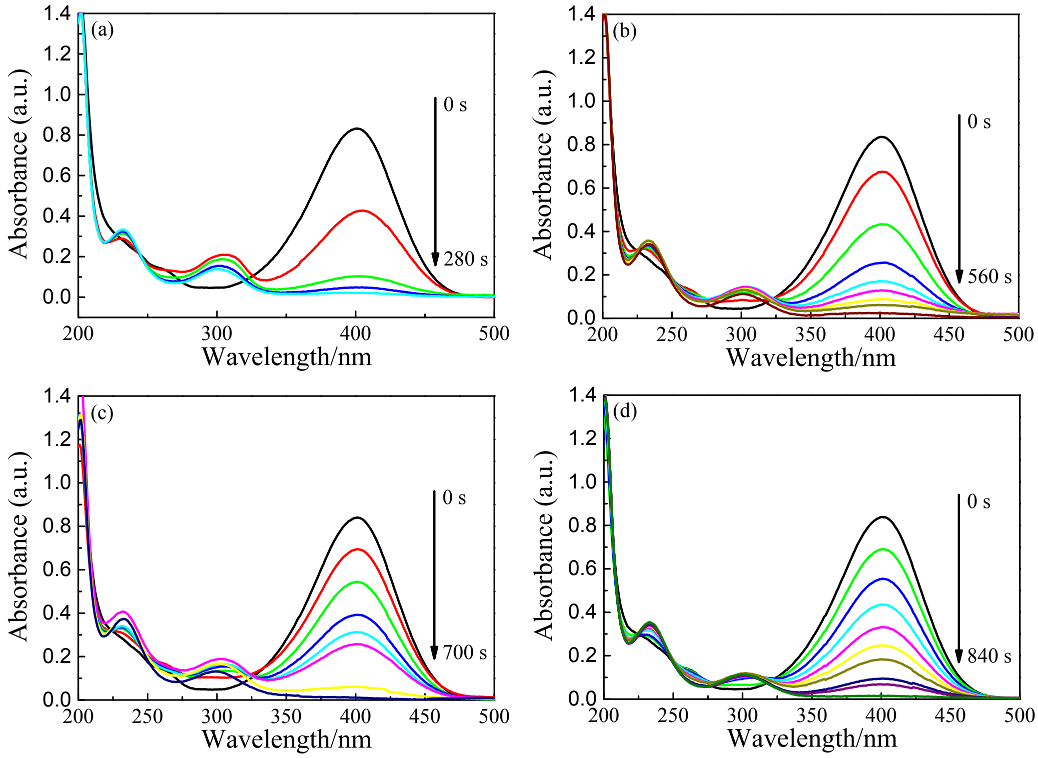

Figure S7. UV-vis spectra of 4-NP in water after the addition of $NaBH_4$ and successive absorption spectra of the conversion from 4-NP to 4-AP with Pd-n catalysts: Pd-1 (a), Pd-2 (b), Pd-3 (c), Pd-4 (d).

9. UV-vis spectra of Pd-5 catalysts for 4-NP reduction reaction

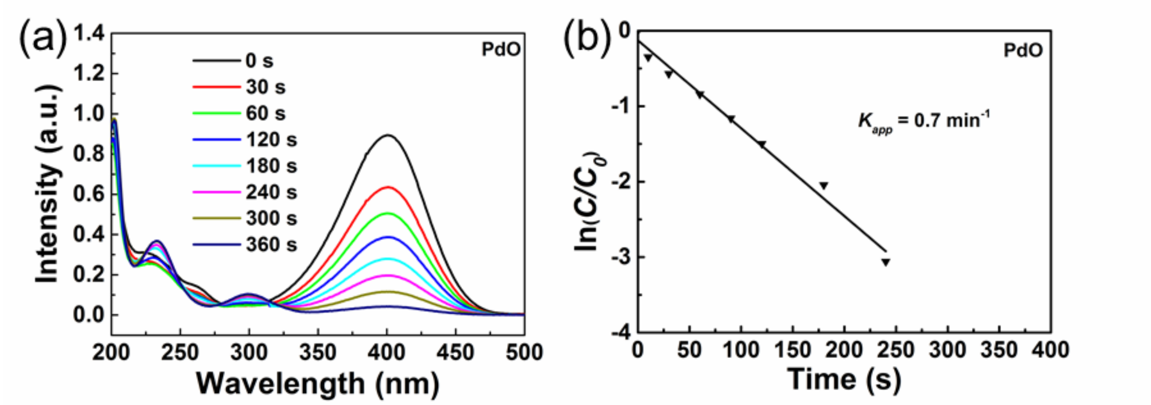

Figure S8. Successive absorption spectra of the conversion from 4-NP to 4-AP with PdO catalysts (a); (f) plots of $\ln(C/C_0)$ versus time for the conversion from 4-NP to 4-AP with Pd-5 catalysts.

10. Apparent rate constant of Pd-n catalysts for 4-NP reduction reaction

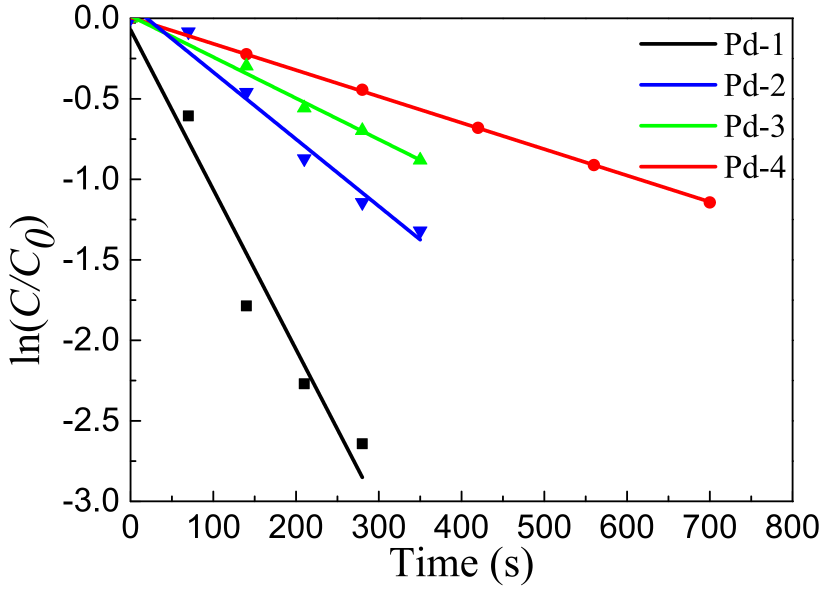

Figure S9. Plots of ln(C/C_0) versus time for the conversion from 4-NP to 4-AP with Pd-n catalysts.

11. The TEM images of the reused Pd-1 catalyst

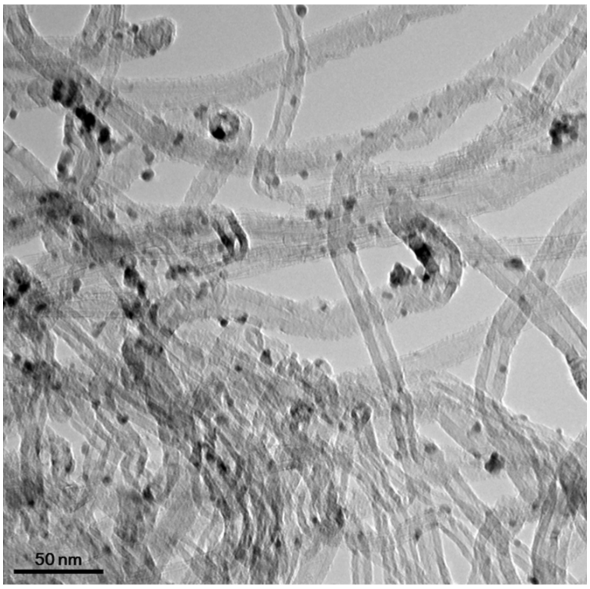

Figure S10. TEM image of Pd-1 catalyst after 10 cycles

Table S1. Pd nanoparticle size (nm)[a] and Pd loading on OCNTs (wt.%)[b].

Sample	Pd-1	Pd-2	Pd-3	Pd-4
Pd-n size (nm)	3.5	3.7	8.6	3.6
Pd loading (wt.%)	9.5	10.0	5.1	8.5

[a] Average size obtained from the size distribution histogram.

[b] Calculated by ICP.

Table S2. Apparent reaction rates k_{app} values for the Pd-n catalysts for 4-NP reduction.

Sample	Pd-1	Pd-2	Pd-3	Pd-4
Apparent reaction rate (min^{-1})[a]	0.60	0.25	0.15	0.1
Apparent reaction rate (min^{-1})[b]	1.00	0.56	0.50	0.21

[a] In quartz cuvette (method A).

[b] In micro-reaction vial (method B).