Supporting Information

Internally Supported Metal-oxide Nanocatalyst for Hydrogenation of Nitroaromatics

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Table S1. Reaction conditions and dosage of reactants and catalysts for hydrogenation of nitroaromatics throughout the whole work.

Nitrobenzene / mmol	Catalyst	Methanol / mL	Reaction Time / min	Data
0.5	10 mg Pd-ZnO, 5% Pd	5	120	Figure 5a
0.5	0.5 mg pure Pd, 10 mg Pd(s)-ZnO, 5% Pd 10 mg Pd(i)-ZnO, 5% Pd	5	60	Figure 6
0.5	10 mg Pd(i)-ZnO, 0.7%, 4.8%, 9.7% and 13% Pd	5	120	Figure 7c
0.5	10 mg Pd(i)-ZnO, 13% Pd	5	80	Figure 7d
0.5	10 mg, 9.5 mg, 8.9 mg, and 8.3 mg Pd(i)-ZnO, all of them contain 0.5 mg Pd	5	40 / 60	Figure 9a / 9b

Table S2. Comparison of reaction conditions and catalytic activity between the literatures and the current work.

Reference	Catalyst	Conditions	Time (min)	TOF (min^{-1})	d_{Pd} (nm)
1) *Rsc Adv.*, **2017**, 7, 3443	GA-Pd-TiO_2	MeOH, r.t., H_2 (1 atm)	120	1.53	5
2) *Adv. Synth. Catal.*, **2008**, 350, 822	NAP-MgO-Pd	THF, r.t., H_2 (8 atm)	120	0.5	
3) *Adv. Synth. Catal.*, **2004**, 346, 661	Pd/SiO_2	EtOH, 308K, H_2 (40 atm)	10	6.9	5
4) *Green Chem.*, **2011**, 13, 1238	Fe_3O_4–NH_2–Pd	N-methyl-2-pyrrolidone, 400 K, H_2 (1 atm)	45	1.38	5-10
5) *Catalysis Science & Technology*, **2013**, 3, 1618	HMMS–NH_2–Pd	EtOH, r.t., H_2 (1 atm)	60	1.64	9
6) *Appl. Surf. Sci.*, **2016**, 390, 100	Pd/HAM@-AlOOH	EtOH, r.t., H_2 (1 atm)	60	1.62	4-8
7) *Tetrahedron Lett.*, **2012**, 53, 4858	Pd-SS	MeOH-H_2O, 323K, $NaBH_4$ (3eq.)	60	0.8	
8) *Tetrahedron*, **2014**, 70, 6050	Pd/$Fe(OH)_x$	Toluene 333K, H_2 (1 atm)	60	2.36	2-5
9) *Appl. Surf. Sci.*, **2013**, 279, 360	CS-Fe_3O_4 -Pd	EtOH, r.t., H_2 (1 atm)	30	4.73	7.2
10) *Int. J. Hydrogen Energy*, **2016**, 41, 17960	Pd/Fe_3O_4@C	EtOH, 333K, $NaBH_4$ (3eq.)	60	2.27	
11) *J. Mol. Catal. A-Chem*, **2016**, 423, 511	Pd/ Fe_3O_4@C	EtOH, 343K, N_2H_4 (3eq.)	60	12.15	10
13) *Cryst. Growth Des.*, **2017**, 17, 5163	Pd/Ni-CNF	MeOH, r.t., H_2 (20 atm)	60	5.68	3-6
14) *ACS Sustain Chem. Eng.*, **2014**, 2, 2155	Fe_3O_4@C-Pd	Isopropanol, r.t., H_2 (1 atm)	40	2.77	
15) *Chem. Commun.*, **2015**, 51, 10419	Pd-MIL-101	MeOH, r.t., H_2 (1 atm)	30	4.85	2-4
16) *ChemCatChem*, **2017**, 9, 3236	Pd- polydopamine	EtOH, 358K, HCOONa	60	2.36	
17) *Appl. Organomet. Chem.*, **2017**, 31	Pd□NPs@G.Tea	EtOH, 323K, $NaBH_4$ (2eq.)	60	0.69	7-10

Current work	Pd-ZnO	MeOH, r.t., H_2 (1 atm)	120	1.15	10

Table S3. The ratio of Pd^{2+}/Pd^0 determined by XPS results for Pd-ZnO, Pd-Cu_2O and Pd-CeO_2 catalysts before and after hydrogenation.

Catalyst	**Pd-ZnO**	**Pd-Cu_2O**	**Pd-CeO_2**
Pd^{2+}/Pd^0 before catalysis	0.141	0	11.8
Pd^{2+}/Pd^0 after catalysis	0.246	0.165	0.596

Table S4. Pd size, metal dispersion and TOF value for Pd(i)-ZnO with different Pd content and Pd(s)-ZnO with 5% of Pd.

Catalyst	**Pd(i)-ZnO (0.7%)**	**Pd(i)-ZnO (4.8%)**	**Pd(i)-ZnO (9.7%)**	**Pd(i)-ZnO (13%)**	**Pd(s)-ZnO (5%)**
Pd size (nm)	10 nm	10 nm	10 nm	10 nm	10 nm
Metal Dispersion (%)	3.04	3.14	1.26	1.29	5.64
TOF (min^{-1})	1.19	0.86	0.48	0.57	1.94

Table S5. BET surface areas and BJH pore diameter of a series of Pd-ZnO particles obtained from the protective etching process and their corresponding weight loss

	Surface area / $m^2 \cdot g^{-1}$	**Pore diameter / nm**	**Weight loss / %**
Pd-ZnO	22.49	4.77	0
Pd-ZnO E1	37.39	4.92	5.3
Pd-ZnO E2	46.07	5.13	11.3
Pd-ZnO E3	47.01	6.82	18.4

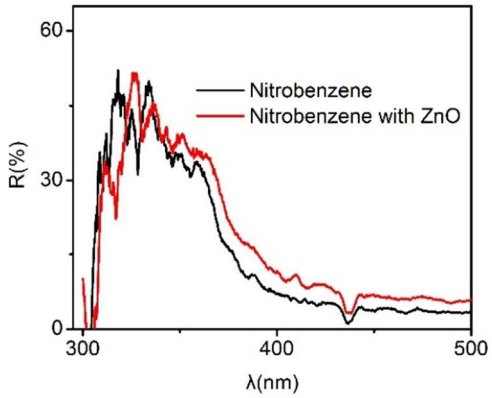

Figure S1. UV-Vis absorption of nitrobenzene with and without the presence of ZnO particles.

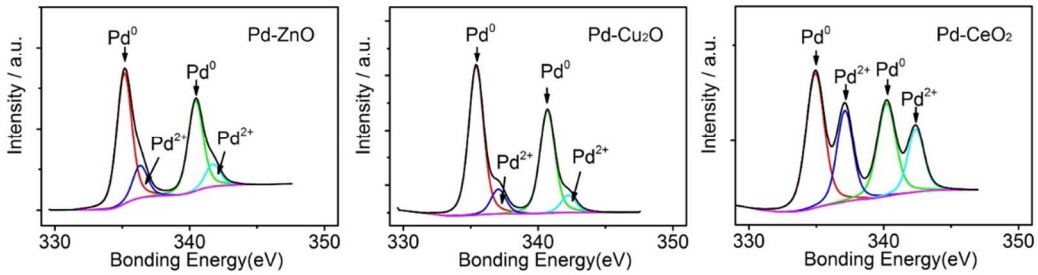

Figure S2. XPS spectra of Pd 3d for Pd-ZnO, Pd-Cu_2O and Pd-CeO_2 catalysts after catalytic hydrogenation.

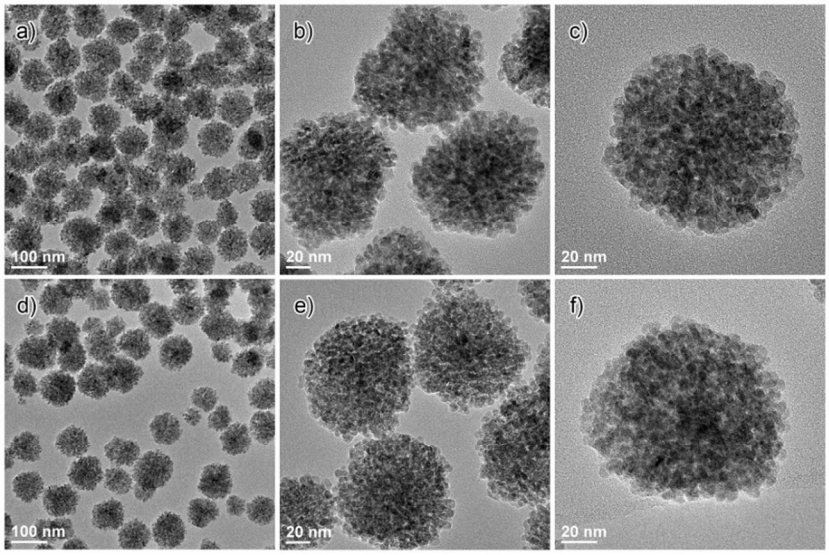

Figure S3. TEM images of Pd-ZnO composite particles before and after hydrogenation.

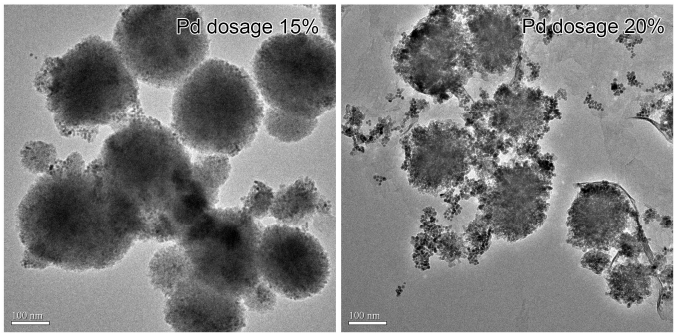

Figure S4. TEM images of Pd-ZnO composite particles when the Pd dosage were set at 15% and 20% respectively.