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Supporting Information

Hierarchical nanospheres based on Pd nanoparticles dispersed on carbon coated magnetite cores with a mesoporous ceria shell: a highly integrated multifunctional catalyst

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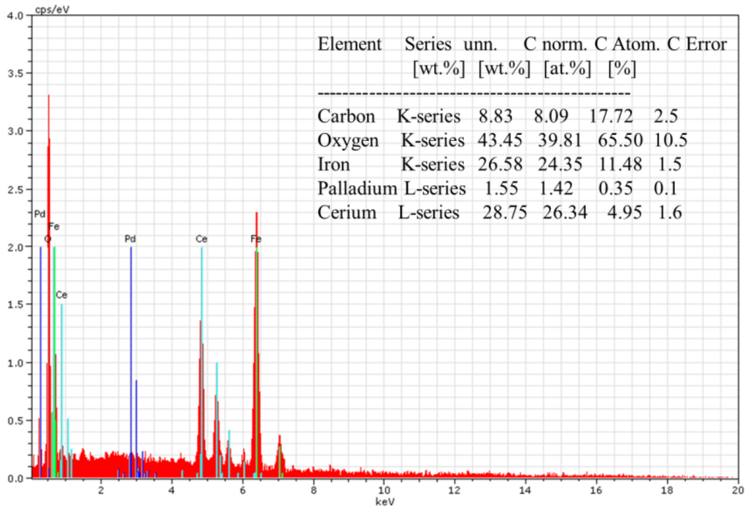


Figure S1 EDX spectrum of Fe_3O_4@C-Pd@*m*CeO_2

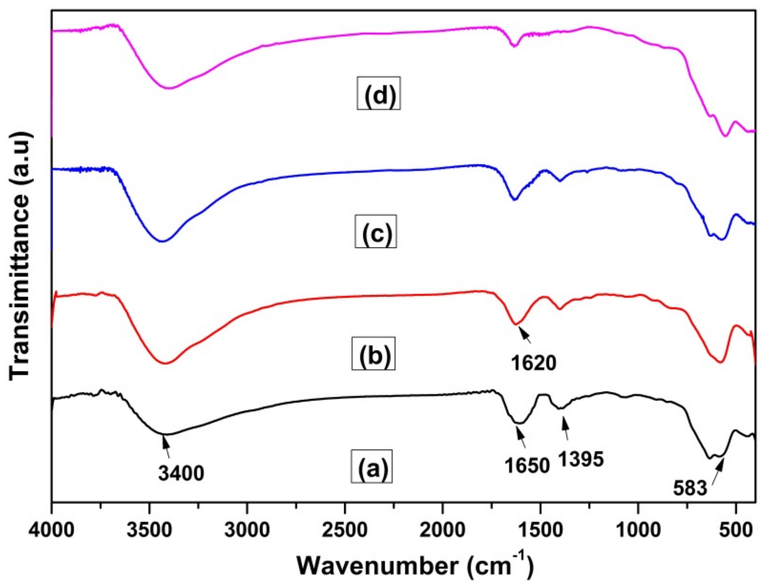


Fig. S2 FT-IR spectra of (a) Fe_3O_4 nanospheres, (b) Fe_3O_4@C nanospheres, (c) Fe_3O_4@C-Pd nanospheres, (d) Fe_3O_4@C-Pd@*m*CeO_2 nanospheres

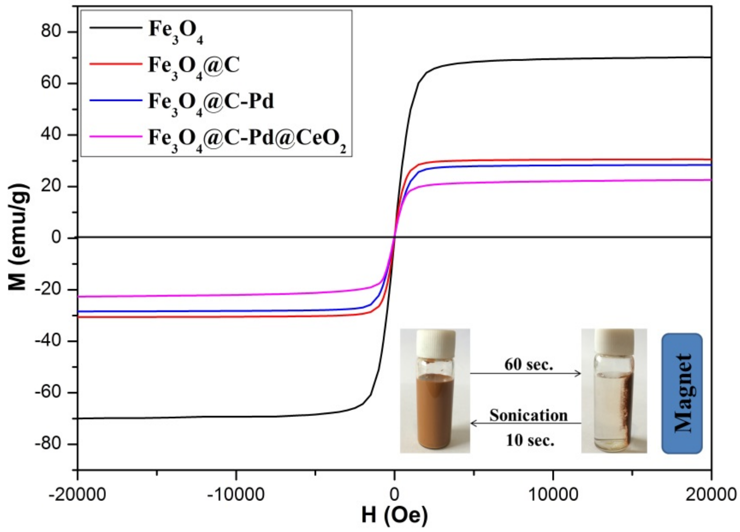


Fig. S3 Magnetization curves at 300 K of the Fe_3O_4 nanospheres (black), Fe_3O_4@C nanospheres (red), Fe_3O_4@C-Pd nanospheres (blue), Fe_3O_4@C-Pd@*m*CeO_2 nanospheres (pink). Inset show the photograph of the dispersion of 5 mg/mL Fe_3O_4@C-Pd@*m*CeO_2 nanospheres in water before and after magnetic separation.

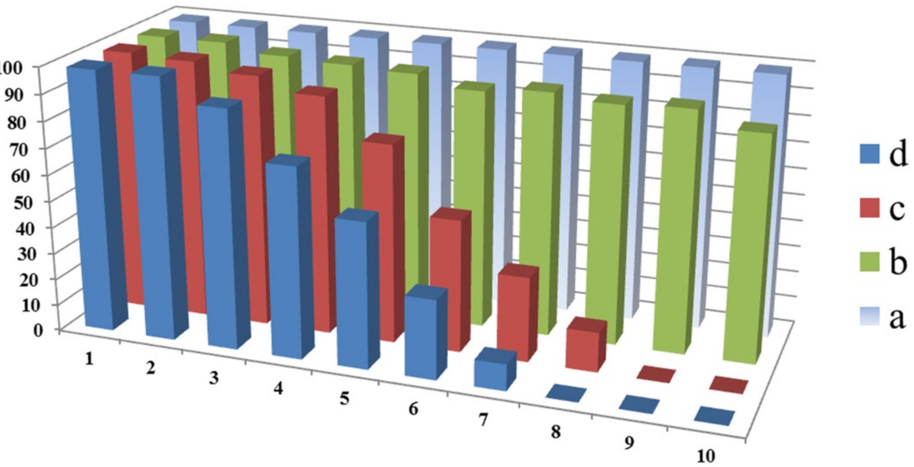


Fig. S4 (a) and (c): The reusability of the Fe_3O_4@C-Pd@*m*CeO_2 and Fe_3O_4@C-Pd as a catalyst for the reduction of 4-NP; (b) and (d): the reusability of the Fe_3O_4@C-Pd@*m*CeO_2 and Fe_3O_4@C-Pd as a catalyst for the Suzuki reaction;

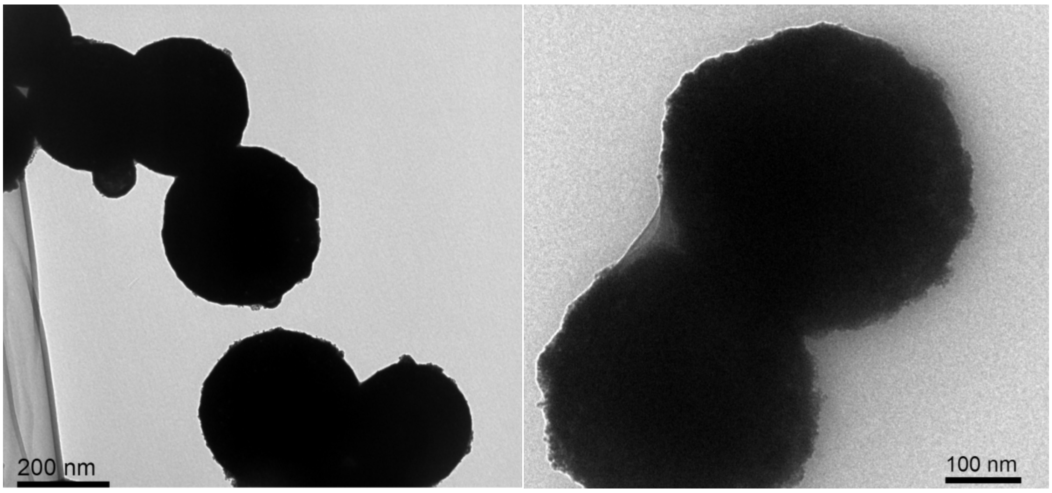
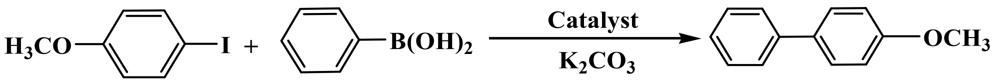


Figure S5 TEM images of Fe_3O_4@C-Pd@*m*CeO_2 after 10 runs of recycling experiments for the Suzuki reactions

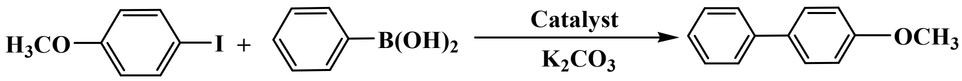
Table S1 Suzuki reactions catalyzed by different catalyst in different solvent[a].



Entry	Catalyst	Solvent	Yield[b]
1	Fe_3O_4@C@*m*CeO_2	ethanol	13
2	Fe_3O_4@C@*m*CeO_2	ethanol	20[c]
3	Fe_3O_4@C@*m*CeO_2	water	N.R.
4	Fe_3O_4@C-Pd	water	75
5	Fe_3O_4@C-Pd	ethanol	90
6	Fe_3O_4@C-Pd	ethanol-water (1:1)	96
7	Fe_3O_4@C-Pd@*m*CeO_2	water	85
8	Fe_3O_4@C-Pd@*m*CeO_2	ethanol	95
9	Fe_3O_4@C-Pd@*m*CeO_2	ethanol-water (1:1)	99

[a]Reaction conditions: 4-Iodoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), potassium carbonate (2 mmol), 5 mL solvent, 10 mg catalyst, at 80 ^{o}C for 3 h. [b] isolated yields. [c] 24 h.

Table S2 Suzuki reactions catalyzed by the Fe_3O_4@C-Pd@*m*CeO_2 in different solvents



Entry	Catalyst	Solvent	Yield[b]
1	Fe_3O_4@C-Pd@*m*CeO_2	Isopropanol	98
2	Fe_3O_4@C-Pd@*m*CeO_2	Tetrahydrofuran	88[c]
3	Fe_3O_4@C-Pd@*m*CeO_2	N,N-Dimethylformamide	92
4	Fe_3O_4@C-Pd@*m*CeO_2	1,4-dioxane	85
5	Fe_3O_4@C-Pd@*m*CeO_2	Dimethyl sulfoxide	90
6	Fe_3O_4@C-Pd@*m*CeO_2	Dimethylacetamide	92
7	Fe_3O_4@C-Pd@*m*CeO_2	toulene	95
8	Fe_3O_4@C-Pd@*m*CeO_2	dimethylbenzene	91

[a]Reaction conditions: 4-Iodoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), potassium carbonate (2.5 mmol), 5 mL solvent, 10 mg catalyst, at 80 ^{o}C for 3 h. [b] isolated yields. [C] 65 ^{o}C for 3 h.

Table S3 the Pd leaching test after ten cycles

	Pd loss after ten cycles (%)
Suzuki reactions	1.8
reduction of 4-NP	0.7

Table S4. Catalytic Performance of Different Magnetically Pd-Based Catalysts in the Coupling Reaction of Iodobenzene and Phenylbronic Acid

entry	catalyst	solvent	base	temp (°C)	time (h)	Yield (%)	ref
1	Pd/$NiFe_2O_4$	DMF	Na_2CO_3	90	2	50	1
2	Pd-Fe_3O_4	DME[a]/H_2O = 3:1	K_2CO_3	reflux	48	92	2
3	Pd-Fe_3O_4@C	ethanol	K_2CO_3	reflux	2	>99	3
4	Pd@Mag-MSN[b]	CH_2Cl_2	K_2CO_3	80	6	85	4
5	Xerogel g1-MNPs[c]	CH_3OH	Na_2CO_3	60	2	99	5
6	Pd@MC[d]	EtOH/H_2O = 1:1	Na_2CO_3	80	1	98	6
7	Pd@polymer[e]	EtOH/H_2O = 1:1	K_2CO_3	50	4	88	7
8	Pd/PS[f]	DMF/H_2O = 1:1	Na_2CO_3	90	12	93	8
9	Pd-SBAM[g]	H_2O	K_2CO_3	60	5	98.3	9
10	Co@C@Pd complexes	THF/H_2O = 1:2	Na_2CO_3	65	2	96	10
11	Fe_3O_4@C-Pd@*m*CeO_2	EtOH/H_2O = 1:1	K_2CO_3	60	0..75	>99	This work

[a] DME = 1,2-dimethoxyethane. [b] Mag-MSN = magnetic mesoporous silica nanocomposites. [c] Xerogel g1-MNPs = Fe_3O_4 nanoparticles supported gel nanofibers + Pd^{2+}. [d] MC = mesoporous carbon. [e] polymer = $(OH)_2$-poly[2-(methacryloyloxy)ethyl phosphorylcholine]$_{40}$-b-PDPAEMA$_{70}$. [f] PS = polystyrene. [g] SBAM = acrylate copolymer monoliths.

Table S5. The comparison of the catalytic performance between the catalyst of Fe_3O_4@C-Pd@*m*SiO_2[11] and our Fe_3O_4@C-Pd@*m*CeO_2

Entry	Reactant A	Reactant B	Conversion[a]	Conversion[b]
1	Iodobenzene	Phenylbronic Acid	92	>99
2	4-Iodoanisole	Phenylbronic Acid	98	98.5
3	4-Iodonitrobenzene	Phenylbronic Acid	73	96
4	4-Iodoacetophenone	Phenylbronic Acid	99	99.2

[a] phenylboronic acid (1.5 equiv.), aryl halide (1.0 mmol), Fe_3O_4@C-Pd@*m*SiO_2 wih Pd (1.5 mol%), K_2CO_3 (1 equiv.), 6 h, 70 °C. [b] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), 5 mL solvent, 10 mg Fe_3O_4@C-Pd@*m*CeO_2 with Pd (0.3 mol%), at 80 °C for 3 h.

References

1 S R. Borhade, S. B Waghmode,. *Beilstein, J. Org. Chem*. 2011, **7**, 310-319.

2 Y. Jang, J. Chung, S. Kim, B. H. Kim, D. W. Lee, B.M. Kim, T. Hyeon, *Phys. Chem. Chem. Phys*. 2011, **13**, 2512-2516.

3 M. Y. Zhu and G. W. Diao, *J. Phys. Chem. C.* 2011, **115**, 24743-24749.

4 S. Shylesh, L. Wang, S. Demeshko,. W. R. Thiel, *ChemCatChem*, 2010, **2**, 1543-1547.

5 Y. Liao, L. He, J. Huang, J. Zhang, L. Zhuang, H. Shen, C. Y. Su, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2333-2338.

6 L. Zhong, S. Wang, X. Y. Su, *Catalysis Today*, 2015, **243**, 195-198.

7 T. Bortolotto, S. E. Facchinetto, S. G. Trindade, V. Schmidt, *J. Colloid Interf. Sci.*, 2015, **439**, 154-161.

8 K. Karami, M. Ghasemi, N. H. Naeini, *Catal. Commun*., 2013, **38**, 10-15.

9 H. y. Shen, C. Shen, C. Chen, P. F. Zhang, *Catal. Sci. Technol*., 2015, **5**, 2065-2071.

10 T. R. Long, R. N. Grass, W. J. Stark, O. Reiser, *Adv. Funct. Mater.* 2010, **20**, 4323-4328.

11 Z. K. Sun, J. P. Yang, Y.H. Deng and D. Y. Zhao, *J. Mater. Chem. A*, 2014, **2**, 6071-6074.