Supplementary Material (ESI) for Green Chemistry

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Electronic Supplementary Information

Magnetically retrievable nanocomposite adorned with Pd nanocatalysts: efficient reduction of nitroaromatics in aqueous media

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Synthesis of Pd NPs using Pluronic copolymer

Pd nanoparticles (NPs) were synthesized by modification of a previously reported method [1]. In brief, aqueous solutions of palladium salts and Pluronic copolymer P123 were mixed. In a typical procedure, 200 mg of K_2PdCl_4 was added to 50 mL aqueous solution containing 100 mg polyvinylpyrrolidone (Mw ~40,000) and 100 mg of triblock Pluronic copolymer P123 at room temperature, and the resulting solution was vigorously stirred for 12 hours. The color of the solution changed from light yellow to a deep brown, indicating the formation of Pd NPs. The product was isolated using a centrifuge, washed several times with water and ethanol, and dried in an oven at 70 ^{o}C for 7 h.

Synthesis of carbon supported Pd NPs

Carbon (1 g) was dispersed in H_2O/EtOH mixture (2:1) and stirred at room temperature for 1 h. While stirring vigorously, 200 mg K_2PdCl_4 dissolved in water was added to the vial and the mixture was stirred for 1 h at room temperature. To this solution, 25 mg $NaBH_4$ dissolved in water was directly added and the solution vigorously stirred at room temperature for 3 h to produce Pd NPs supported on carbon. The product was isolated using a centrifuge, washed several times with water and ethanol, and dried in an oven at 70 ^{o}C for 7 h.

Synthesis of silica NPs supported Pd NPs

Silica NPs were readily synthesized by modifying a previously reported method (Stöber *et al.* 1968) [2]. In a typical synthesis, 300 mL ethanol and 50 mL H_2O were mixed and stirred vigorously at room temperature for 15 min. To this solution, 5 mL tetraethyl orthosilicate (TEOS) was directly added. While vigorous stirring, 5 mL ammonia was rapidly added, and the mixture was stirred for 12 h at room temperature to yield silica NPs. The resulting product was centrifuged, washed with water and ethanol, and dried in an oven at 80 ^{o}C for 12 h. The synthesized silica NPs (1 g) was dispersed in H_2O/EtOH mixture (2:1) and stirred at room temperature for 1 h. While stirring vigorously, 200 mg K_2PdCl_4 dissolved in water was added to the vial and the mixture was stirred for 1 h at room temperature. To this solution, 25 mg $NaBH_4$ dissolved in water was directly added and the solution was vigorously stirred at room temperature for 3 h to produce Pd NPs supported on silica. The product was isolated using a centrifuge, washed several times with water and ethanol, and dried in an oven at 70 ^{o}C for 7 h.

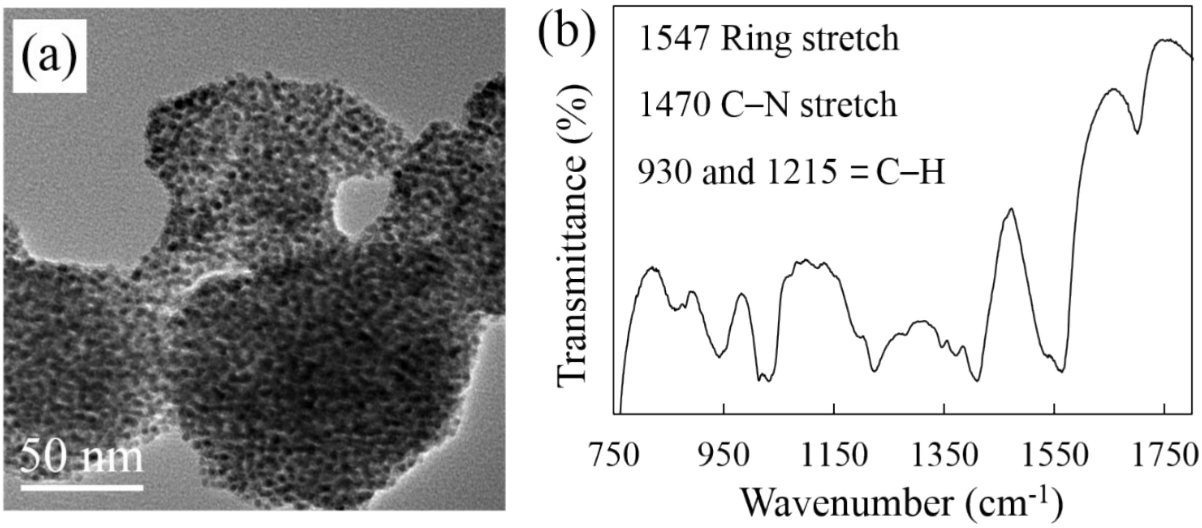


Fig. S1. (a) TEM image and (b) FT–IR spectrum of polypyrrole–supported Pd NPs catalysts.

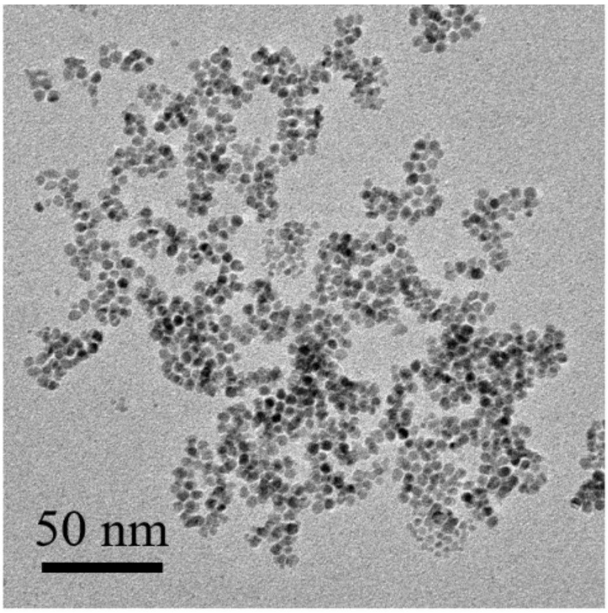


Fig. S2. TEM image of Pd NPs synthesized using Pluronic copolymer P123 catalysts.

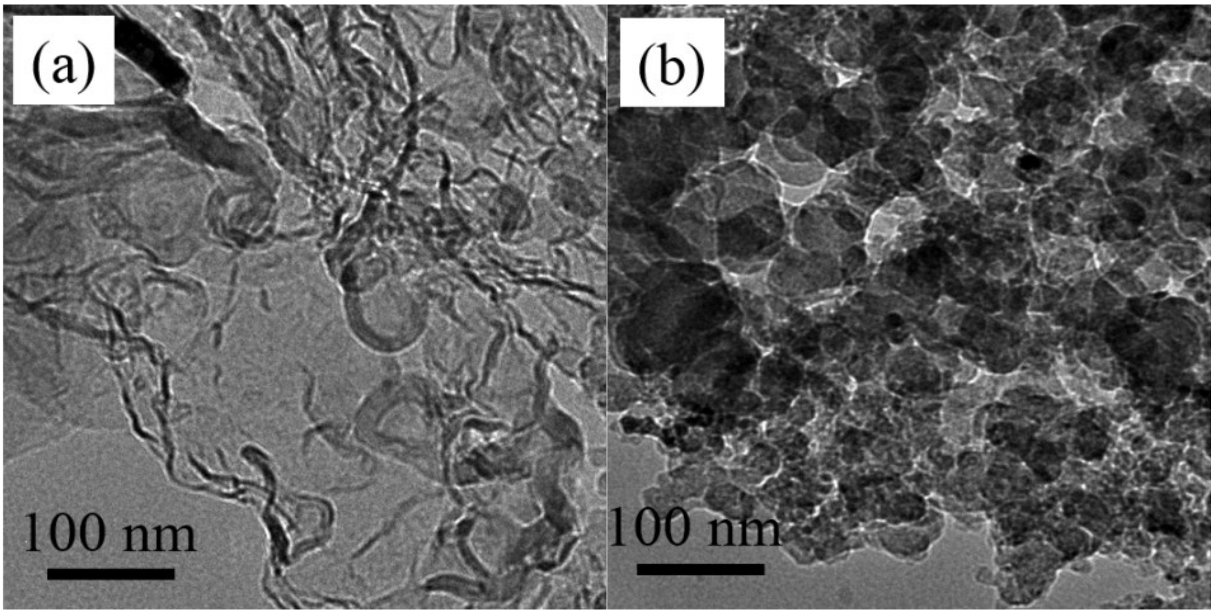


Fig. S3. TEM images of (a) carbon and (b) carbon–supported Pd NPs catalysts.

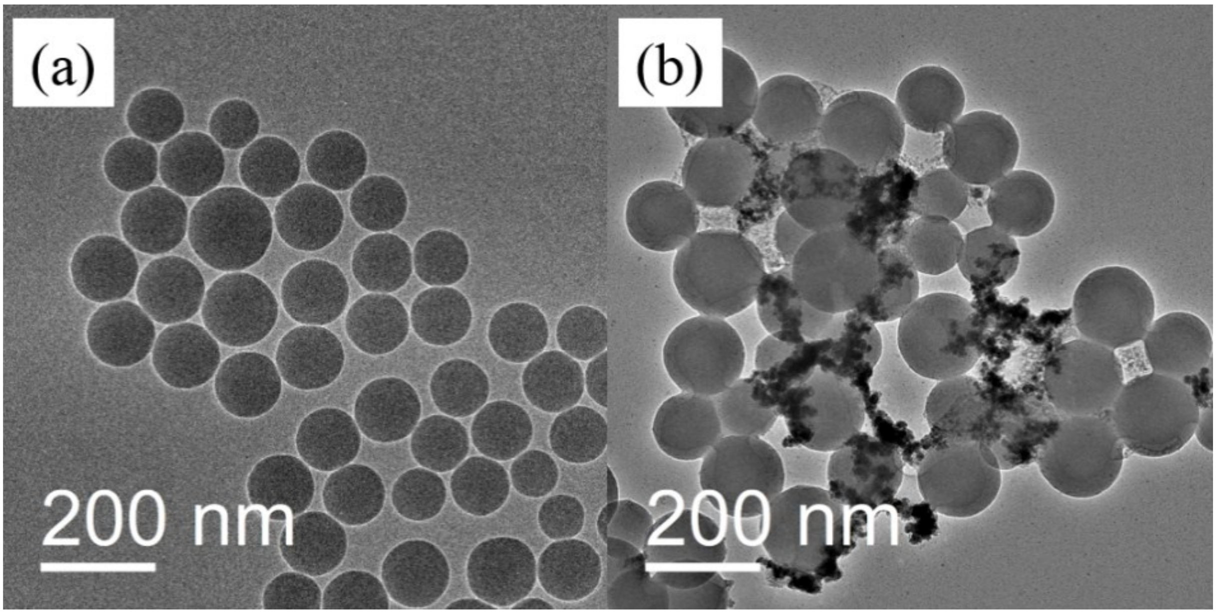


Fig. S4. TEM images of (a) silica NPs and (b) silica NPs supported Pd NPs catalysts.

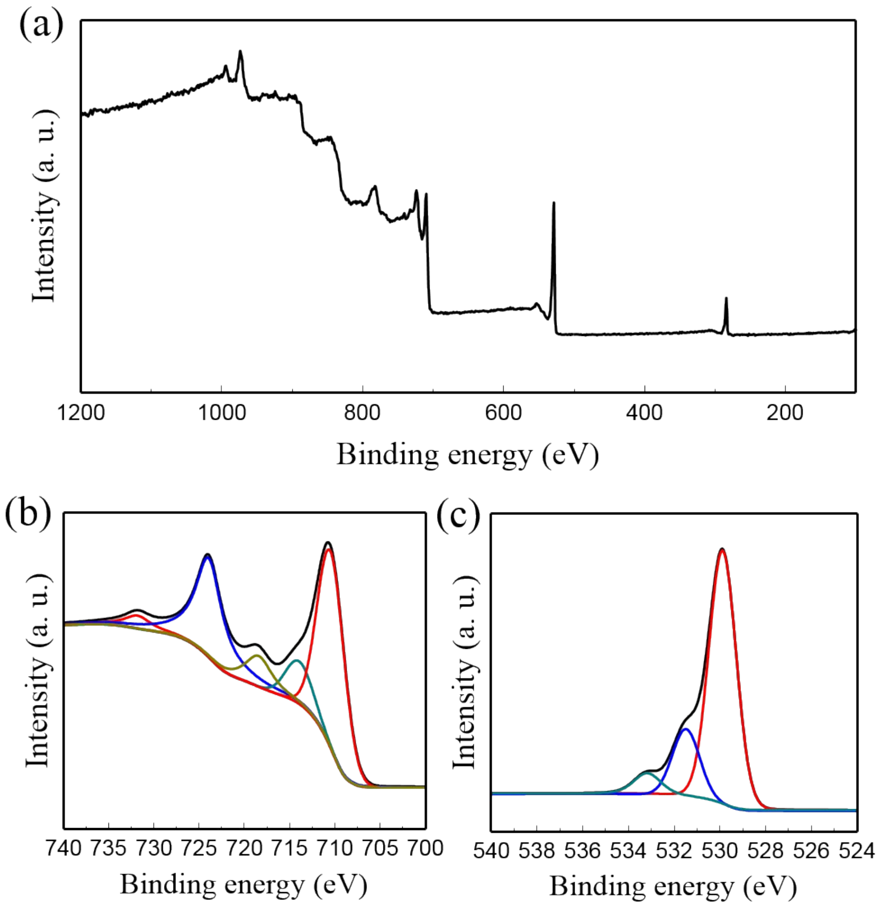


Fig. S5. XPS analysis of (a) survey scan, (b) Fe 2p and (c) O 1s for iron nanopowders.

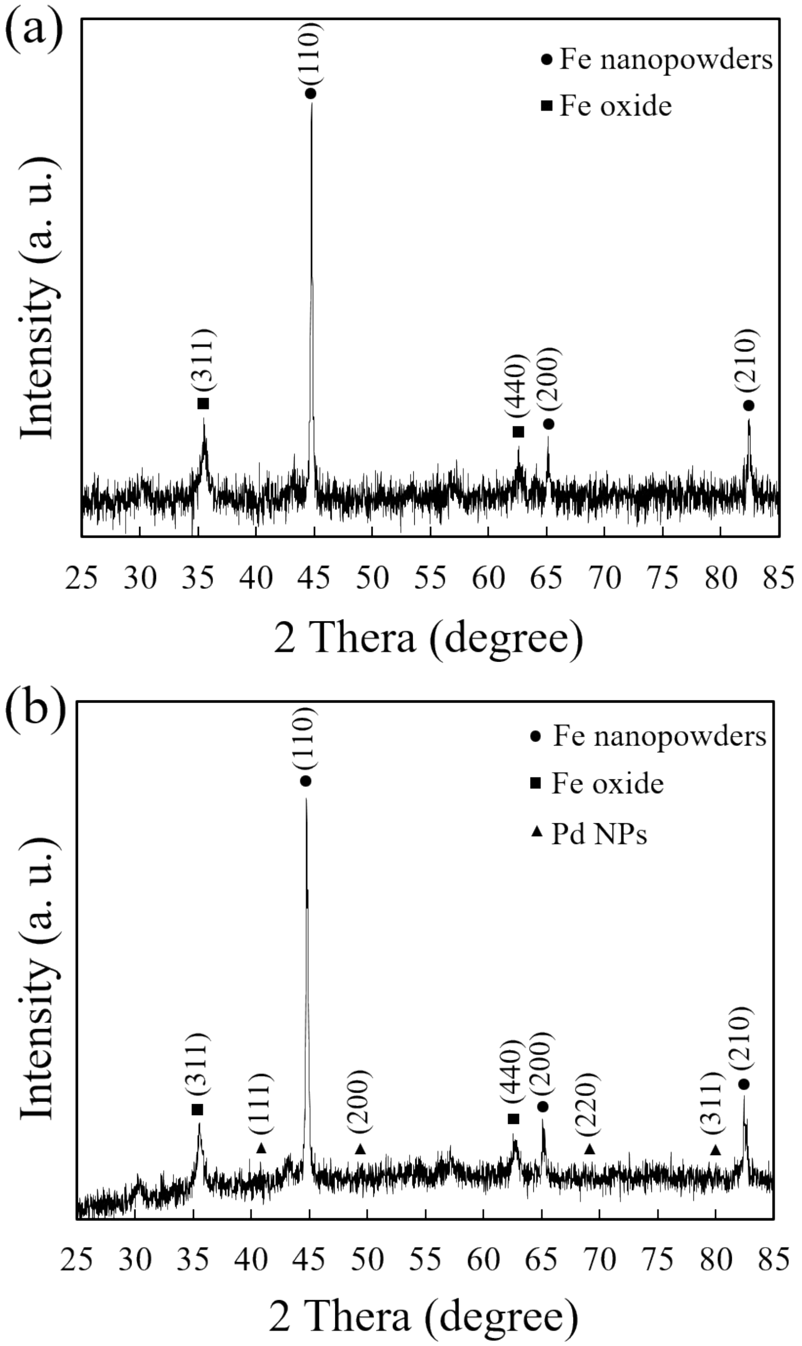


Fig. S7. XRD patterns of (a) iron nanopowders and (b) MRN–Pd catalysts.

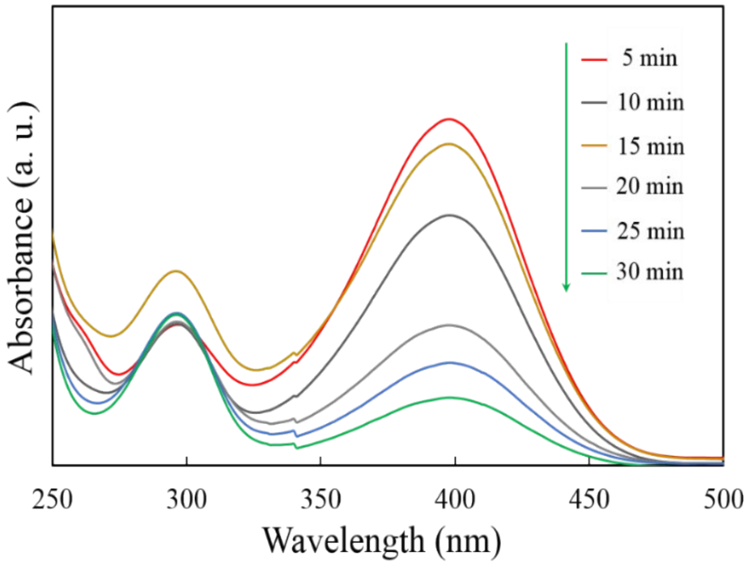


Fig. S8. UV–vis spectra for the catalytic reduction of nitrophenol using MRN–Pd catalysts.

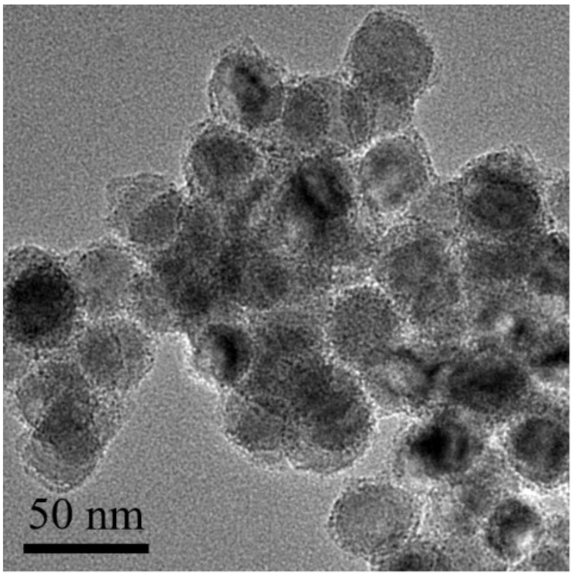


Fig. S9. TEM image of the iron oxide nanocomposite catalyst.

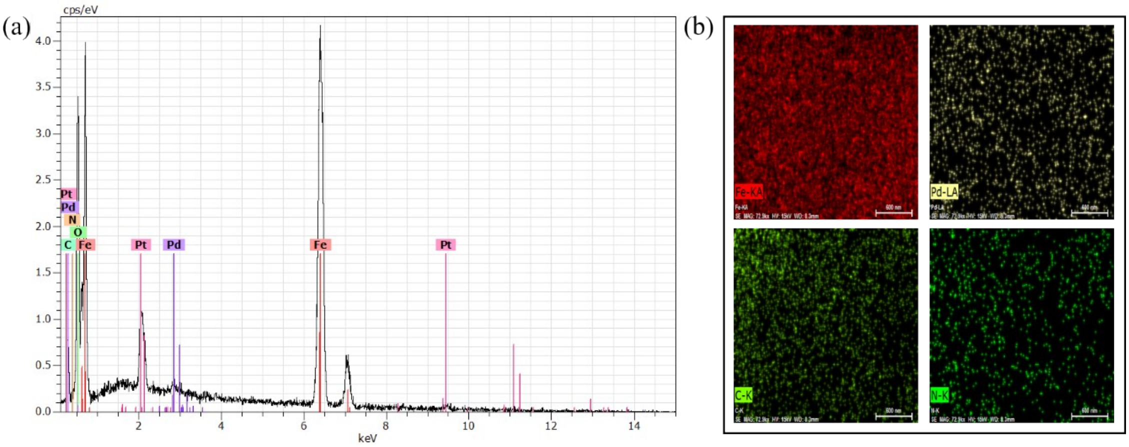


Fig. S10. (a) EDX spectrum, and (b) EDX map of iron, carbon, nitrogen, and Pd of the MRN–Pd catalysts after recycling.

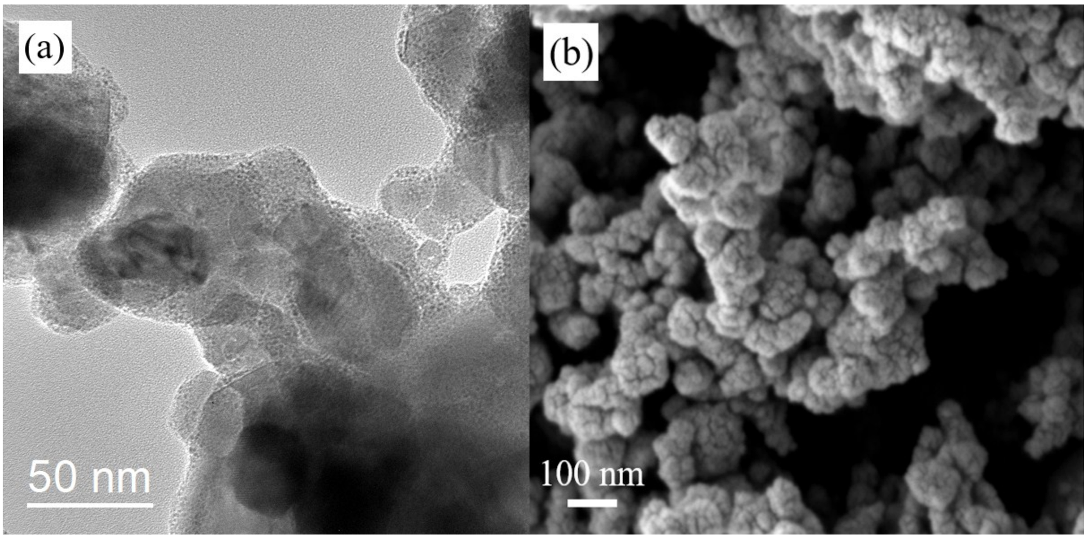


Fig. S11. (a) TEM image, and (b) FESEM image of the MRN–Pd catalysts after recycling.

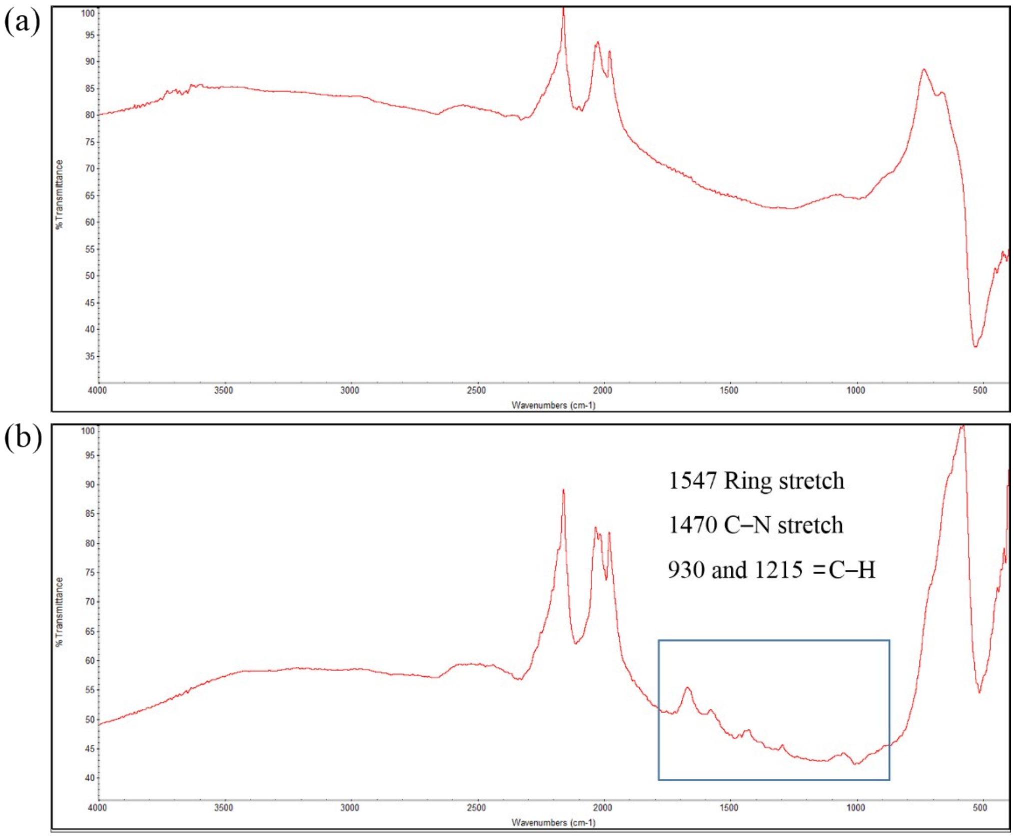


Fig. S12. FT–IR spectrum of (a) iron nanopowders, and (b) the MRN–Pd catalysts after recycling.

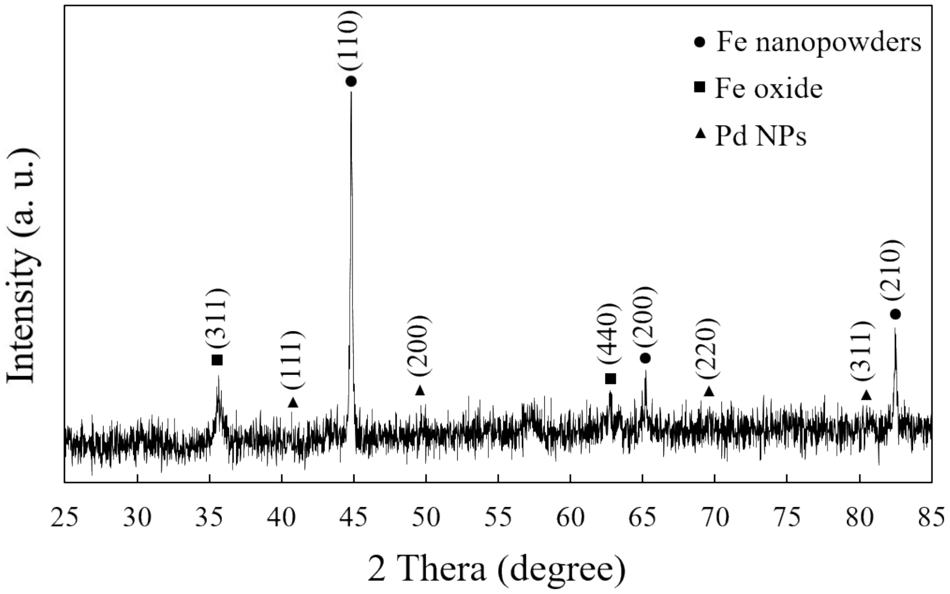


Fig. S13. XRD pattern of the MRN–Pd catalysts after recycling.

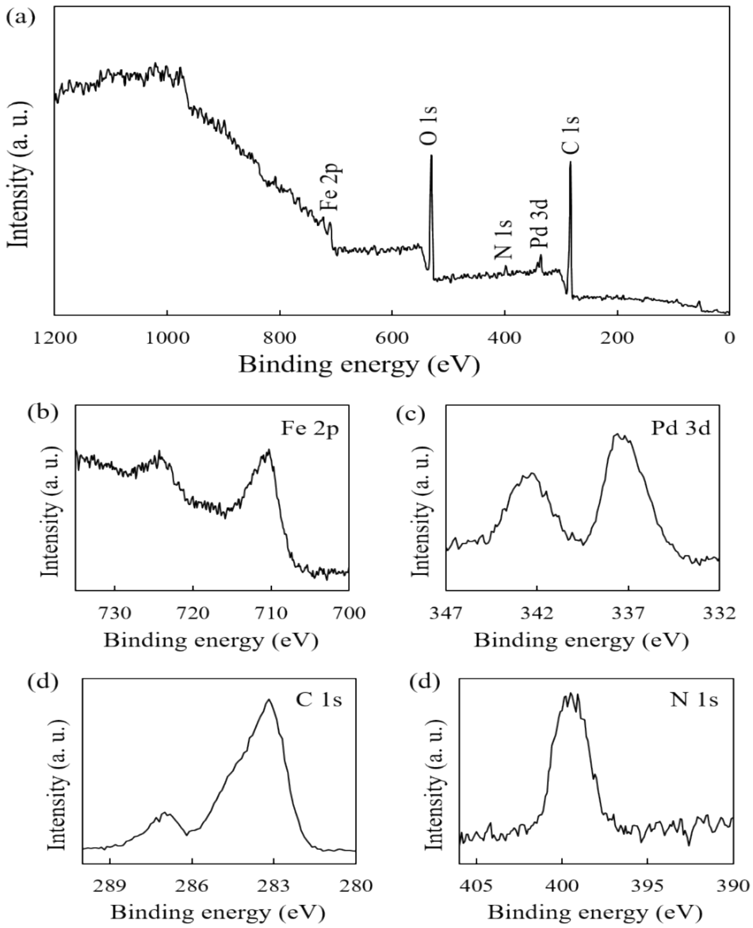


Fig. S14. XPS analysis (a) survey scan, (b) Fe 2p, (c) Pd 3d, (d) C 1s, and (e) N 1s for the MRN–Pd catalysts after recycling.

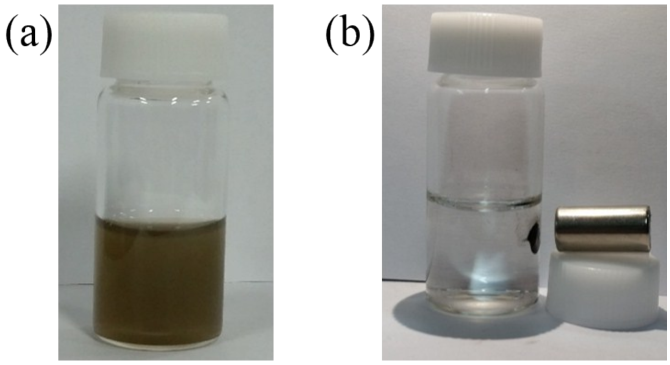
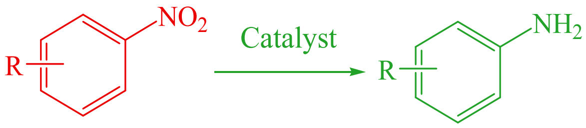


Fig. S15. Photographs of MRN–Pd catalysts kept under the reductive condition for five months; (a) before magnetic separation and (b) after magnetic separation.

Table S1. The CHN elemental analysis results of poly pyrrole supported Pd NPs catalyst and MRN–Pd catalysts.

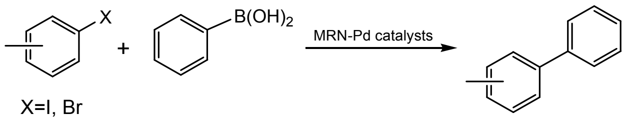
Sample	Elemental Contents (wt %)		
	C	H	N
Polypyrrole–supported Pd NPs	32.5	8.7	7.5
MRN–Pd catalysts	11.2	5.8	4.1

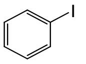
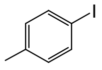
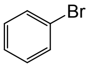
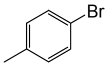
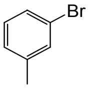
Table S2. Comparative catalytic studies for the reduction of nitroaromatics using known heterogeneous catalysts.



Entry	Catalyst	Reaction condition	Yield (%)	Refs.
1	Hollow nanocomposite catalyst (Rh 1 mol%)	Hydrazine (mmol), EtOH, 80 °C, 2.5 h	91–99	3
2	Magnetic carbon nanocomposite catalysts (Pt 1 mol%)	Hydrazine (mmol), EtOH, 80 °C, 3 h	94–99	4
3	Nanocatalysts confined in mesoporous silica (Pd 1 mol%)	Hydrazine (mmol), EtOH, 80 °C, 4 h	91–99	5
4	Core–shell nanocatalysts (Pd 1 mol%)	Hydrazine (mmol), EtOH, 80 °C, 4 h	92–99	6
5	Silver nanocomposites (Ag 5 mol%)	$NaBH_4$ (10 mmol), H_2O, room temperature, 0.5–6 h.	71–94	7
6	Pd NPs on cyclodextrin (Pd 0.5 mol%)	$NaBH_4$ (3 mmol), H_2O, room temperature, 3 h.	93–99	8
7	MRN–Pd catalysts (Pd 1 mol%)	$NaBH_4$ (1.2 mmol), H_2O, room temperature, 45 min	93–99	This work

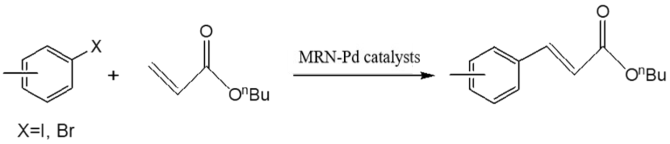
Table S3. Suzuki cross–coupling reaction of aryl halides with phenylboronic acid catalyzed by MRN–Pd catalysts.[a]

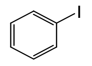
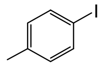
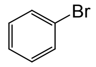
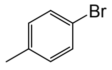
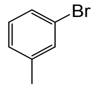


Entry	**Aryl halide**	**Time (h)**	**Yield (%)**[b]
1		2	98
2		2	94
3		4	93
4		4	91
5		4	89

[a] Aryl halide (1 mmol), phenylboronic acid (1.2 eq.), MRN–Pd catalysts (1 mol%), K_2CO_3 (1.5 eq.), DMF/H_2O (5:1), 100 °C. [b] Yields were determined by GC–MS.

Table S4. Heck cross–coupling reaction of aryl halides with *n*–butylacrylate catalyzed by MRN–Pd catalysts.[a]



Entry	Aryl halide	Time (h)	Yield (%)[b]
1		3	95
2		3	93
3		5	94
4		5	90
5		5	85

[a] Aryl halide (1 mmol), n–butylacrylate (1.2 eq.), MRN–Pd catalysts (1 mol %), tributylamine (1.5 eq.), dimethylformamide (10 mL), 130 °C. [b] Yields were determined by GC–MS.

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