Supporting Information

Magnetically Recyclable Catalytic Carbon Nanoreactors

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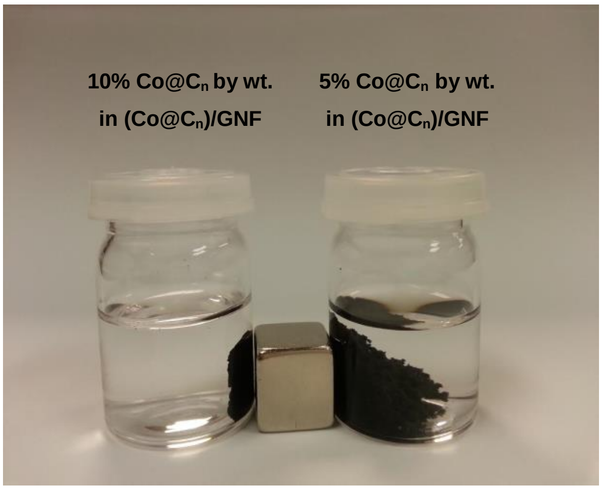


Figure S1. Comparison of the effectiveness of the magnetic separation for (Co@C$_n$)/GNF with a 10 % (wt) (left) and a 5 % (wt) (right) Co@C$_n$ loading where (Co@C$_n$)/GNF was dispersed in hexane by ultrasonication and exposed to a magnet (0.1 T).

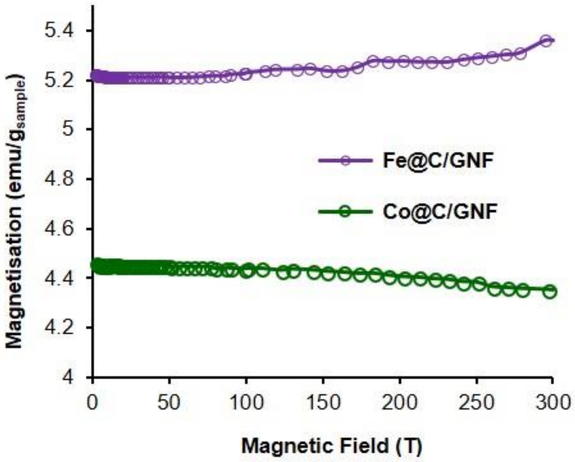


Figure S2. Magnetic hysteresis loops for (Co@C$_n$)/GNF and (Fe@C$_n$)/GNF recored at 2-300 K (inset: expanded region at low magnetic fields between -0.5 and 0.5 T).

Table 1. Magnetisation, remanent and coercity magnetic fields for (Co@C$_n$)/GNF and (Fe@C$_n$)/GNF at 2 K and 300 K.

	Magnetisation at 5T (emu/g$_{sample}$)	**Remanent magnetisation (emu/g$_{sample}$)**	**Coercivity magnetic field (T)**	**Magnetisation at 0.1 T (emu/g$_{sample}$)**
(Co@C$_n$)/GNF at 2K	11.65	6.91	0.14	5.22
(Co@C$_n$)/GNF at 300 K	10.76	1.56	0.045	5.36
(Fe@C$_n$)/GNF at 2 K	15.84	1.59	0.04	4.45
(Fe@C$_n$)/GNF at 300 K	15.58	1.42	0.026	4.35

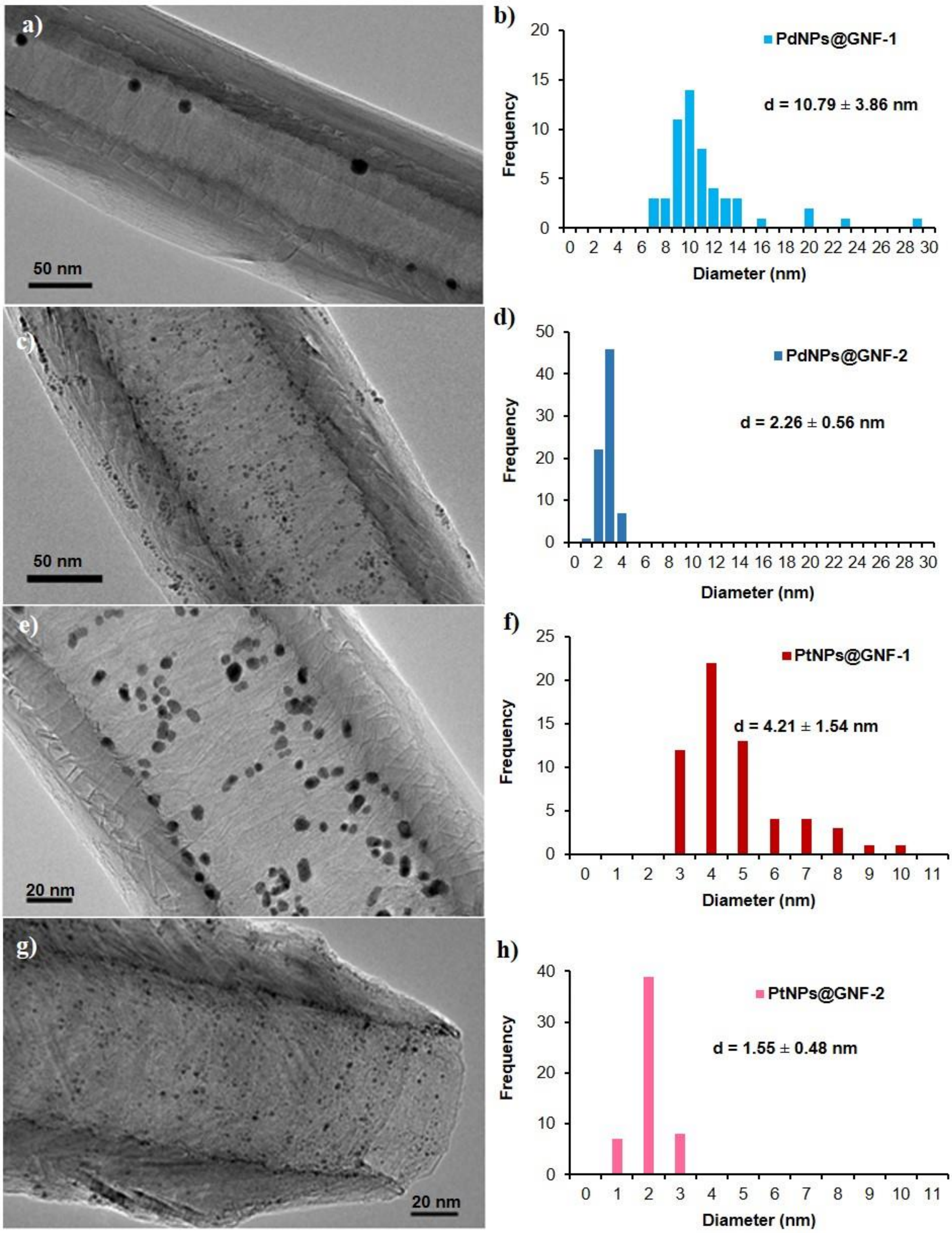


Figure S3. a) Representative HRTEM images of a) PdNPs@GNF-1, c) PdNPs@GNF-2, e) PtNPs@GNF-1, and g) PtNPs@GNF-2 with b, d, f, and h) showing the corresponding size distribution of the PdNPs and PtNPs composites.

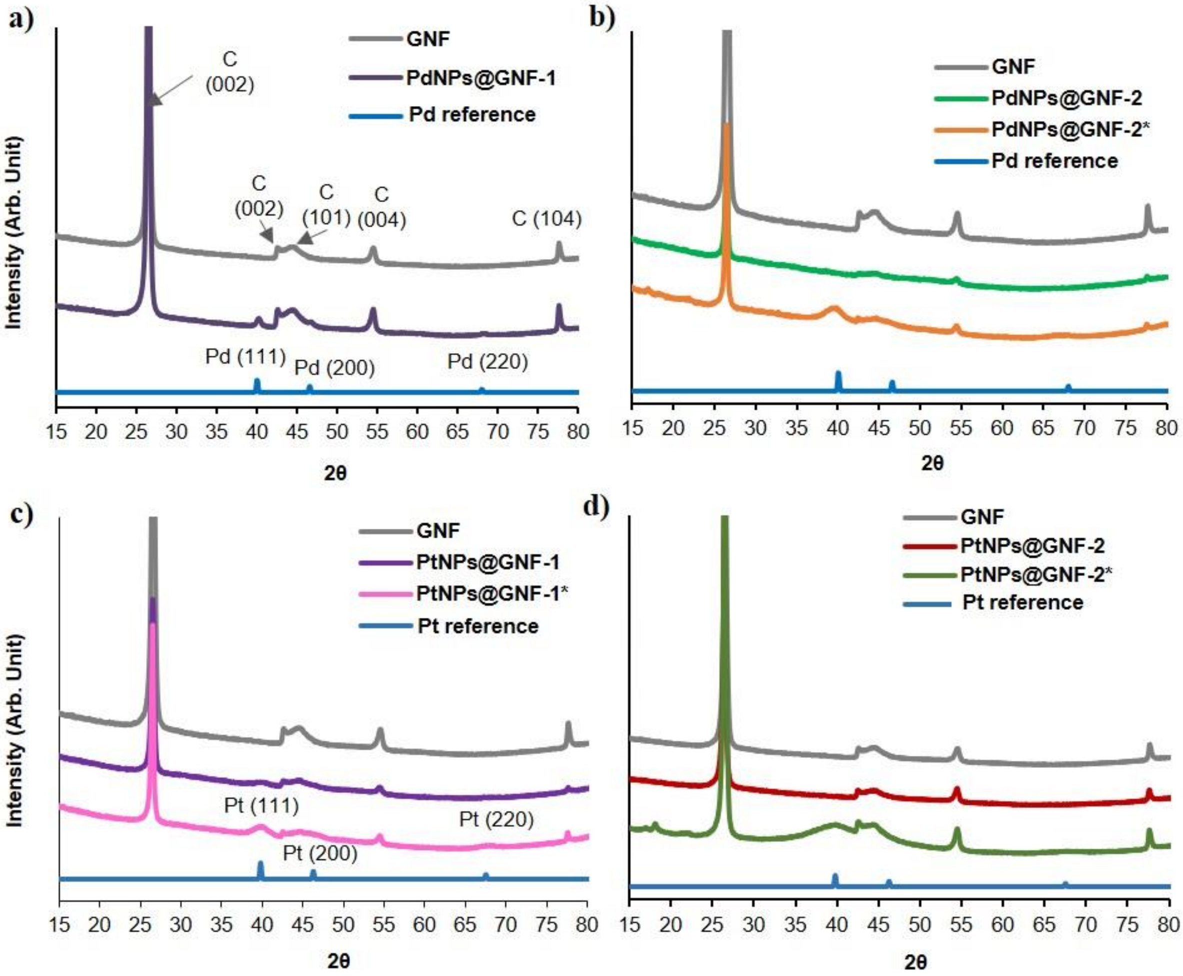


Figure S4. Powder XRD patterns of a) PdNPs@GNF-1, b) PdNPs@GNF-2 and PdNPs@GNF-2*, c) PtNPs@GNF-1 and PtNPs@GNF-1* and d) PtNPs@GNF-2 and PtNPs@GNF-2*. Diffractograms for Pd[S1] and Pt[S2] references and GNF (annealed at 450 °C for 1 h) are shown for comparison. All * composites show 15 % by wt. loading of Pt or Pd respectively for comparison.

Table S2. BET measurements for GNF, PdNPs@GNF-2 and PtNPs@GNF-1.

	Pore volume, cm³/g	**Pore sizes, Å**	**BET surface area, m²/g**
GNF[3]	0.023237	32/54/63/93/252/503	12.08
PdNPs@GNF-2	0.033801	32/54/63/93/252/503	16.06
PtNPs@GNF-1	0.030408	32/54/63/93/252/503	15.67

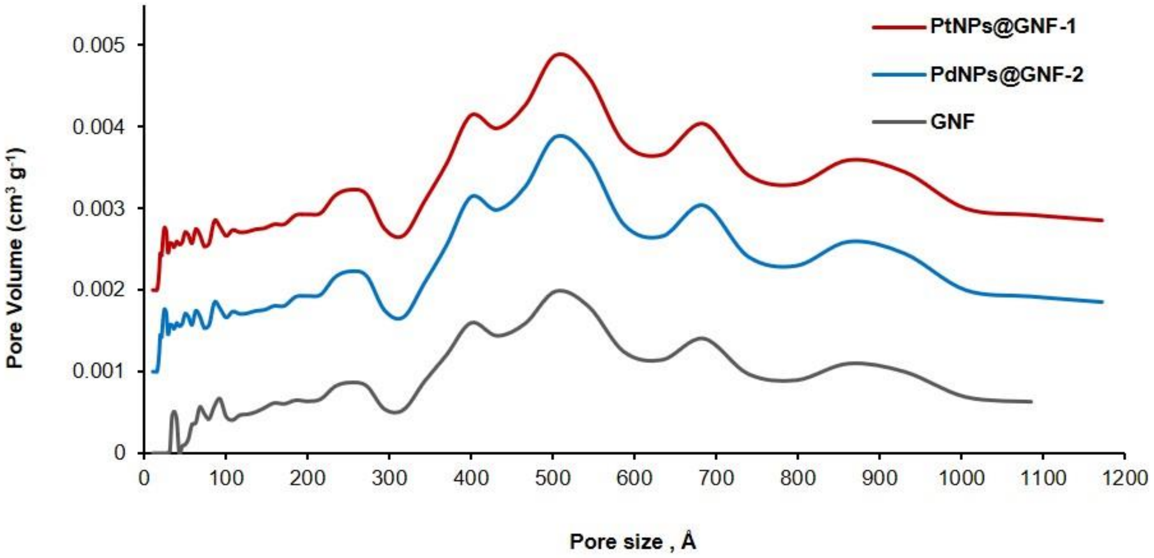
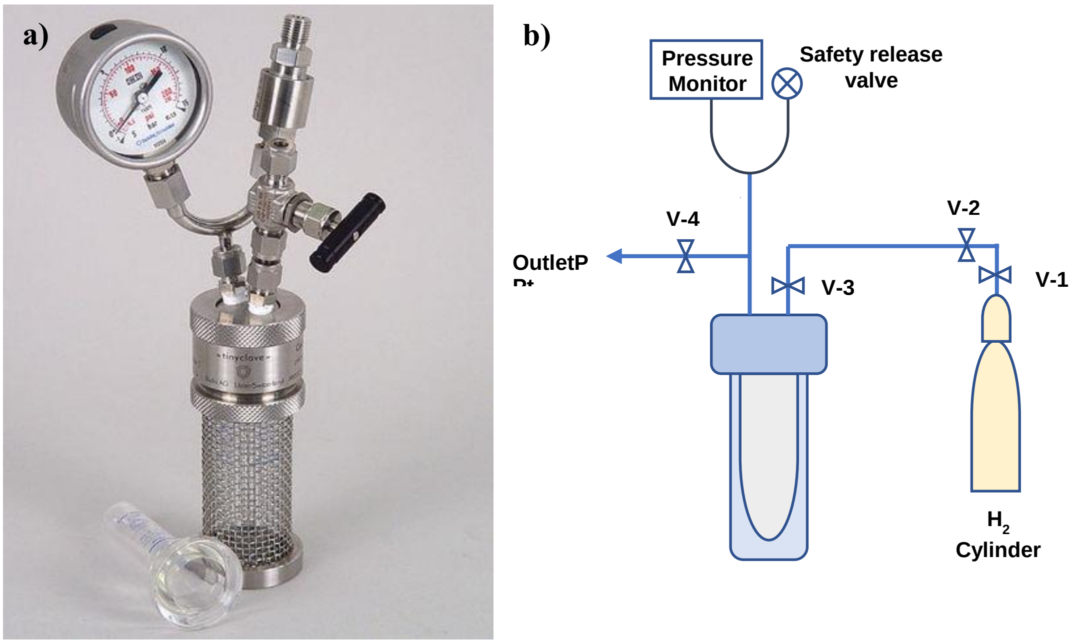


Figure S5. Pore size distributions for GNF[S3], PdNPs@GNF-2 and PtNPs@GNF-1.



Scheme S1. a) The high-pressure glass reactor, and b) a schematic of the high-pressure glass hydrogenation batch system (right).

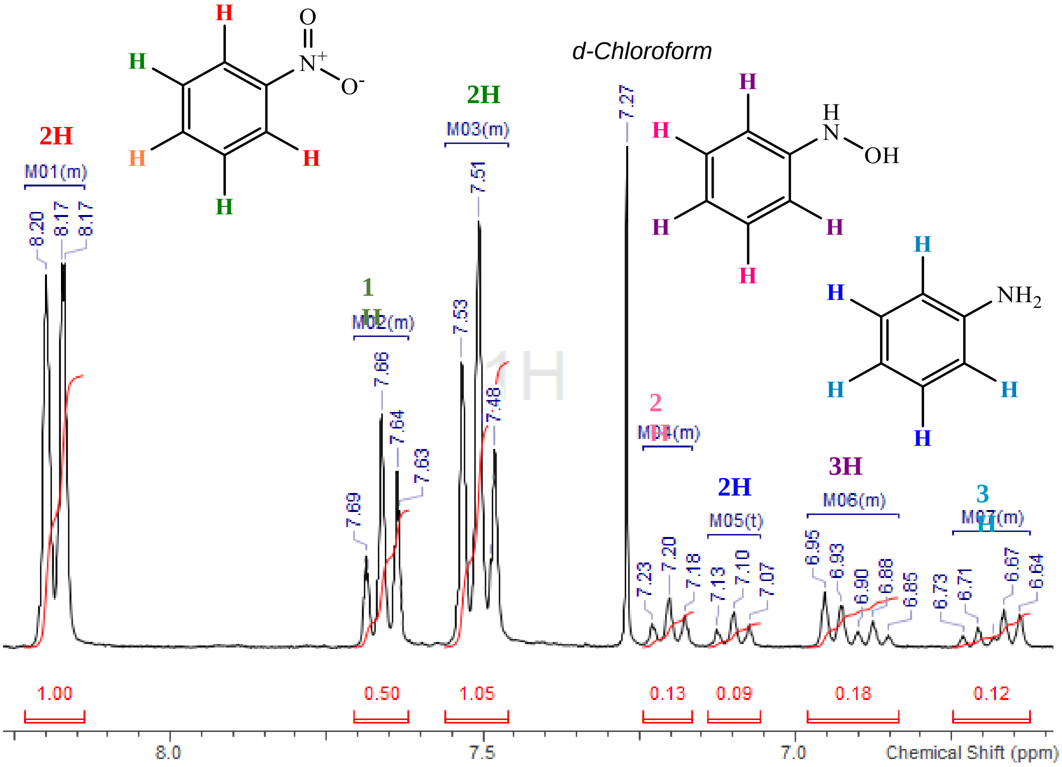


Figure S6. ^{1}H NMR of spectrum of the reaction mixture of catalytic reduction of nitrobenzene (Ph-NO_2) to phenylhydroxylamine (Ph-NHOH) and aniline (Ph-NH_2) recorded in $CDCl_3$ at 300 MHz.

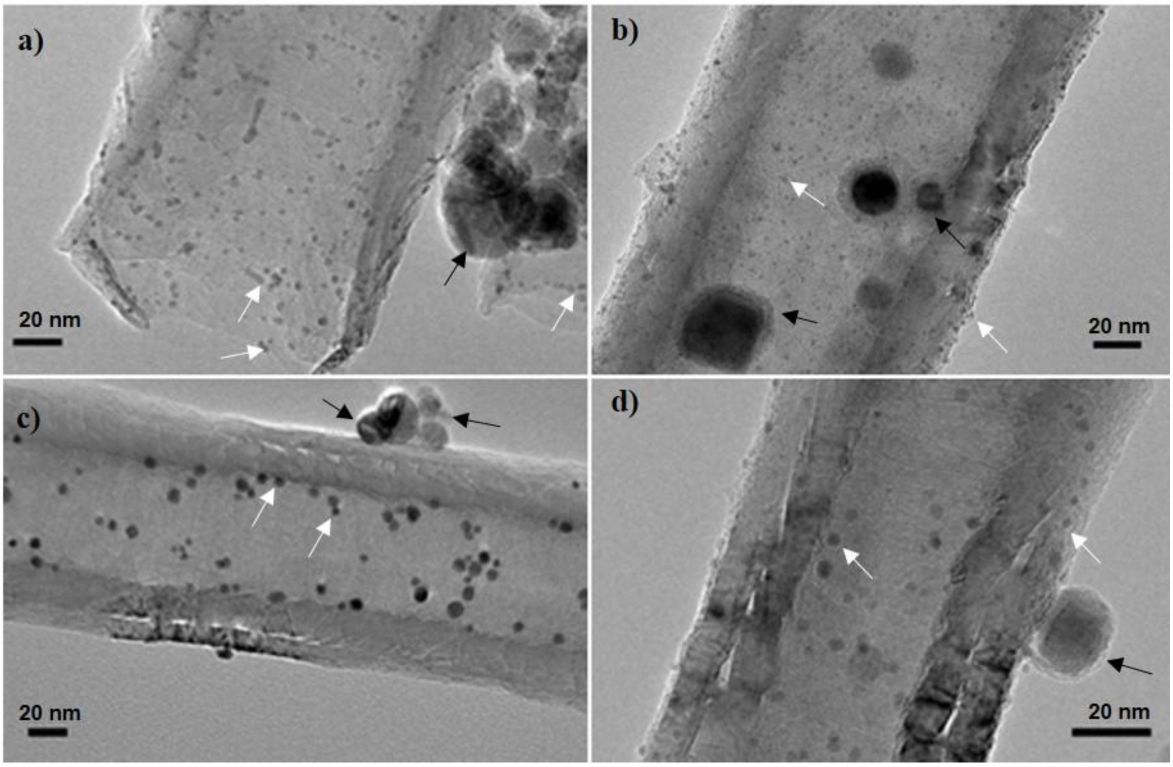


Figure S7. Representative HRTEM image of a), PdNPs@((Co@C$_n$)/GNF), b), PdNPs@((Fe@C$_n$)/GNF), c), PtNPs@((Co@C$_n$)/GNF), and d), PtNPs@((Fe@C$_n$)/GNF), white show catalytic Pd or PtNPs while black arrows show Co@C$_n$ or Fe@C$_n$ both attached to the GNF, respectively.

Table S3. Stability test data showing the activity of PdNPs@GNF-1 in the reduction of nitrobenzene in sequential reactions after conventional recovery based on the filtration using a PTFE membrane paper vs. PdNPs@(Co@C_n)/GNF and PdNPs@(Fe@C_n)/GNF in the reduction of nitrobenzene in sequential reactions after magnetic recovery.

Experiment no.	**Catalyst**	**Conversion of Ph-NO_2 (%) / TOF (min^{-1})**	**Selectivity (%)**	
			Ph-NHOH	**Ph-NH_2**
1st cycle	**PdNPs@GNF-2**[a]	77 / 72.3	15	85
	PdNPs@(Co@C_n)/GNF[b]	74 / 69.5	14	86
	PdNPs@(Fe@C_n)/GNF[b]	72 / 69.1	16	84
2nd cycle	**PdNPs@GNF-2**[a]	57 / 57.3	18	82
	PdNPs@(Co@C_n)/GNF[b]	70 / 65.7	17	83
	PdNPs@(Fe@C_n)/GNF[b]	68 / 64.4	13	87
3rd cycle	**PdNPs@GNF-2**[a]	48 / 45.1	20	80
	PdNPs@(Co@C_n)/GNF[b]	64 / 60.1	17	83
	PdNPs@(Fe@C_n)/GNF[b]	59 / 55.8	20	80
4th cycle	**PdNPs@GNF-2**[a]	50 / 46.9	26	74
	PdNPs@(Co@C_n)/GNF[b]	42 / 39.4	28	72
	PdNPs@(Fe@C_n)/GNF[b]	55 / 52.1	22	78
5th cycle	**PdNPs@GNF-2**[a]	37 / 35.6	29	71
	PdNPs@(Co@C_n)/GNF[b]	46 / 43.2	26	74
	PdNPs@(Fe@C_n)/GNF[b]	47 / 44.5	19	81

Reaction conditions: Nitrobenzene (0.08 mL, 0.78 mmol), ethanol (0.5 mL), catalyst (0.00051 mmol), H_2 (8 bar), room temperature, 30 min. All reactions were performed in duplicate and nitrobenzene conversion was determined by ^1H NMR with an error of ± 2 %. The TOFs were calculated as the ratio of the number of molecules of substrate consumed in the reaction per the number of true active catalyst sites calculated by BET measurements per minute. [a]Recovered by filtration. [b]Recovered by magnetic separation.

Table S4. Stability test data showing the activity of PtNPs@GNF-1 in the reduction of nitrobenzene in sequential reactions after conventional recovery based on the filtration using a PTFE membrane paper vs. PtNPs@(Co@C_n)/GNF and PtNPs@(Fe@C_n)/GNF in the reduction of nitrobenzene in sequential reactions after magnetic recovery.

Experiment no.	**Catalyst**	**Conversion of Ph-NO_2 (%) / TOF (min^{-1})**	**Selectivity (%)**	
			Ph-NHOH	**Ph-NH_2**
1st cycle	**PtNPs@GNF-1**[a]	24 / 25.2	36	64
	PtNPs@(Co@C_n)/GNF[b]	23 / 24.2	43	57
	PtNPs@(Fe@C_n)/GNF[b]	22 / 23.1	32	68
2nd cycle	**PtNPs@GNF-1**[a]	18 / 21.8	41	59
	PtNPs@(Co@C_n)/GNF[b]	20 / 21	50	50
	PtNPs@(Fe@C_n)/GNF[b]	19 / 19.9	52	48
3rd cycle	**PtNPs@GNF-1**[a]	15 / 15.6	50	55
	PtNPs@(Co@C_n)/GNF[b]	19 / 19.9	47	53
	PtNPs@(Fe@C_n)/GNF[b]	16 / 16.8	56	44
4th cycle	**PtNPs@GNF-1**[a]	15 / 15.6	43	57
	PtNPs@(Co@C_n)/GNF[b]	15 / 15.7	47	53
	PtNPs@(Fe@C_n)/GNF[b]	16 / 16.8	53	47
5th cycle	**PtNPs@GNF-1**[a]	13 / 13.5	48	52
	PtNPs@(Co@C_n)/GNF[b]	15 / 15.7	47	53
	PtNPs@(Fe@C_n)/GNF[b]	15 / 15.7.	53	47

Reaction conditions: Nitrobenzene (0.08 mL, 0.78 mmol), ethanol (0.5 mL), catalyst (0.00051 mmol), H_2 (8 bar), room tepmerature, 30 min. All reactions were performed in duplicate and nitrobenzene conversion was determined by ^{1}H NMR with an error of ± 2 %. The TOFs were calculated as the ratio of the number of molecules of substrate consumed in the reaction per the number of true active catalyst sites calculated by BET measurements per minute. [a]Recovered by filtration. [b]Recovered by magnetic separation.

Table S5. Data showing the precise loading of Pd and Pt metal in PdNPs@GNF-2 and PtNPs@GNF-1, for the catalyst materials as synthesised and after five rection cycles measured by ICP-OES.

	PdNPs (% wt.) in PdNPs@GNF-2 Before the reaction	PdNPs (% wt.) in PdNPs@GNF-2 After the 5. recovery	PtNPs (% wt.) in PtNPs@GNF-1 Before the reaction	PtNPs (% wt.) in PtNPs@GNF-1 After the 5. recovery
% amount of catalyst by ICP-OES	0.532 ±0.04	0.512 ±0.02	0.842 ±0.06	0.813 ±0.02

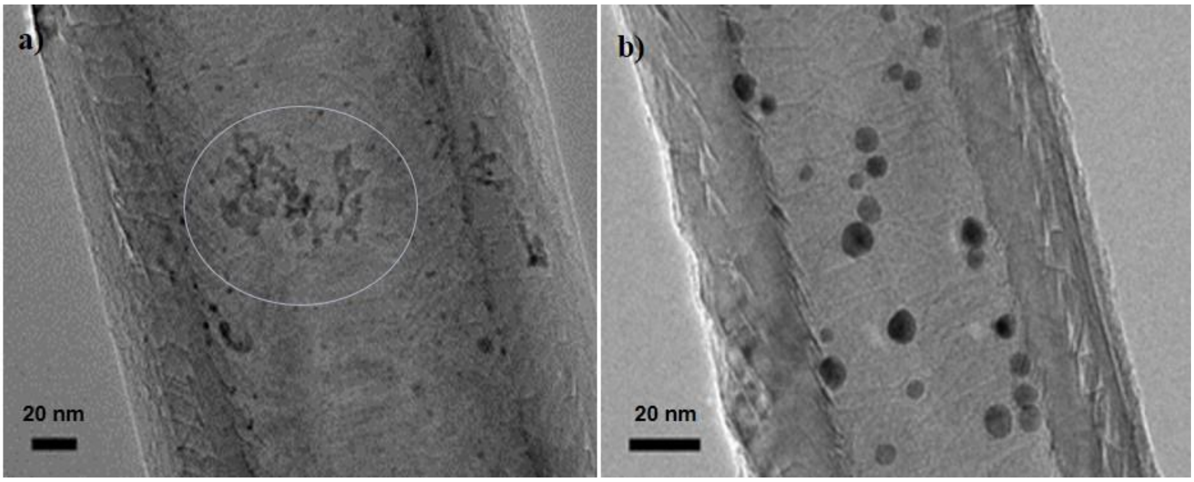


Figure S8. HRTEM images of a) PdNPs@GNF-2, and b) PtNPs@GNF-1 after five cycles of the catalyst tested in the reduction of nitrobenzene.

References

[S1] A.W. Hull, W.P. Davey, *Physical Review*, **1921**, *17*, 571-587.

[S2] H.E. Swanson, E., Tatge, Standard X-ray diffraction powder patterns I, National Bureau of Standards (U.S.), Circular, **1953**.

[S3] M. Aygün, C.T. Stoppiello, M. A. Lebedeva, E. F. Smith, M. D. C. Gimenez-Lopez, A. N. Khlobystov, T. W. Chamberlain, *J. Mater. Chem. A*, **2017**, *5*, 21467-21477.