Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Seed-engineering Approach toward Hollow Nanoreactor Suitable for the Confined Synthesis of Less-noble Ni-based Nanocrystals

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General consideration. All reagents, including $FeCl_3 \cdot 6H_2O$ (Acros), Sodium oleate (TCI), oleic acid (Aldrich), 1-Octadecene (Aldrich), Igepal CO-520 (Aldrich), tetraethyl orthosilicate (Acros), $NaBH_4$ (Samchun chem.), H_2O_2 (Samchun chem.), ascorbic acid (Samchun chem.), NH_3BH_3 (Aldrich), $N_2H_4 \cdot H_2O$ (Junsei), $HAuCl_4 \cdot xH_2O$ (Strem), $Na_2PdCl_4 \cdot 3H_2O$ (Strem), $Na_2PtCl_4 \cdot xH_2O$ (Strem), $Ni(NO_3)_2 \cdot 6H_2O$ (Strem), $NiCl_2 \cdot 6H_2O$ (Aldrich), $CoCl_2 \cdot 6H_2O$ (Kanto), 1-chloro-4-nitrobenzene (Aldrich), 1-bromo-4-nitrobenzene (Aldrich), 1-iodo-4-nitrobenzene (Aldrich), 4-nitroaniline (Aldrich), 4-nitrophenol (Aldrich), 4-nitroanisole (Aldrich), Ethyl 4-nitrobenzoate (Alfa Aesar), and 4-nitrostyrene (TCI), were used as purchased.

Transmission electron microscopy analyses (TEM) were conducted with JEOL JEM-2100 and JEM-ARM200F instruments. Samples were suspended in water by sonication and then dropped (20 μL) on a carbon-coated copper grid. X-ray diffraction patterns were obtained sith an X-Ray Diffractometer (18kW, Rigaku, Japan). The metal contents were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES) using Direct Reading Echelle ICP (Leeman Labs, Inc., NH USA). ^1H NMR spectra were recorded with a Bruker Avance III (300 MHz, 600 MHz) FT-NMR spectrometer. The analysis of the field dependent magnetization property was performed by using a MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer at 300 K and 5 K.

Synthesis of less-noble Ni-based nanocrystals inside the cavity.

Control experiments for Ni growth inside a Au@h-SiO_2 cavity with various reducing agent. Au@*h*-SiO_2 nanospheres were prepared through a previously reported procedure,[S1] which included the encapsulation of an Fe_3O_4/Au hybrid nanocrystal with a silica shell via a microemulsion technique and the selective etching of Fe_3O_4 from the silica nanosphere by reacting with $NaBH_4$. The resulting **Au@*h*-SiO_2** used in this study had a 3.3 nm Au nanocrystal inside the cavity. For the Ni growth reaction, **Au@*h*-SiO_2** nanospheres (2 mg) and $NiCl_2$ (10 mg) were mixed in distilled water (1 mL). Then, an aqueous solution containing 2.2 mmol of L-ascorbic acid, H_2O_2, $N_2H_4 \cdot H_2O$, or $NaBH_4$ (1 mL) was added to the suspension. The reaction was stirred gently at 45 °C with a magnetic stirrer. After 1.5 h, the resulting solids were collected by centrifugation and purified by three cycles of dispersion in an water and collection by centrifugation.

Preparation of the (Fe_3O_4/Au)@(SiO_2/M^{2+}) (M = Pd, Ni) and (Fe_3O_4/$AuPt^{2+}$)@SiO_2 nanospheres. Fe_3O_4 nanocrystals with an average core size of 10 nm were prepared through the previously reported procedure.[S2] The **(Fe_3O_4/Au)@(SiO_2/M^{2+})** (M = Pd, Ni) and **(Fe_3O_4/$AuPt^{2+}$)@SiO_2** nanospheres were made by a modification of the previously reported reverse microemulsion technique.S1 Igepal CO-520 (0.6 mL) was dispersed by sonication in a round-bottom flask containing cyclohexane (10 mL). Next, Fe_3O_4 nanoparticles (3 mg) dispersed in cyclohexane were added. An aqueous solution of $HAuCl_4$ (16 mg/mL, 0.05 mL) was added dropwise to the reaction mixture to form a transparent solution. Then, Na_2PdCl_4, $Ni(NO_3)_2$, or Na_2PtCl_4 aqueous solution (16 mg/mL, 0.05 mL) was introduced, followed by ammonium hydroxide solution (28–30%, 0.16 mL) with vigorous stirring. Finally, tetraethyl orthosilicate (TEOS, 0.2 mL) was added, and stirring was continued for 21 h. The resulting nanospheres were purified by repeating the redispersion in EtOH and water and then by centrifugation.

Control experiments excluding either TEOS or both $HAuCl_4$ and TEOS during the silica encapsulation procedure. Igepal CO-520 (0.6 mL) was dispersed in a round-bottom flask containing cyclohexane (10 mL). Next, Fe_3O_4 (3 mg) nanoparticles dispersed in cyclohexane were added. An aqueous solution of $HAuCl_4$ (16 mg/mL, 0.05 mL) was added dropwise to the reaction mixture to form a transparent solution (this step was omitted during the experiment excluding $HAuCl_4$). The subsequent introduction of Na_2PdCl_4, $Ni(NO_3)_2$, or Na_2PtCl_4 solution (16 mg/mL, 0.05 mL) was followed by the addition of ammonium hydroxide solution (28–30%, 0.16 mL) with vigorous stirring. The resulting nanospheres were purified by repeated cycles of dispersion in EtOH and water and followed by centrifugation.

Control experiments excluding $HAuCl_4$ during the silica encapsulation procedure. Igepal CO-520 (0.6 mL) was dispersed in a round-bottom flask containing cyclohexane (10 mL). Next, Fe_3O_4 (3 mg) nanoparticles dispersed in cyclohexane were added. An aqueous solution of Na_2PdCl_4, $Ni(NO_3)_2$, or Na_2PtCl_4 solution (8mg/mL, 0.1 mL) was added dropwise to the reaction mixture to form a transparent solution). Then, ammonium hydroxide solution (28–30%, 0.16 mL) was added with vigorous stirring. Finally, tetraethyl orthosilicate (TEOS, 0.2 mL) was added, and stirring was continued for 21 h. The resulting nanospheres were purified by repeating the redispersion in EtOH and water and then by centrifugation.

Sodium borohydride treatment of Fe_3O_4@SiO_2/M^{2+} (M = Pd, Ni, Pt). An aqueous solution of $NaBH_4$ (0.2 M, 1 mL) was added to an aqueous suspension (2 mL) of

Fe_3O_4@SiO_2/M^{2+} (M = Pd, Ni, Pt) (3 mg) at 40 °C; the reactions were stirred for 1 h at a constant temperature. The brown color of the suspension changed to black with the evolution of H_2 gas. The resulting solids were collected by the centrifugation and purified by repeated dispersion in water followed by centrifugation.

Control experiments for preparation of the (Fe_3O_4/Au)@(SiO_2/M^{2+}) (M = Pd, Ni) with various Pd^{2+} and Ni^{2+} contents. Aqueous stock solutions were prepared for Na_2PdCl_4 at 4, 8, 32 and 64 mg/mL and $Ni(NO_3)_2$ at 16 and 32 mg/mL. Igepal CO-520 (0.6 mL) was dispersed by sonication in a round-bottom flask containing cyclohexane (10 mL). Next, Fe_3O_4 nanoparticles (3 mg) dispersed in cyclohexane were added. An aqueous solution of $HAuCl_4$ (16 mg/mL, 0.05 mL) was added dropwise to form a transparent suspension. The desired Na_2PdCl_4 or $Ni(NO_3)_2$ stock solution (0.05 mL) was added, followed by ammonium hydroxide solution (28–30%, 0.16 mL) with vigorous stirring. Finally, TEOS (0.2 mL) was added, and stirring was continued for 21 h. The resulting nanospheres were purified by repeated cycles of dispersion in EtOH and water followed by centrifugation.

Reductive etching of Fe_3O_4 from (Fe_3O_4/Au)@(SiO_2/M^{2+}) (M = Pd, Ni) and (Fe_3O_4/AuPt^{2+})@SiO_2. An aqueous solution of $NaBH_4$ (0.2 M, 1 mL) was added to an aqueous suspension (2 mL) of **(Fe_3O_4/Au)@(SiO_2/M^{2+})** (M = Pd, Ni) (3 mg) or **(Fe_3O_4/AuPt^{2+})@SiO_2** (3 mg) at 40 °C; the reactions were stirred for 1 h at a constant temperature. The brown color of the suspension changed to black with the evolution of H_2 gas. The resulting solids were collected by the centrifugation and purified by repeated dispersion in water followed by centrifugation.

Growth of Ni nanoparticle inside (Au/Pd)@h-SiO_2 cavities. To form the Ni-hydrazine complex, $NiCl_2$ (50 mg, 0.2 mmol) was dissolved in deionized water (0.5 mL), and hydrazine (0.109 mL, 2.2 mmol) was added. Violet precipitates were formed immediately. The resulting solids were collected by centrifugation and purified twice by repeated dispersion in water. An aqueous solution of Ni-hydrazine complex (15 mg) and hydrazine (0.054 mL, 1.1 mmol) were prepared in distilled water (1.5 mL) in a capped vessel. The solution was degassed by sparging with N_2 for 30 min. **(Au/Pd)@*h*-SiO_2** nanospheres (2 mg) dispersed in degassed water (0.5 mL) were transferred to the solution via syringe and stirred for 1.5 h at 45 °C in a closed vessel without ventilation. The color of the suspension slowly changed from violet, through light brown, to black with the evolution of H_2 gas. The **Ni@SiO_2** was collected by placing a small magnet on the side wall of the reaction vessel and removing the supernatant solution by using a syringe. The resulted **Ni@SiO$_2$** were re-dispersed in a degassed water and stored as a suspension under the nitrogen environment.

Growth of Ni/Co alloy nanoparticles inside (Au/Pd)@h-SiO$_2$ cavities. An aqueous solution of Ni-hydrazine complex (10 mg) and hydrazine (0.054 mL, 1.1 mmol) were prepared in distilled water (1.5 mL) in a capped vessel. The solution was degassed by sparging with N_2 for 30 min. (Au/Pd)@*h*-SiO$_2$ nanospheres (2 mg) dispersed in degassed water (0.5 mL) were transferred to the solution via syringe and stirred for 20 min at 45 °C in a closed vessel. Then, the aqueous solution of $CoCl_2$ (0.42 M, 0.075 mL) was added and the solution was maintained for 40 min at 45 °C in a closed vessel. The resulting solids were collected by the centrifugation and purified by repeated dispersion in water followed by centrifugation.

Control experiment for Co growth inside (Au/Pd)@h-SiO$_2$ cavities. (Au/Pd)@*h*-SiO$_2$ nanoparticles (2 mg) and hydrazine (1.1 mmol) were suspended in water (2 mL). Aqueous $CoCl_2$ (0.42 M, 0.075 mL) was added to the suspension and stirred at 45 °C for 1 h in the closed vessel. The resulting solid was collected by centrifugation and washed with water three times.

Evaluation of catalytic effectiveness of the Ni@SiO$_2$.

Hydrolytic dehydrogenation of NH$_3$BH$_3$. A one-necked Schlenk flask containing a stir bar was placed on a magnetic stirrer. A burette filled with water was connected to a reaction flask to measure the volume of hydrogen gas evolved from the reaction. The other end of the burette was connected to a pressure-equalization funnel. The **Ni@SiO$_2$** (0.064, 0.053, 0.043, and 0.032 mM, based on Ni content) in water (1.5 mL) was introduced into the flask. Then, aqueous NH_3BH_3 solution (0.5 mL, 30.8 mg, 1 mmol) was added into the reaction flask to initiate the reaction. The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature under ambient atmosphere. Recycling experiments were carried out by additionally injecting a aliqout of the NH_3BH_3 solution (0.5 mL, 1 mmol) to the flask after each run.

Catalytic hydrogenation of nitroarene compounds. **N**itroarenes (0.1 mmol), hydrazine (4 mmol, 0.2 mL), and H_2O (0.8 mL) were mixed in reaction tube, and then the **Ni@SiO**$_2$ catalyst (15 mol%) was added to the solution. The mixture was stirred until nitroarenes was completely consumed at room temperature, as determined by TLC (0.25 mm E. Merck silica gel plates (60F-254), with UV light detection). After completion, the reaction mixture was extracted with ethyl acetate (3 × 1 mL) and filtered to remove the catalysts. The combined organic layers were evaporated at reduced pressure. The products were identified by ^{1}H NMR. For investigating the recylability of the **Ni@SiO$_2$** catalyst, the catalyst was collected after the reaction by placing a small magnet on the side wall of the reaction vessel and decanting the product solution, which was followed by the succesive washing with 1 ml of distilled water and 1 ml of actone. The consecutive run was performed by adding the reactants solution to the reaction vessel containing the recovered **Ni@SiO$_2$** catalyst.

References for the Supporting Information

[S1] K. M. Yeo, J. Shin and I. S. Lee, *Chem. Commun.*, 2010, **46**, 64-66.

[S2] J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang and T. Hyeon, *Nat. Mater.*, 2004, **3**, 891-895.

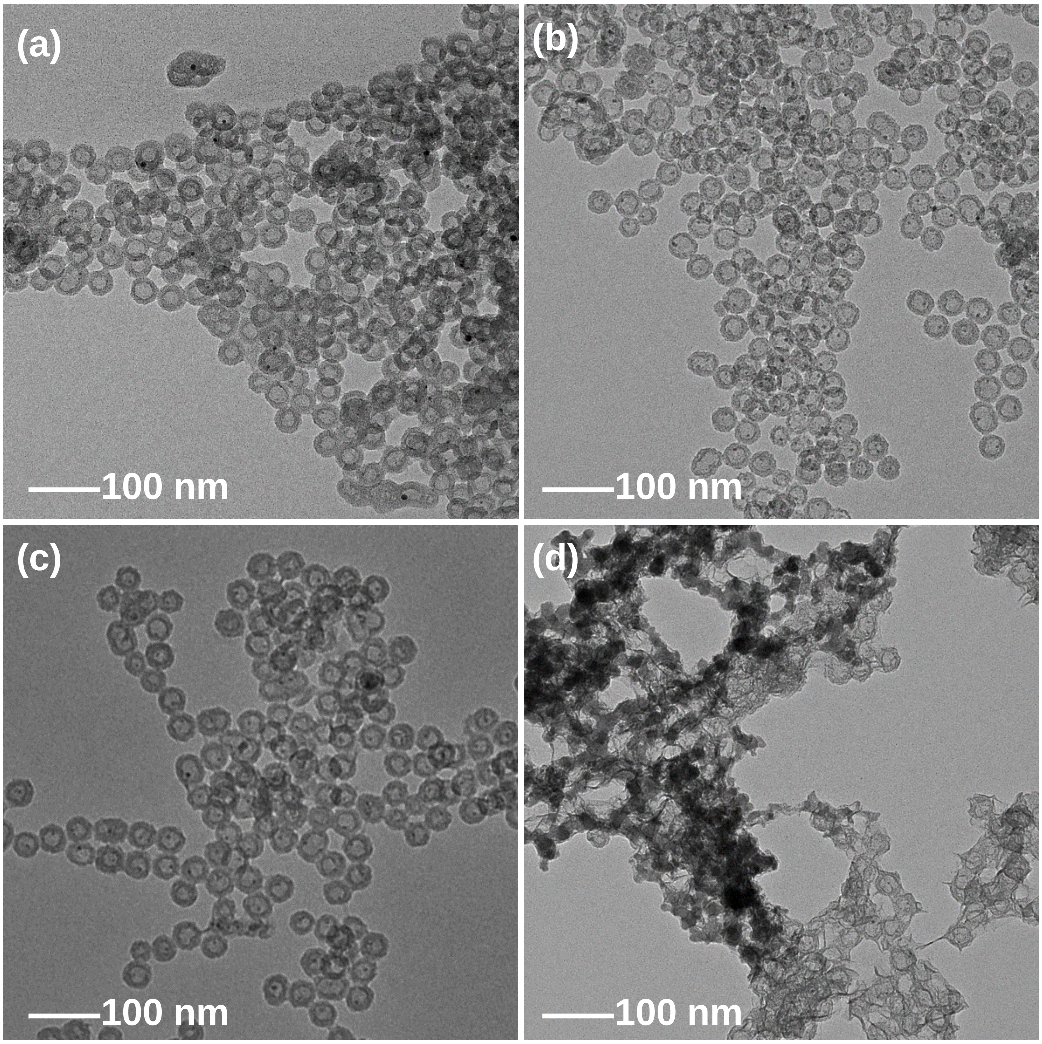
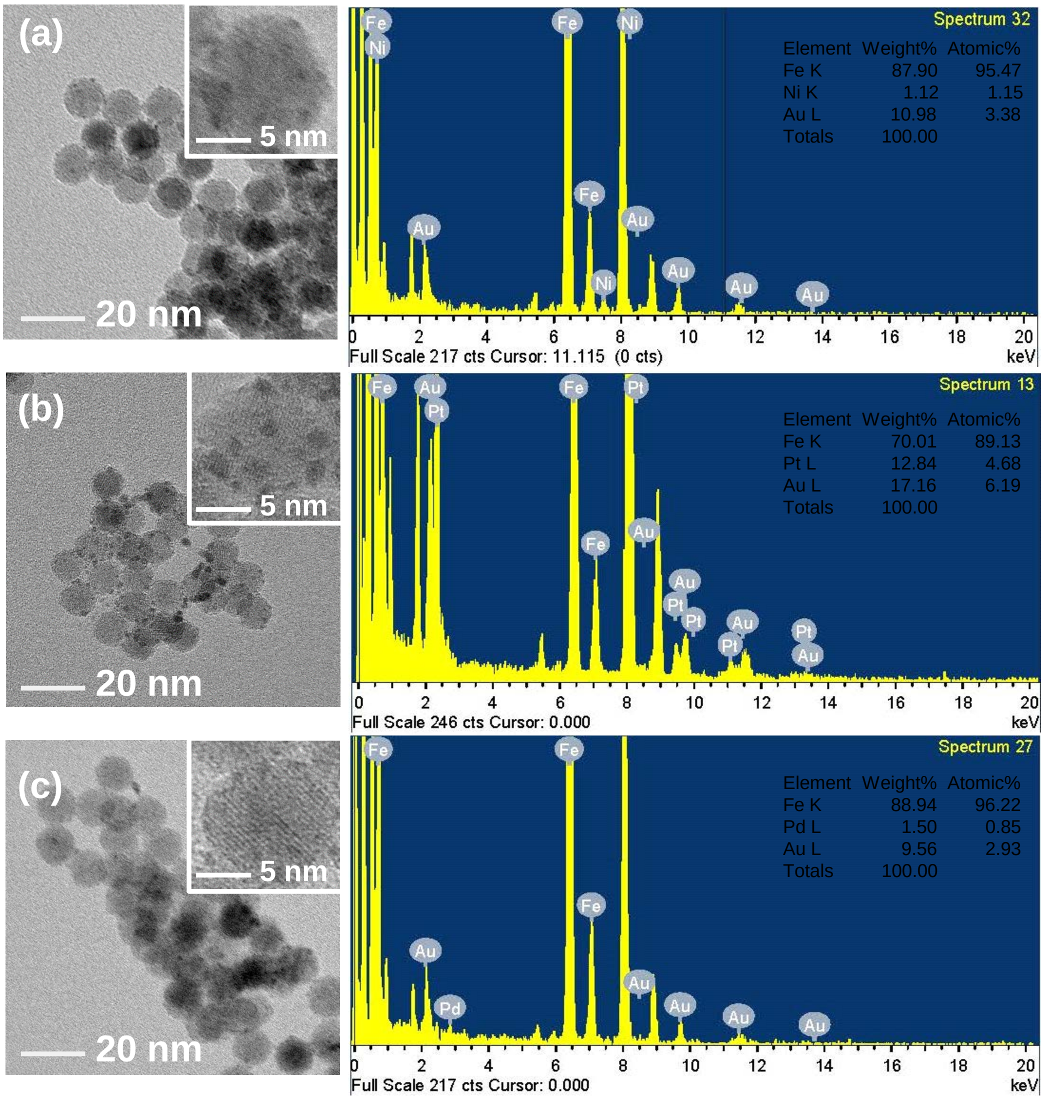


Fig. S1 TEM image of the isolated nanoparticles from the trial reaction to growth Ni nanoparticles inside **Au@*h*-SiO$_2$** with mild reducing agents such as (a) ascorbic acid, (b) H_2O_2, and (c) hydrazine and (d) more strongly reducing $NaBH_4$.

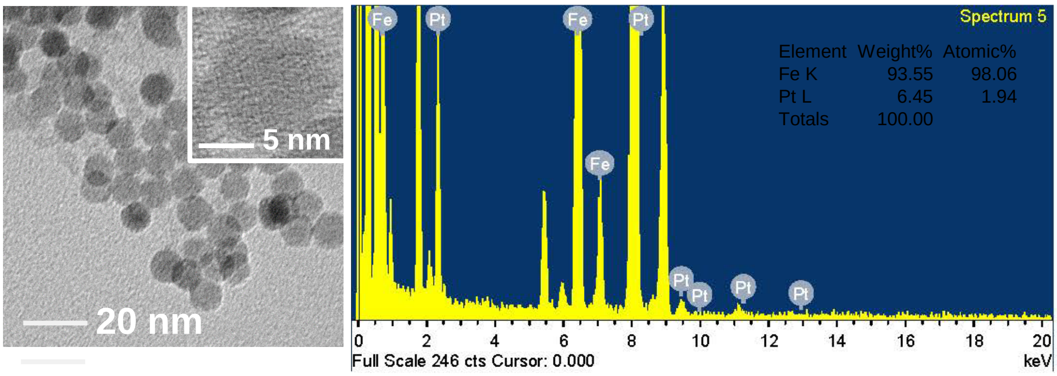


Element	Weight%	Atomic%
Fe K	87.90	95.47
Ni K	1.12	1.15
Au L	10.98	3.38
Totals	100.00	

Element	Weight%	Atomic%
Fe K	70.01	89.13
Pt L	12.84	4.68
Au L	17.16	6.19
Totals	100.00	

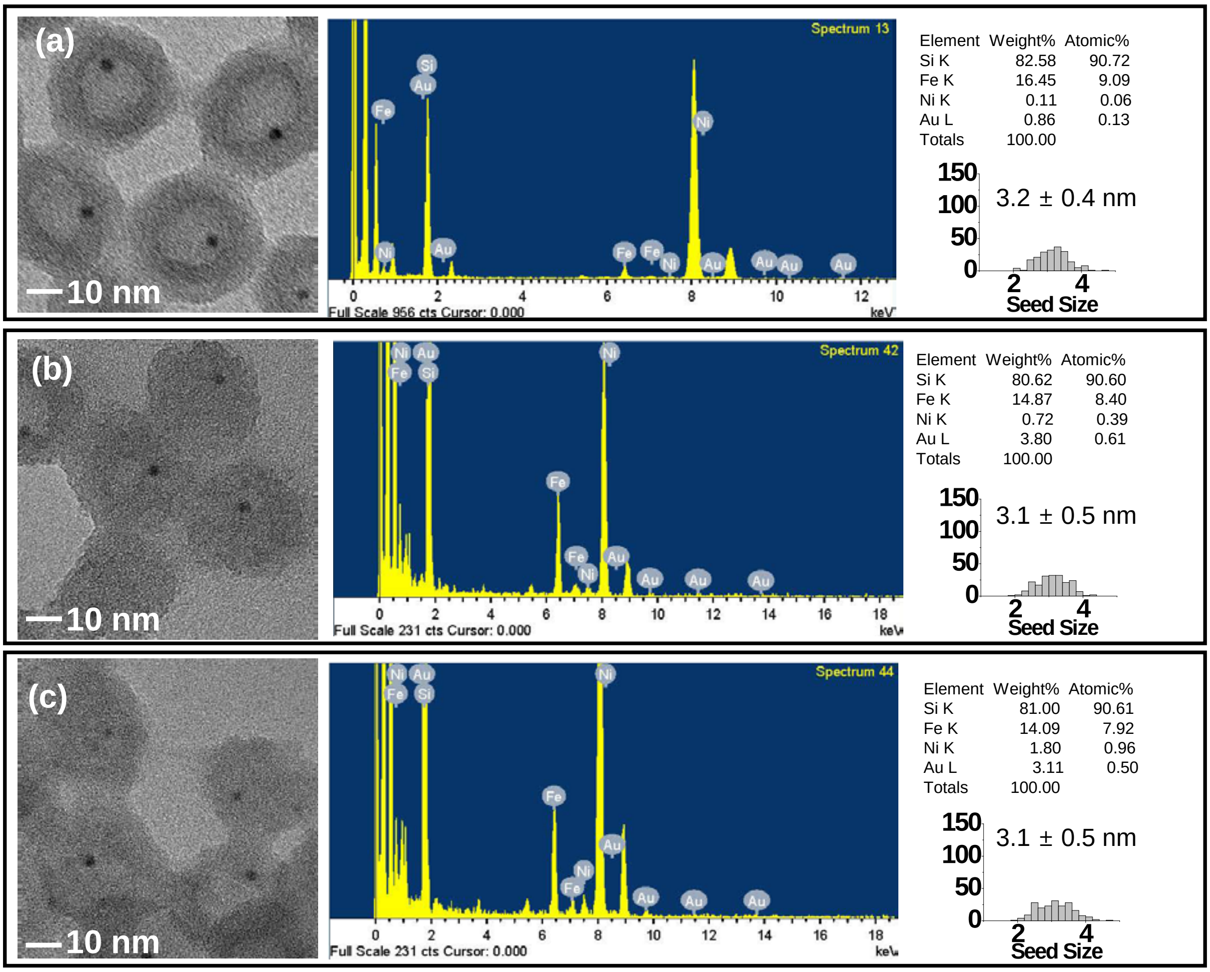
Element	Weight%	Atomic%
Fe K	88.94	96.22
Pd L	1.50	0.85
Au L	9.56	2.93
Totals	100.00	

Fig. S2 TEM and HRTEM (insets) images and EDS data of resultant nanopraticles from the control reactions without TEOS, where Fe_3O_4 nanoparticles were treated with equlimolar mixtures of $HAuCl_4$ and (a) $Ni(NO_3)_2$, (b) Na_2PtCl_4, and (c) Na_2PdCl_4, respectively, in microemulsion solutions.



Element	Weight%	Atomic%
Fe K	93.55	98.06
Pt L	6.45	1.94
Totals	100.00	

Fig. S3 TEM and HRTEM (insets) images and EDS data of resultant nanopraticles from the control reactions without TEOS and $HAuCl_4$, where Fe_3O_4 nanoparticles were treated with Na_2PtCl_4, in microemulsion solutions.



(a)

Element	Weight%	Atomic%
Si K	82.58	90.72
Fe K	16.45	9.09
Ni K	0.11	0.06
Au L	0.86	0.13
Totals	100.00	

(b)

Element	Weight%	Atomic%
Si K	80.62	90.60
Fe K	14.87	8.40
Ni K	0.72	0.39
Au L	3.80	0.61
Totals	100.00	

(c)

Element	Weight%	Atomic%
Si K	81.00	90.61
Fe K	14.09	7.92
Ni K	1.80	0.96
Au L	3.11	0.50
Totals	100.00	

Fig. S4 TEM images and EDS data of resultant **Au@*h*-SiO$_2$** nanoparticles from the NaBH$_4$ treatement of the **(Fe$_3$O$_4$/Au)@(SiO$_2$/Ni^{2+})** nanospheres with various Ni^{2+} contents, which were prepared by varying the concentration of the injected Ni(NO$_3$)$_2$ solution of (a) 16 mg/mL, (b) 32 mg/mL, and (c) 48 mg/mL. Histograms are showing the size distribution of Au nanocrystal inside the cavity.

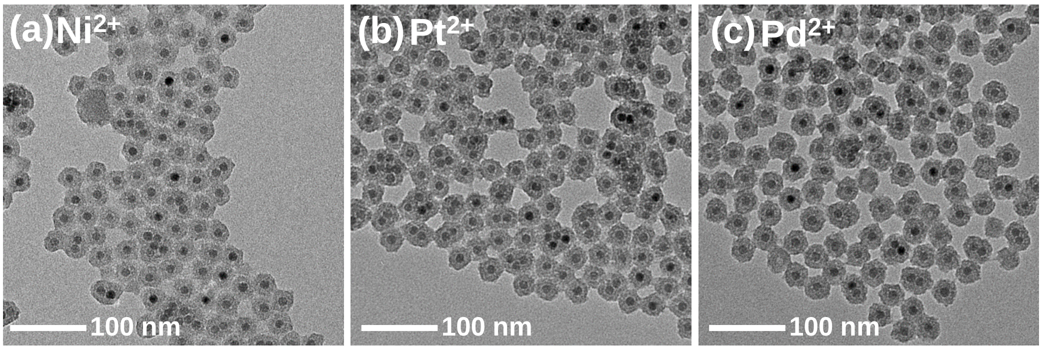
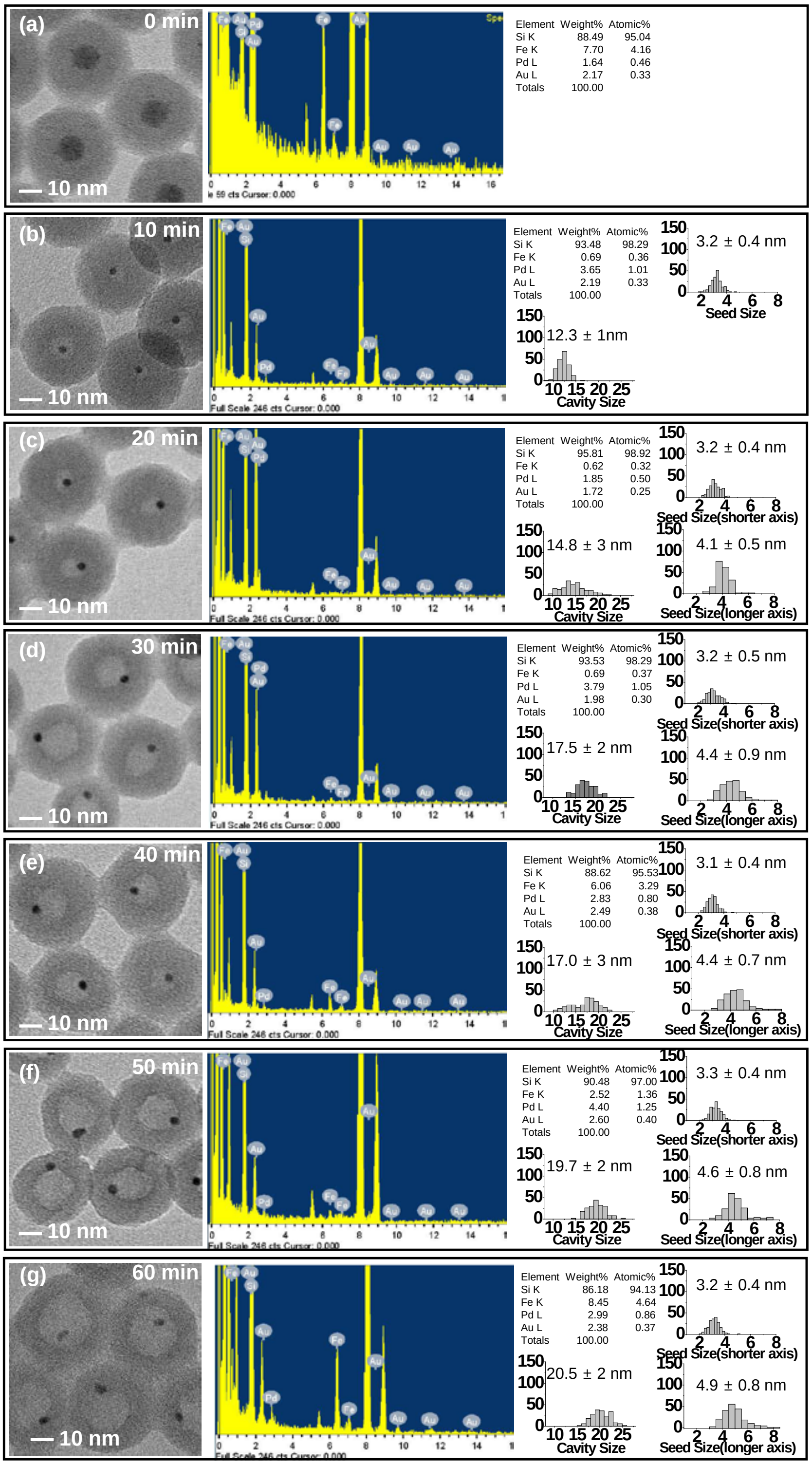


Fig. S5 TEM images of the **Fe_3O_4@SiO_2/M^{2+}**, M = (a) Ni, (b) Pt, (c) Pd, treated with $NaBH_4$.



(a)

Element	Weight%	Atomic%
Si K	88.49	95.04
Fe K	7.70	4.16
Pd L	1.64	0.46
Au L	2.17	0.33
Totals	100.00	

(b)

Element	Weight%	Atomic%
Si K	93.48	98.29
Fe K	0.69	0.36
Pd L	3.65	1.01
Au L	2.19	0.33
Totals	100.00	

(c)

Element	Weight%	Atomic%
Si K	95.81	98.92
Fe K	0.62	0.32
Pd L	1.85	0.50
Au L	1.72	0.25
Totals	100.00	

(d)

Element	Weight%	Atomic%
Si K	93.53	98.29
Fe K	0.69	0.37
Pd L	3.79	1.05
Au L	1.98	0.30
Totals	100.00	

(e)

Element	Weight%	Atomic%
Si K	88.62	95.53
Fe K	6.06	3.29
Pd L	2.83	0.80
Au L	2.49	0.38
Totals	100.00	

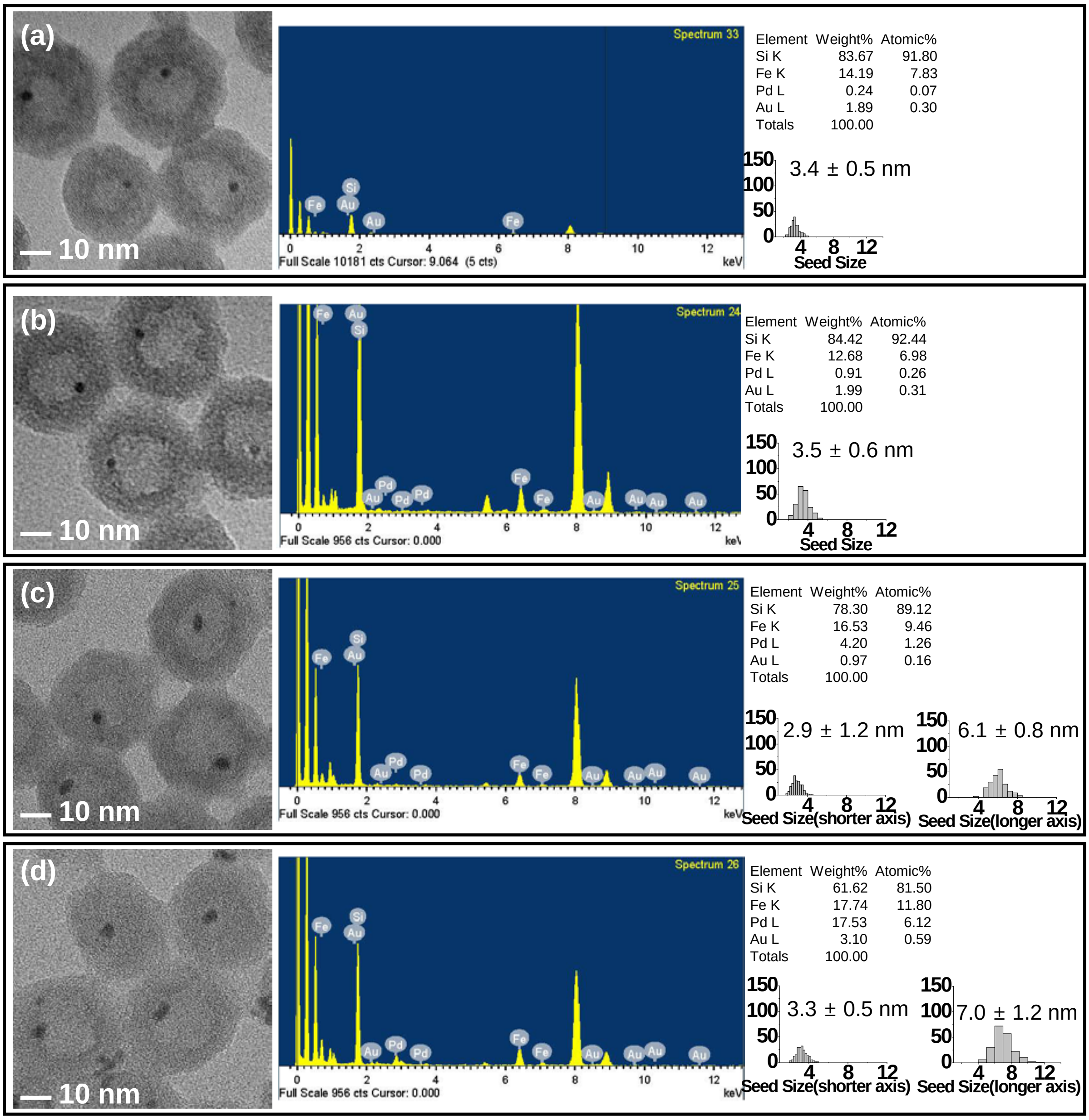
(f)

Element	Weight%	Atomic%
Si K	90.48	97.00
Fe K	2.52	1.36
Pd L	4.40	1.25
Au L	2.60	0.40
Totals	100.00	

(g)

Element	Weight%	Atomic%
Si K	86.18	94.13
Fe K	8.45	4.64
Pd L	2.99	0.86
Au L	2.38	0.37
Totals	100.00	

Fig. S6 TEM images and histograms, for showing the size distribution of the interior cavity and core nanoparticle, of samples isolated during the reaction of the **$(Fe_3O_4/Au)@)SiO_2/Pd^{2+}$** with $NaBH_4$ at (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, and (g) 60 min, respectively. Histograms are showing the size distribution of cavity and internal nanocrystal with ellipsoidal shape.



(a)

Element	Weight%	Atomic%
Si K	83.67	91.80
Fe K	14.19	7.83
Pd L	0.24	0.07
Au L	1.89	0.30
Totals	100.00	

(b)

Element	Weight%	Atomic%
Si K	84.42	92.44
Fe K	12.68	6.98
Pd L	0.91	0.26
Au L	1.99	0.31
Totals	100.00	

(c)

Element	Weight%	Atomic%
Si K	78.30	89.12
Fe K	16.53	9.46
Pd L	4.20	1.26
Au L	0.97	0.16
Totals	100.00	

(d)

Element	Weight%	Atomic%
Si K	61.62	81.50
Fe K	17.74	11.80
Pd L	17.53	6.12
Au L	3.10	0.59
Totals	100.00	

Fig. S7 TEM images, EDS data, and histograms for for showing the size distribution of the core nanoparticle inside the cavity, of resultant **(Au/Pd)@*h*-SiO_2** from the $NaBH_4$ treatement of the **(Fe_3O_4/Au)@(SiO_2/Pd^{2+})** nanospheres with various Pd^{2+} contents, which were prepared by varying the concentration of the injected Na_2PdCl_4 solution of (a) 4 mg/mL, (b) 8 mg/mL, (c) 32 mg/mL, and (d) 64 mg/mL. Histograms are showing the size distribution of Au/Pd heterojection-nanocrystal inside the cavity.

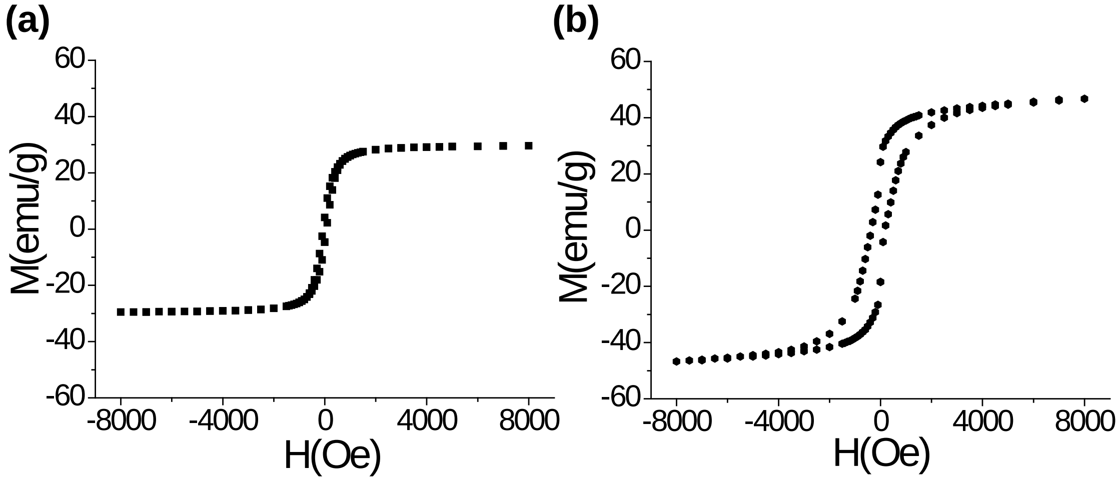


Fig. S8 Field dependent magnetization curves of the **Ni@SiO$_2$** measured at (a) 300 K and (b) 5 K.

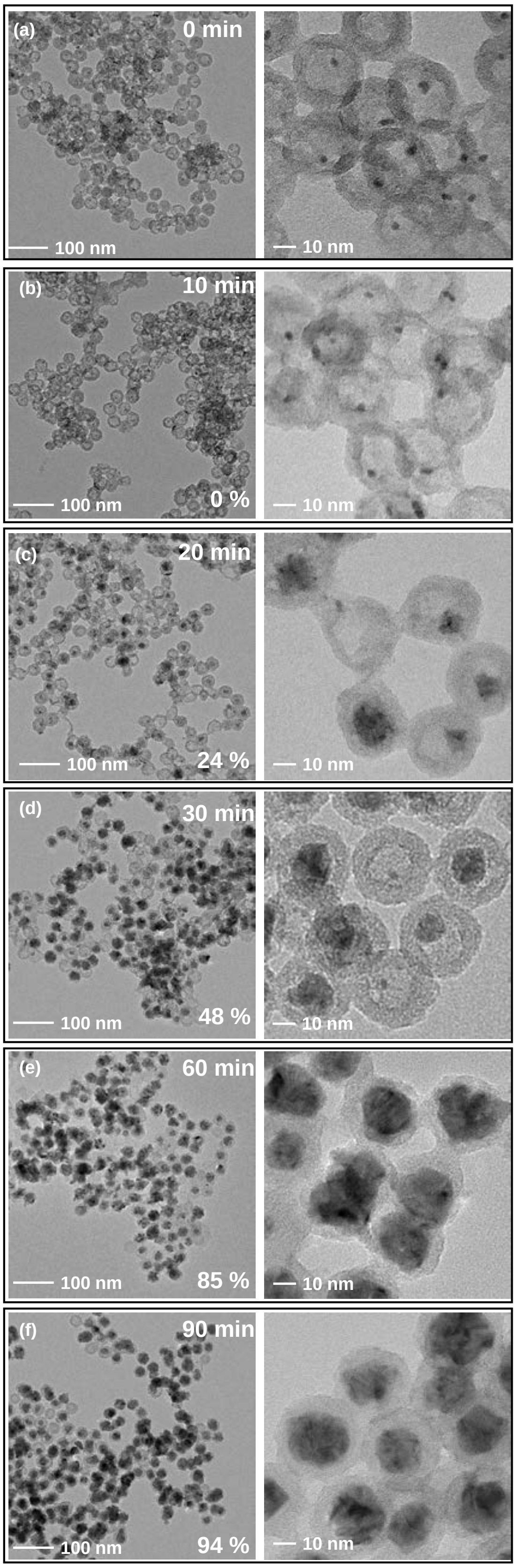


Fig. S9 TEM images of samples isolated during the Ni-growing reaction with the **(Au/Pd)@*h*-SiO$_2$** at (a) 0, (b) 10, (c) 20, (d) 30, (e) 60, and (f) 90 min, respectively.

Fig. S10 Photographes of the aqueous suspenison of the **Ni@SiO$_2$** before (left) and 5 min after placing a magnet (right).

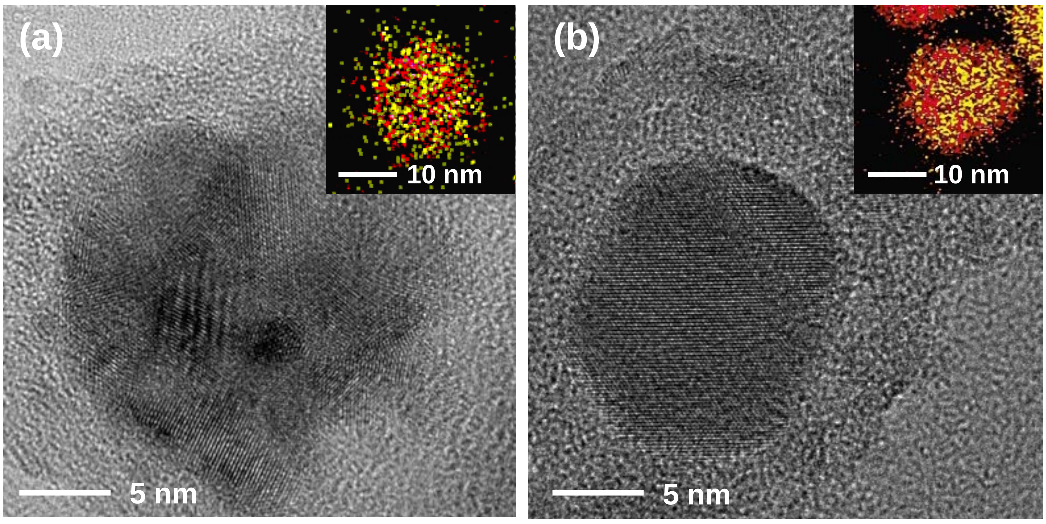
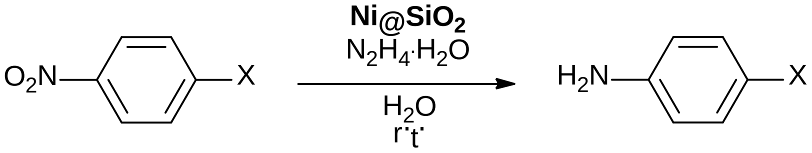
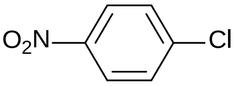
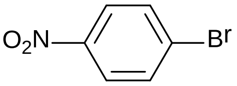
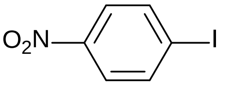
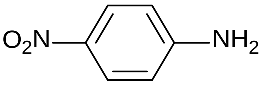
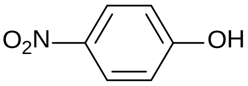
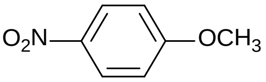
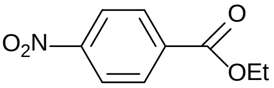
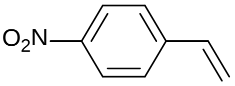


Fig. S11 HRTEM images and EDX elementary maps (insets, Ni: red, Co: yellow) of the **(Ni/Co@SiO$_2$)** (a) before and (b) after post-annealing treatment at 700 °C.

Table S1. Catalytic reduction of nitroarenes to the corresponding anilines[a].



Entry	Substrate	Time [h]	Conversion [%]	Selectivity [%]
1		2	>99	>99
2		2	>99	83
3		2	>99	95
4		0.5	>99	>99
5		1	>99	>99
6		4	>99	>99
7		2	>99	>99
8		1	>99	88

[a]Condition: 0.1 mmol of nitroarene, 15 mol% catalyst, 0.2 mL of $N_2H_4 \cdot H_2O$, room temperature.