Electronic Supplementary Material (ESI) for Nanoscale.

A simple route to diverse noble metal-decorated iron oxide nanoparticles for catalysis

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SUPPLEMENTARY INFORMATION

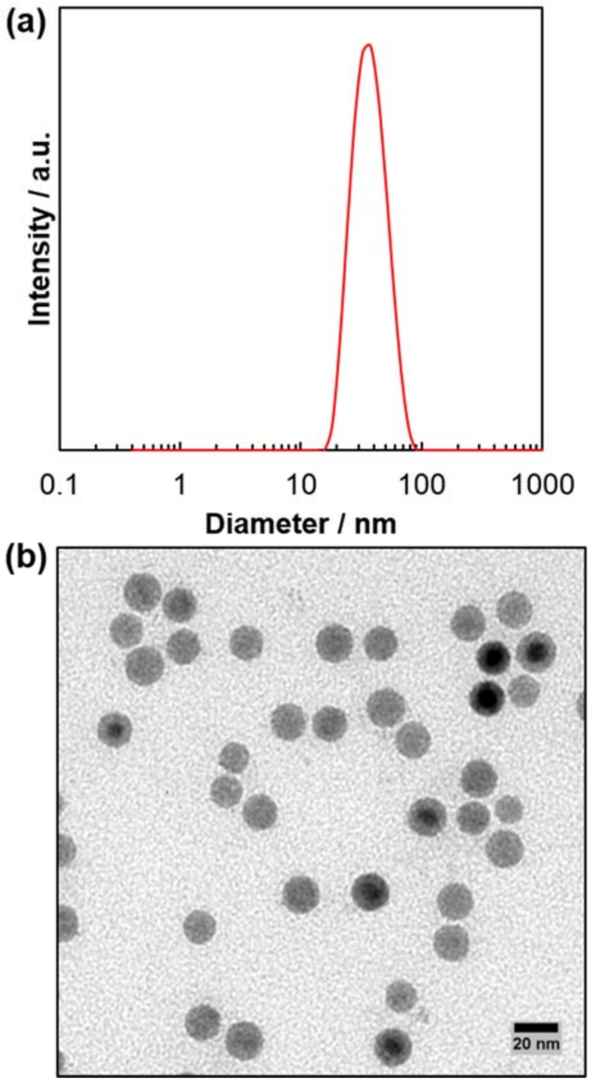

Figure S1. The IONP cores are coated with a thin layer of trialkoxysilane. (a) The DLS trace shows a narrow size distribution (Z_{ave} = 36.9 +/- 0.4 nm; PDI 0.2), and (b) the nanoparticles appear as non-aggregated separate particles in TEM images.

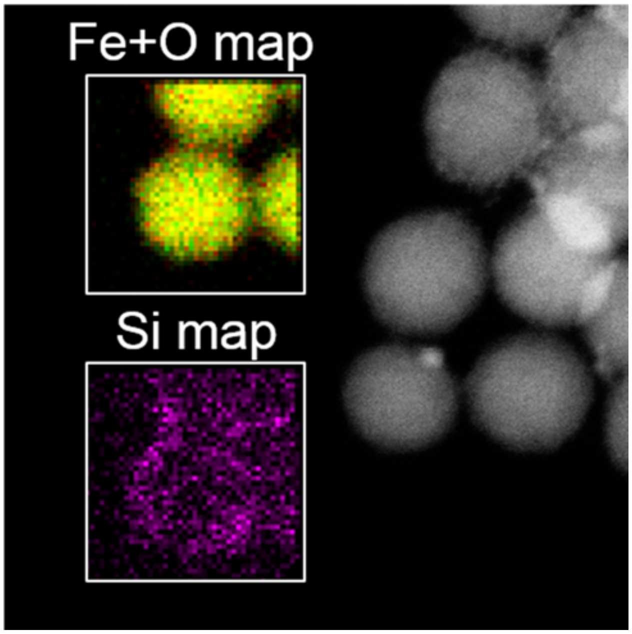

Figure S2. EDX mapping reveals the presence of a thin shell containing Si (shown in magenta) around the IONP cores (Fe in green and O in red, rendering their co-localization as yellow). *n.b.* The sample shown here is Fe_3O_4@SiO_2-Ag.

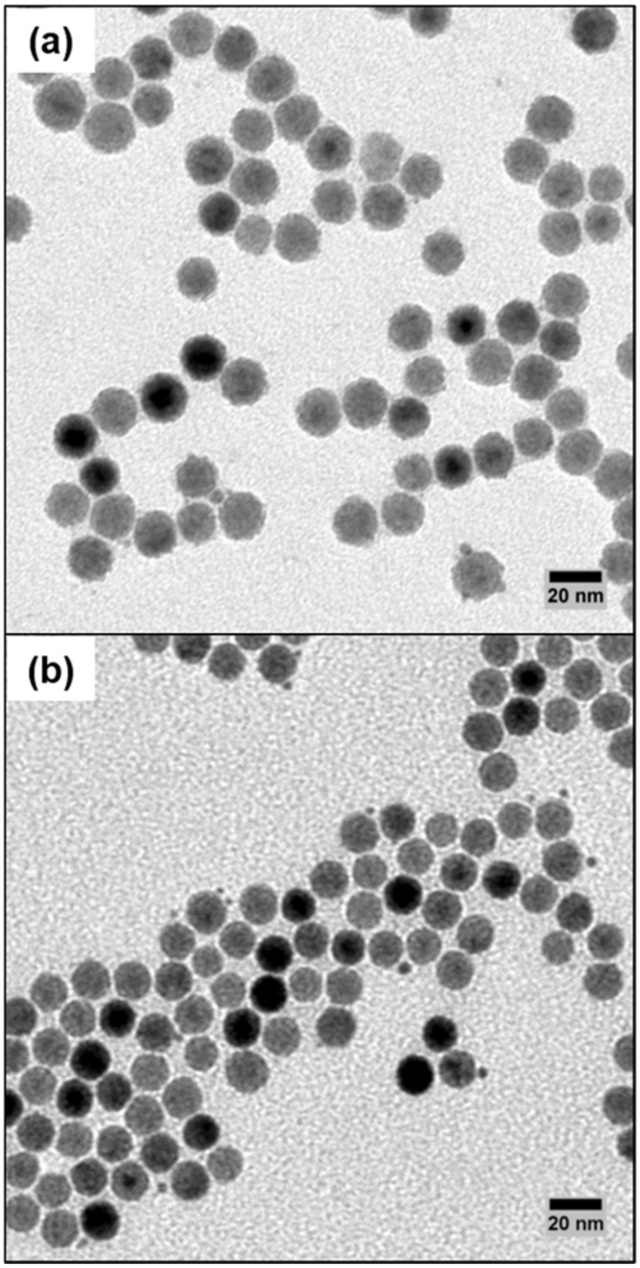

Figure S3. Two synthetic controls were performed to illustrate the silver-thiol attachment in the preliminary steps. (a) By increasing the amount of $AgNO_3$ added to the $Fe_3O_4@SiO_2$ material fivefold, small silver particles are visible in the product. (b) Alternatively, by decreasing the amount of MPTMS in the SiO_2 coating by half, the silver is forced into a smaller surface area once it is reduced, rendering small visible particles.

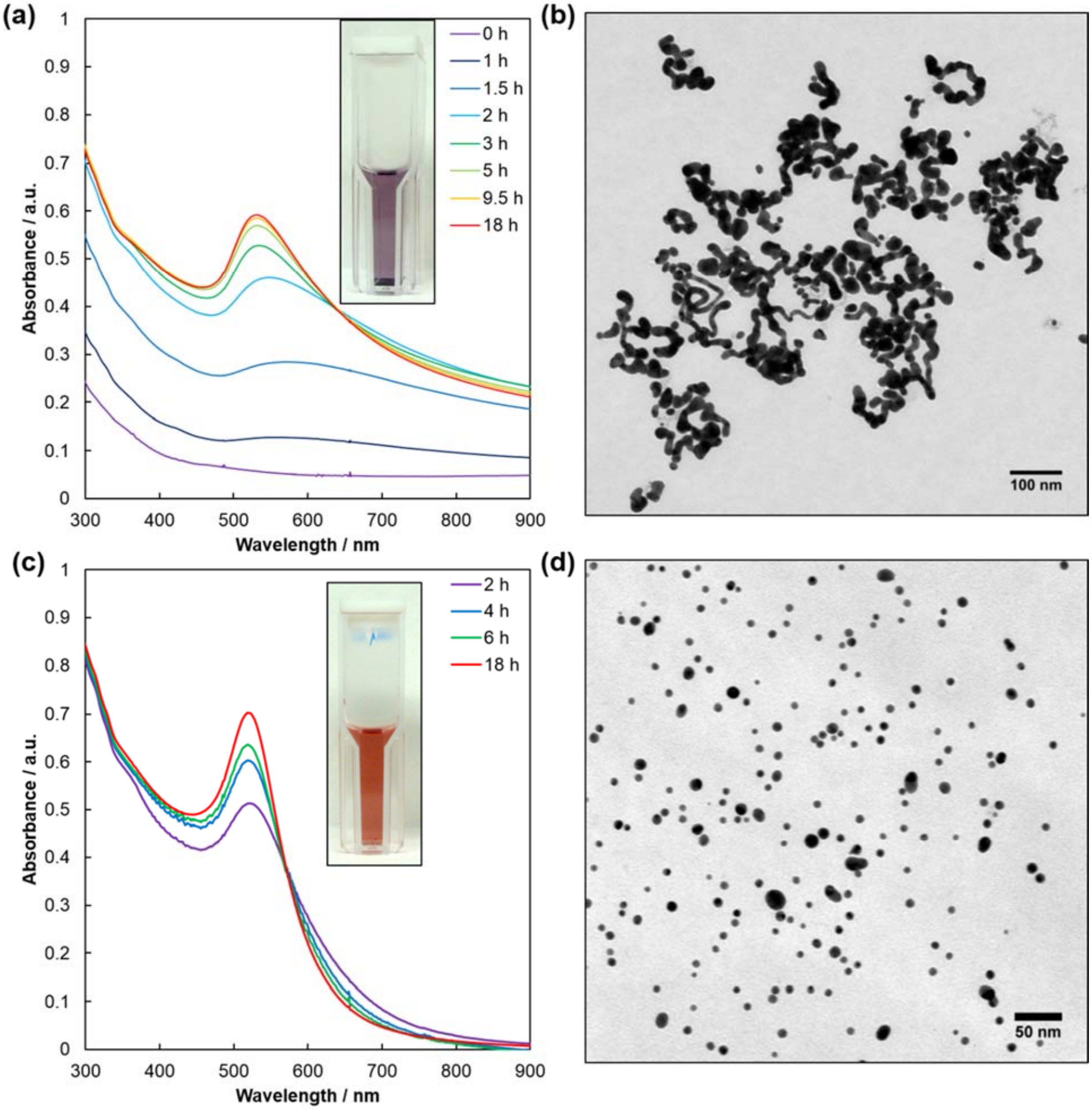

Figure S4. Control reductions of Au. (a) A solution of $HAuCl_4$, CTAB, and NaOH (1:250:500) slowly forms Au^0 over 18 h, as indicated by the solution color change and solid material visualized by TEM (b). By adding a sub-stoichiometric amount of silver seeds (0.37 eq), the reduction accelerates appreciably (c), developing a red color within 2 h and ultimately spheroid particles (d). This indicates that small silver seeds are able to direct the reduction and subsequent growth of noble metal particles.

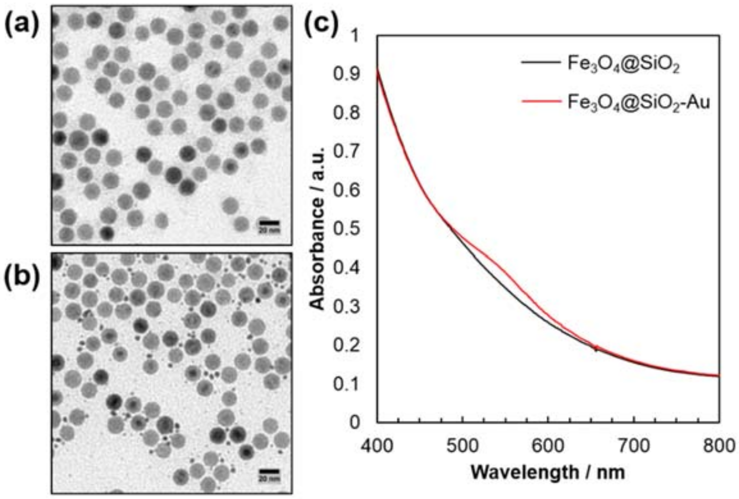

Figure S5. The presence of the Ag10 intermediate is crucial to the successful growth of noble metal seeds on the IONPs. TEM images of the products of parallel reactions (a) without and (b) with silver show that little to no Au decoration occurs without silver as a directing agent, and (c) UV-vis spectra of the starting material and Au-decorated iron oxide sample show the growth of the Au surface plasmon absorbance between 500 and 600 nm, confirming the presence of gold seeds.

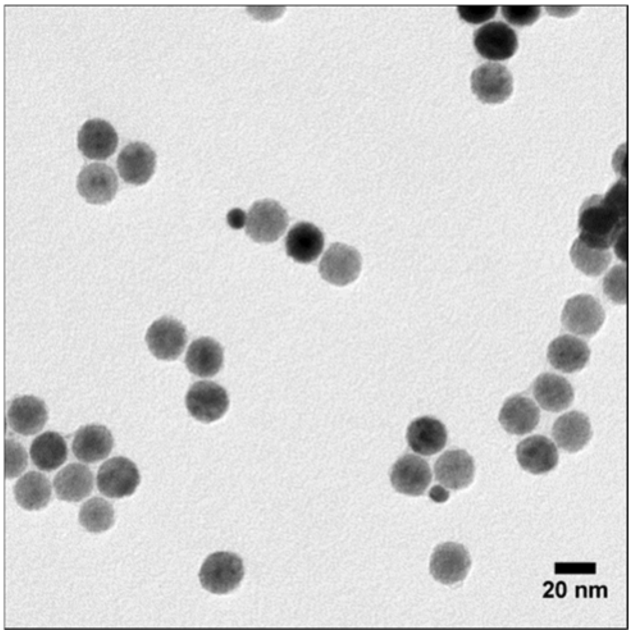

Figure S6. TEM image of Fe_3O_4@SiO_2-Ag10 after heating at 60 °C for 6 h, illustrating that the elevated temperature required for the successful reduction of Ag and Pt in the seed decoration reaction also can rearrange the distributed silver intermediate content into larger Ag particles.

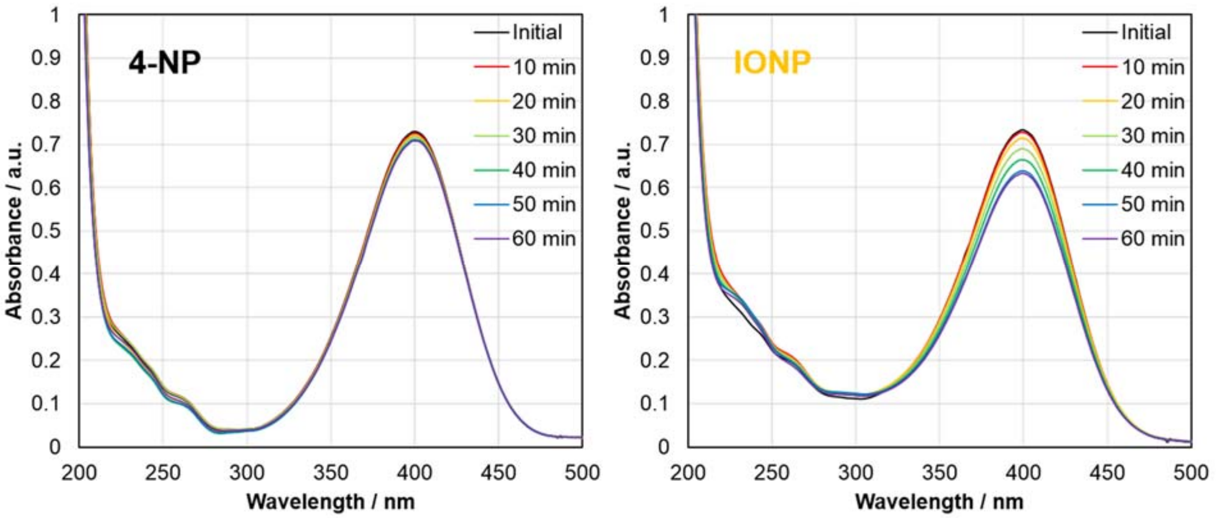

Figure S7. The stock catalysis solution is relatively stable over 60 min. Adding un-decorated $Fe_3O_4@SiO_2$ provides a weak catalytic surface.

Ref.	**M**	**k_{obs} / s^{-1}**	**k_{norm} / $s^{-1}mol^{-1}$**	**mol%**
this work	Au	4.41E-03	5.52E+06[a]	1.97
Chem. Asian J. **2013** (8) 1160	Au	8.37E-02	2.14E+06	3.90
JPCC **2013** (117) 6363	Au	4.50E-03	1.95E+06	0.46
RSC Adv. **2014** (4) 5012	Au	1.94E-02	1.50E+06[a]	*
JPCC **2011** (115) 1614	Au	3.00E-03	1.21E+06	0.50
Nanoscale **2013** (5) 4894	Au	1.43E-02	1.14E+06[a]	5.00
Appl. Catal. A **2014** (486) 32	Au	2.68E-02	7.70E+05	19.00
RSC Adv. **2014** (4) 6454	Au	9.30E-03	3.00E+05	3.00
Cryst. Eng. Comm. **2012** (14) 7229	Au	4.90E-02	2.73E+05	25.00
J. Mat. Chem. A **2013** (1) 11641	Au	1.62E-02	1.87E+05	17.26
RSC Adv. **2015** (5) 5131	Au	6.12E-03	1.00E+05	0.04
Nanoscale **2014** (6) 7025	Au	1.00E-02	5.15E+04	78.00
Appl. Surf. Sci. **2012** (263) 471	Au	6.80E-03	1.94E+04	2.30
RSC Adv. **2015** (5) 44018	Au	1.47E-02	1.56E+02	25.00
this work	Pd	1.26E-02	1.68E+07[a]	1.97
JPCC **2014** (118) 3062	Pd	2.01E-02	8.50E+06	0.17
New J. Chem. **2015** (39) 6474	Pd	4.60E-03	1.50E+06	1.00
RSC Adv. 2015 (5) 91340	Pd	4.40E-02	6.5E+05	30.50
J. Mat. Chem. A **2013** (1) 12732	Pd	1.05E-02	3.10E+05	1.13
RSC Adv. **2015** (5) 44018	Pd	1.36E-02	7.24E+02	5.00
this work	Ag	2.16E-03	6.66E+05[a]	10.80
Appl. Surf. Sci. **2012** (258) 2717	Ag	1.38E-02	2.70E+04	100.00
J. Coll. Int. Sci. **2012** (383) 96	Ag	7.67E-03	4.92E+03[a]	43.00

RSC Adv. **2015** (5) 50505	Ag	2.5E-02	4.80E+03[a]	1.30
J. Mat. Chem. A **2013** (1) 2118	Ag	1.72E-02	1.20E+02[a]	3541.00
ACS Appl. Mat. Int. **2014** (6) 2671	Pt/Pd	2.02E+01	1.20E+10	36.00
JPCC **2012** (116) 22432	Au/Ag	1.58E-02	1.29E+06	12.20
RSC Adv. **2014** (4) 38040	Ag/Cu	1.23E-01	2.50E+06	*
this work	Pt/Ag	1.69E-03	5.21E+05[a]	10.80
IEC Res. **2012** (51) 5608	Pt	4.98E-02	1.27E+05	79.30
Chem. Comm. **2011** (47) 11924	Ag/Pd	3.30E-02	1.00E+05	110.00
J. Mat. Chem. A **2013** (1) 12732	Au/Pd	3.95E-03	1.35E+04	10.00

Table S1. Comparison table of the reported performance for the reduction of 4-NP of selected magnetically-recoverable catalysts from the recent literature. * Value could not be determined from the published data. For normalization purposes, the amount of metal was determined from [a]reported synthetic parameters, unless otherwise directly stated in the publication.

Glass assembly experimental procedures

Glass surface preparation. Glass capillaries (1.5 mm O.D.) were cleaned by a modified RCA procedure, using a 1:1:5 mixture of H_2O_2:NH_4OH:H_2O, incubated at 80 °C for 15 minutes. The capillaries were rinsed with 18 MΩ water and air dried. Silane coating was achieved by 1 h incubation at RT in a 10% ethanol solution of APTMS or MPTMS, followed by curing at 120 °C for 1 h.

Method 1: *in situ* growth. The prepared APTMS or MPTMS coated capillaries were first incubated in 1 mM $AgNO_3$ for 1 h at RT and then briefly dipped in 10 mM $NaBH_4$. A growth solution of 0.5 mL (0.4 mM) metal salt solution ($HAuCl_4$, $PdCl_2$/2HCl, or K_2PtCl_4), 0.5 mL (0.1 M) CTAB, and 100 μL (1 M) NaOH was prepared. The coated capillaries were soaked in the growth solution for 3 h at RT.

Method 2: direct reduction. The prepared APTMS or MPTMS coated capillaries were incubated in 1 mM metal salt solution ($HAuCl_4$, $PdCl_2$/2HCl, or K_2PtCl_4) for 1 h at RT and then briefly dipped in 10 mM $NaBH_4$.

Method 3: seed attachment. Noble metal seeds were separately prepared in the presence of CTAB by mixing 125 μL (10 mM) metal salt solution ($HAuCl_4$, $PdCl_2$/2HCl, or K_2PtCl_4) with 5 mL (0.1 M) CTAB. Seed were instantaneously formed through the addition of 0.25 mL $NaBH_4$ and were allowed to rest undisturbed for 1 h at RT. The prepared APTMS or MPTMS coated capillaries were incubated in 1 mL of the seed solution for 2 h at RT.

Catalysis. The treated capillaries were placed in 1 mL catalysis solution (4-NP, $NaBH_4$) and the absorbance at 400 nm was monitored for 1 h at 30 s intervals.

Table S2. Catalysis results (k_{obs} / s^{-1}) for decorated glass substrates.

method	APTMS			MPTMS		
	Pd	Au	Pt	Pd	Au	Pt
in situ growth	-4.19E-03	-3.92E-03	-1.23E-03	-6.08E-03	-8.25E-05	-6.13E-04
direct reduction	-4.01E-04	-6.99E-04	-1.20E-03	-7.29E-05	-2.07E-05	-1.36E-05
seed attachment	-8.25E-03	-4.94E-03	-2.23E-03	-5.74E-05	-3.06E-05	-1.99E-05