

# Supplementary Information

## Iron Oxide Nanocluster Synthesis

0.86 g FeCl<sub>2</sub> and 2.35 g FeCl<sub>3</sub> were dissolved completely in 40 ml deionized (DI) water by bath sonication. 0.05 g citric acid was dissolved in 2 ml DI water. Both these solutions were injected into a 3-necked reaction flask that had been evacuated twice and nitrogen flow was maintained during the reaction to avoid oxygen exposure. The reactant solution was stirred and heated up to 95°C, and 10 ml of ammonia (28-30%) was injected to initiate Fe<sub>3</sub>O<sub>4</sub> nucleation. After one hour, the reactor was cooled down to room temperature slowly and the product was centrifuged at 6000 rpm for 6 minutes. The resulting completely clear supernatant was decanted and the precipitated particles were re-dispersed by probe sonication in 25 ml of buffer solution containing citric acid (20 mg/ml) with NaOH at a pH of 5.2. This centrifugation and re-dispersion procedure was repeated 2 more times until all the particles were well dispersed in the buffer solution and would no longer settle under centrifugation. The dispersion was then dialyzed against DI water for 24 hours using 25 kDa dialysis tubing (Spectra/Pro 7, Spectrum Laboratories Inc.) to remove excess citrate.

Table S1. Mean Size and Standard Deviation of Gold Coated Iron Oxide Nanoparticles in Fig. 2.

Au <sup>3+</sup> /Fe ratio	Mean (nm)	Variance (nm)	% Standard deviation
0.125	44	2.9	7.0
0.250	49	3.1	6.5
0.500	57	3.0	5.3
1.5	73	4.6	6.3
3.0	73 and 146	2.5 and 5.6	3.4 and 3.8
6.0	30 and 159	1.9 and 15.6	6.3 and 9.8

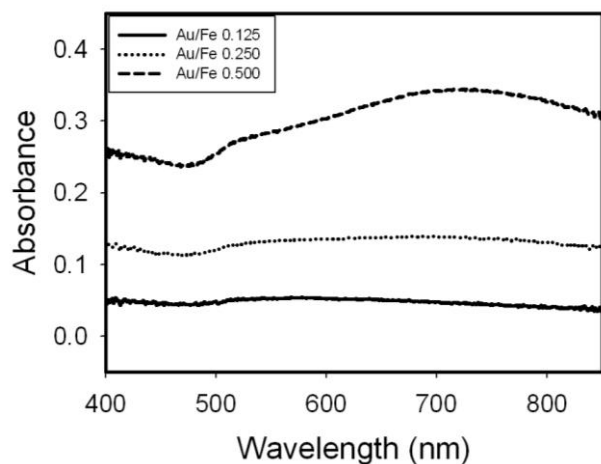
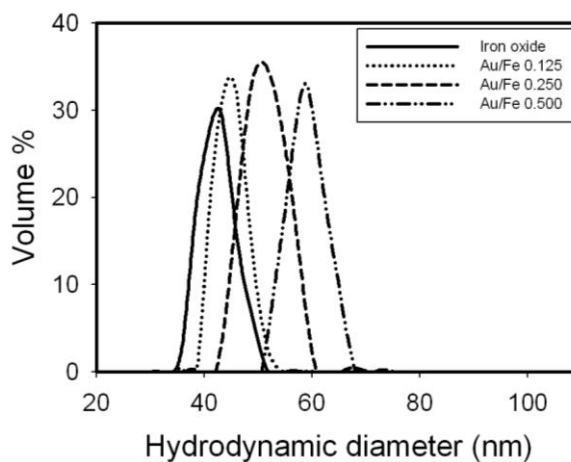
**A****B**

Figure S1. The evolution of absorbance spectra and hydrodynamic diameters at each step of the 5 iteration addition of gold precursor at a total Au/Fe mass ratio of 0.50. Iteration sequence: Au/Fe mass ratio = 0.05, 0.10, 0.125, 0.25, 0.5.

Table S2. Mean Size and Standard Deviation of Textured Thin Gold Coated Iron Oxide Nanoparticles Au/Fe= 0.5, reached with 5 Iterations

Au/Fe ratio	Mean (nm)	Variance (nm)	% Standard deviation
Iron oxide	42	3.2	7.5
0.125	45	2.8	6.1
0.25	51	3.6	7.0
0.5	58	3.3	5.7

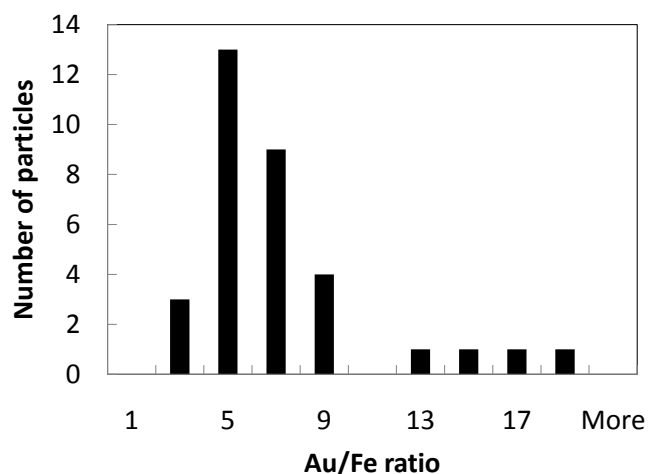


Figure S2. Au/Fe ratio determined by TEM-EDS for 30 individual particles with a feed  $\text{Au}^{3+}/\text{Fe}$  ratio of 0.5 added in 1 iterations shown in Figs 4A, 5A and 5B in the paper.

### Comparison with control experiments

In order to determine the effect of iron oxide, control experiments were conducted in which all the conditions were maintained the same except that iron oxide nanoparticles were not added to the reaction mixture. In this case, the reaction kinetics were observed to be a lot slower for the case when there was no iron oxide in the system. The observed UV-vis spectra shown in figure S3 were also very different from the UV-vis spectra that were observed for the reactions with iron oxide in them.

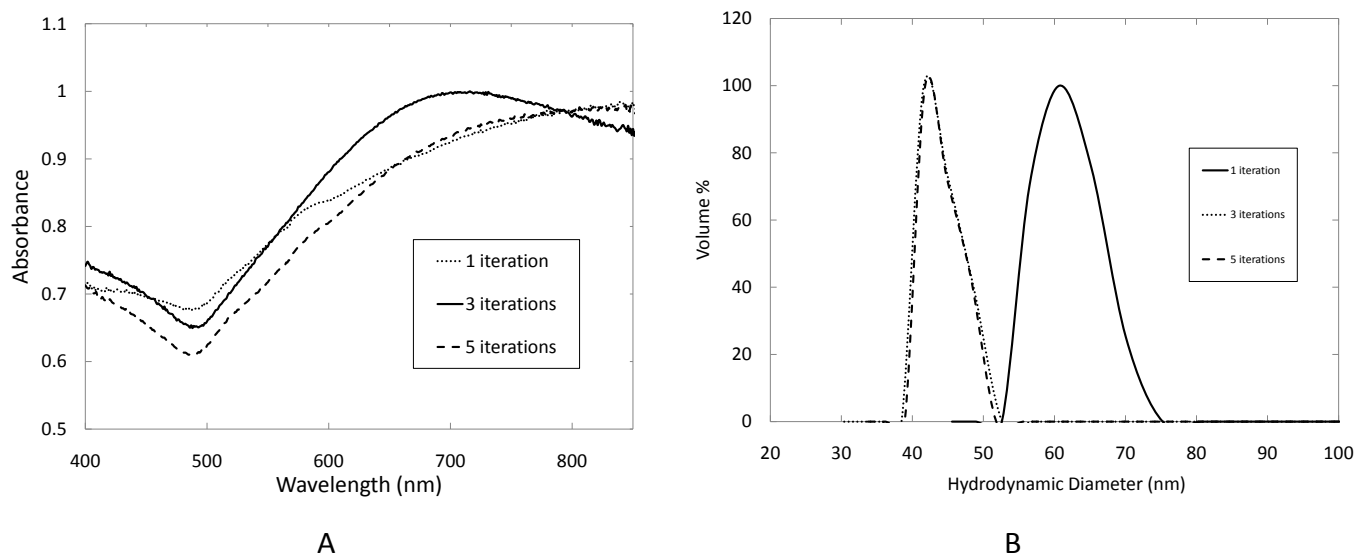


Figure S3. Absorbance spectra and DLS size for the control experiments without iron oxide to contrast

gold only particles with composite particles

## The estimation of centrifugation speed for particle sedimentation

For a spherical particle, the centrifugation process is governed by sedimentation coefficient without considering diffusion. Therefore, this estimation does not take into account steric or electrostatic interactions between particles.<sup>1</sup>

$$S = (1 - \rho_1/\rho_2) * m/f \quad (1)$$

$\rho_1$  = density of the solvent ( $\text{g}\cdot\text{cm}^{-3}$ )

$\rho_2$  = density of the particle ( $\text{g}\cdot\text{cm}^{-3}$ )

$m$  = mass of the particle (g)

$f$  = friction factor ( $\text{g}\cdot\text{s}^{-1}$ )

The density of solvent was assumed to be close to water at 300K,  $\rho_1 = 1.0 \text{ (g}\cdot\text{cm}^{-3}\text{)}$ . The density of gold coated iron oxide particles was calculated as  $\rho_2 = (M_{\text{Au}} + M_{\text{Fe}_3\text{O}_4})/V$ . Knowing the particle diameter ( $D$ ) and the viscosity of the solvent ( $\eta$ ), we can calculate the friction factor  $f$ . In this case, a viscosity  $\eta = 0.001 \text{ kg}\cdot\text{m}^{-1}\text{s}^{-1}$  from water at 300k was used for diluted particle reactant mixture.

$$f = \pi * \eta * D \quad (2)$$

$\eta$  = viscosity of the solvent ( $\text{kg}\cdot\text{m}^{-1}\text{s}^{-1}$ )

$D$  = particle diameter (m)

$$S = \ln(l_1/l_2)/(\omega^2 * t) \quad (3)$$

$l_1$  = initial distance of the particle from the axis of the centrifuge

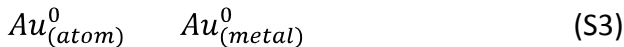
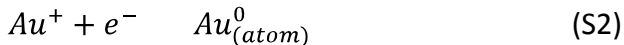
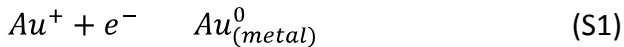
$l_2$  = final distance of the particle from the axis of the centrifuge

$\omega$  = angular speed of rotation of the centrifuge ( $\text{s}^{-1}$ )

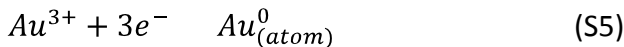
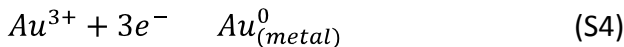
t = time for which the centrifugation is carried out (s)

Assuming the centrifugation duration 360 s, we can calculate the centrifugation speed required to precipitate the particles from initial position to the bottom of the centrifuge tube (l1/l2=3.2/3.97). The thermodynamic driving force for reduction of Au<sup>3+</sup> on gold surfaces versus homogeneous reduction in solution

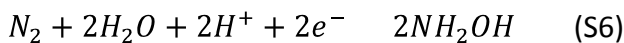
The thermodynamic driving forces of the autocatalytic growth of gold on Au<sup>0</sup> metal and homogeneous nucleation from Au<sup>0</sup> atom can be derived from reduction potentials.



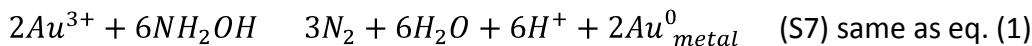
The reduction potential versus NHE for Au<sup>0</sup><sub>(metal)</sub>/Au<sup>+</sup> is 1.68 V and for Au<sup>0</sup><sub>(atom)</sub>/Au<sup>+</sup> is -1.5 V.<sup>2,3</sup> From eq. (S3) = (S1) - (S2), cell potential of Au<sup>0</sup><sub>(metal)</sub>/Au<sup>0</sup><sub>(atom)</sub> is 3.18 V.



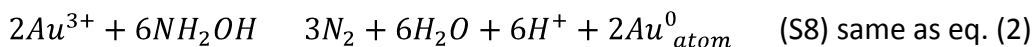
The reduction potential versus NHE for Au<sup>0</sup><sub>(metal)</sub>/Au<sup>3+</sup> is 1 V.<sup>3,4</sup> From eq. (S5) = (S4) - (S3), the reduction potential versus NHE for Au<sup>0</sup><sub>(atom)</sub>/Au<sup>3+</sup> is -2.18 V.



The reduction potential versus NHE for NH<sub>2</sub>OH/N<sub>2</sub> is -0.936 V.<sup>5</sup>



From eq. (S7) = (S4) - (S6), E<sub>cell</sub> = 1.936 V.



From eq. (S8) = (S5) - (S6), E<sub>cell</sub> = -1.244 V.

Table S3 Calculated centrifugation speed for sedimentation of gold coated iron oxide nanoparticles

	Au/Fe ratio	Diameter (nm)	Centrifugation (rpm)
Iron oxide	0.00	42.0	8303
Au coated iron oxide	0.84	43.5	6415
	1.30	44.3	5776
	2.40	46.0	4859
	3.80	48.0	4188

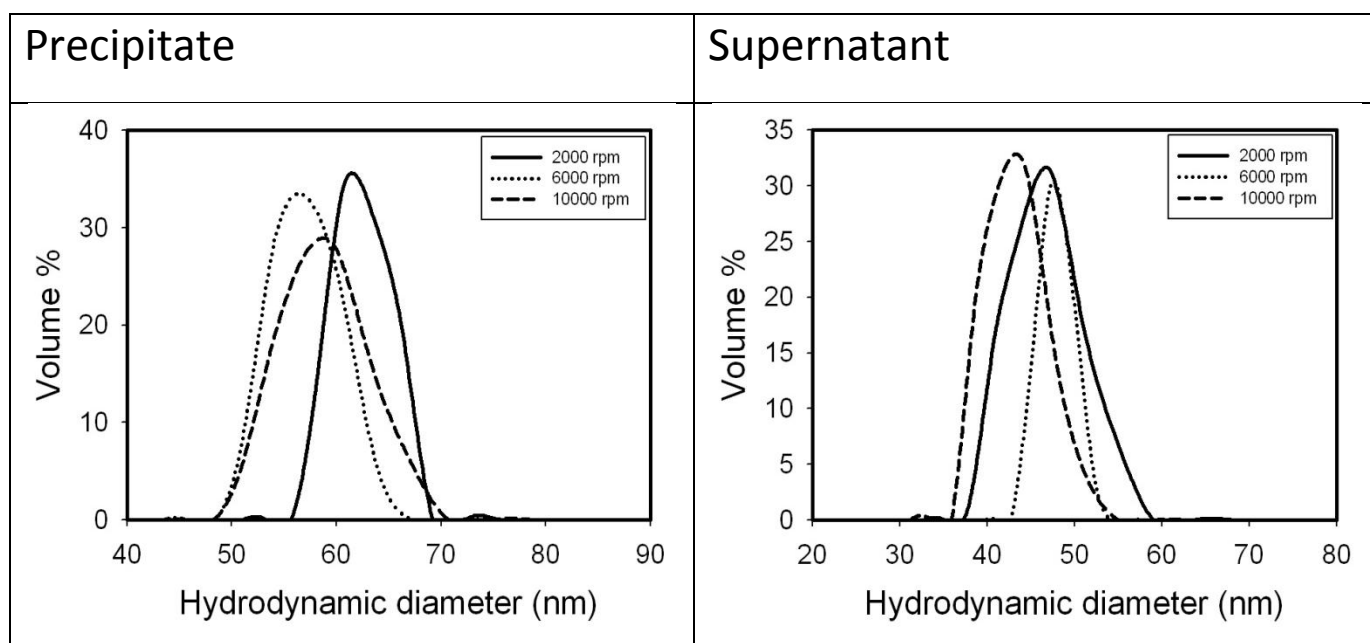


Figure S4. Hydrodynamic diameter distribution of nanoparticles in precipitate and supernatant after centrifugation under different speeds. Au precursor was added by 5 iterations at Au/Fe mass ratio 0.500.

The hydrodynamic diameters of nanoparticles in the precipitate and supernatant phases were measured after centrifugation for the case of Au<sup>3+</sup>/Fe of 0.5. The size distribution of particles in the supernatant was almost identical to that of the uncoated iron oxide nanoclusters. The mean hydrodynamic diameter of Au coated particles in the precipitate at the lowest speed of 2000 rpm were

larger than those at the higher speeds, indicating fewer of the smaller particles settled with the weakest centrifugal force.

Table S4. Detailed elemental analysis results of Fe and Au before and after centrifugation

Sample	Initial Au/Fe ratio	Final Au/Fe ratio	% Fe yield	% Au yield
0.125 R	0.125	0.094	100.3	88.8
0.25 R	0.250	0.264	100.8	108.6
0.5 R	0.500	0.445	100.4	100.9
0.125 2000 S	0.125	0.093	90.7	79.8
0.125 6000 S	0.125	0.014	92.5	12.2
0.125 10000 S	0.125	0	91.0	0
0.125 2000 P	0.125	0	0.82	0
0.125 6000 P	0.125	0.145	3.83	4.6
0.125 10000 P	0.125	0.095	7.84	7.0
0.25 2000 S	0.250	0.137	106.7	60.3
0.25 6000 S	0.250	0.030	98.2	12.0
0.25 10000 S	0.250	0.011	98.5	4.3
0.25 2000 P	0.250	0.073	1.1	0.3
0.25 6000 P	0.250	0.281	4.0	5.3
0.25 10000 P	0.250	0.176	9.7	7.1
0.5 2000 S	0.500	0.151	94.8	32.5
0.5 6000 S	0.500	0.068	90.8	14.0
0.5 10000 S	0.500	0.028	86.6	5.5
0.5 2000 P	0.500	0.396	1.1	1.0
0.5 6000 P	0.500	0.691	4.6	7.2
0.5 10000 P	0.500	0.465	8.8	9.3

\* R indicated reactant before centrifugation

S indicated supernatant after centrifugation

P indicated precipitate after centrifugation

Table S5. Mass balance sheet of Fe and Au after centrifugation

		Au/Fe 0.125	Au/Fe 0.25	Au/Fe 0.5
Fe	2000 rpm	92 %	98 %	96 %
	6000 rpm	96 %	93 %	95 %
	10000 rpm	99 %	98 %	95 %
Au	2000 rpm	89.9 %	55.8 %	33.2 %
	6000 rpm	19.4 %	15.3 %	21.1 %
	10000 rpm	7.9 %	10.4 %	14.6 %

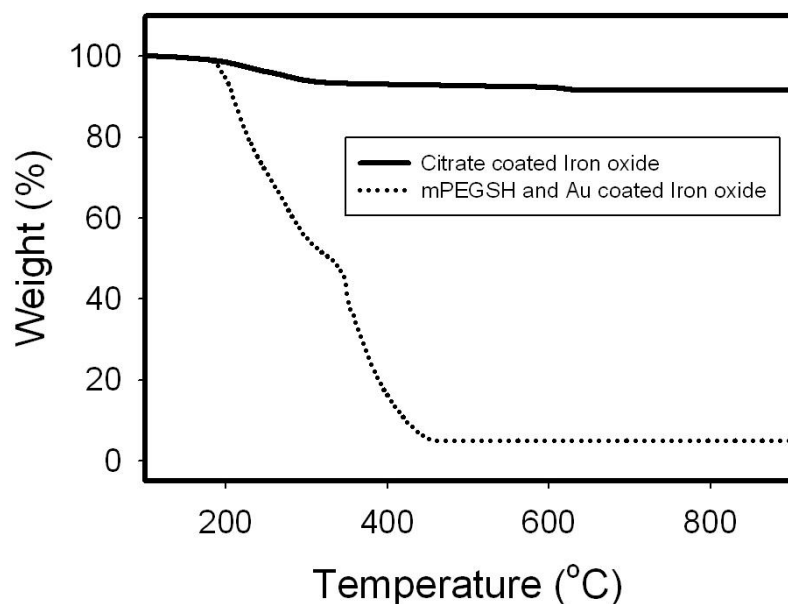


Figure S5. TGA measurements of citrate coated iron oxide nanoclusters, mPEG-SH and gold coated iron oxide nanoparticles. At 900 °C, 9.5 % weight loss occurred from citrate and 95.0 % weight loss occurred from mPEG-SH.



- (1) Hiemenz, P. C.; Rajagopalan, R.; Editors *Principles of Colloid and Surface Chemistry, Third Edition, Revised and Expanded*, 1997.
- (2) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Chem Mater* **2001**, *13*, 2313.
- (3) Gachard, E.; Remita, H.; Khatouri, J.; Keita, B.; Nadjio, L.; Belloni, J. *New J Chem* **1998**, *22*, 1257.
- (4) Brown, K. R.; Natan, M. J. *Langmuir* **1998**, *14*, 726.
- (5) Huang, W.; Tamilmani, S.; Raghavan, S.; Small, R. *Int J Miner Process* **2003**, *72*, 365.