Supplementary Material (ESI) for Chemical Communications

The influence of trace water concentration on iron oxide nanoparticle size

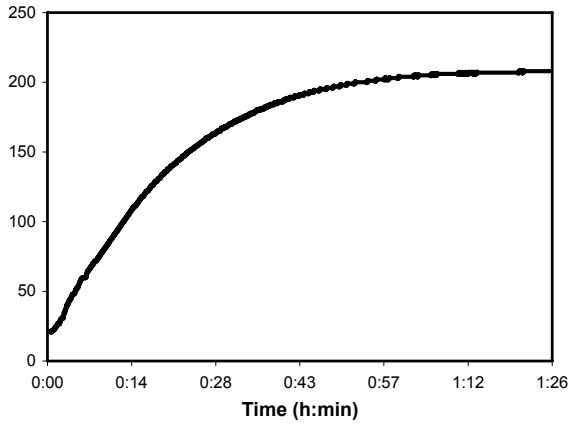
Janet E. Macdonald, Christopher J. Brooks and Jonathan G. C. Veinot

Supporting Information

Preparation of iron oxide nanoparticles

A stock solution of 5:1 (volume) benzyl ether and oleic acid (90%) was prepared. Water was added to ~60 mL aliquots of the solvent mixture and the water concentration was determined by Karl Fischer titrations. The lowest concentrations of water were achieved by drying the aforementioned solvent/surfactant mixtures over $MgSO_4$ or by vacuum distillation of the benzyl ether over Na prior the preparation of the solvent/surfactant mixture. In a typical reaction, the surfactant/solvent mixture was bubbled for 1h with argon. Using standard Schlenk techniques, 10 mL of the solution (5.3 mmol oleic acid) was transferred into an oven-dried, argon flushed reflux apparatus. $Fe(CO)_5$ (0.3 mL, 2.3 mmol) was added. Heat was applied at a controlled heating rate such that the temperature equilibrated at ~200 ^oC after 1h.

SI Chart 1: Example heating curve of sand bath.

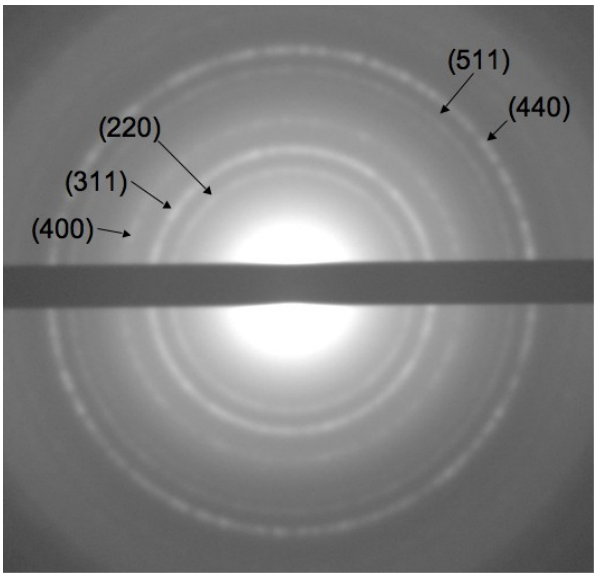


The reaction mixture remained at 192- 217 ^oC for 16 h upon which time the yellow solutions had turned black. Multiple experiments were performed for each concentration of water. Particles were isolated by repetitive precipitation with methanol and dissolution with tetrahydrofuran. Oxidation of the resulting particles was achieved by exposure to air.

Transmission Electron Microscopy samples were prepared by suspending particles in tetrahydrofuran and dropcoating the solution onto carbon coated, 200 mesh Cu grid (SPI Supplies). Samples were evaluated using a JEOL 2010 Transmission Electron

Microscope (TEM) at 200 keV accelerating voltage and a LaB_6 filament. Systematic error in the particle size measurements is less than 3%.

Selected Area Electron Diffraction (SAED) was performed on the samples.



SI Fig 1: Representative SAED of particles showing characteristic reflections of γ-Fe_2O_3.[1, 2]

Fourier Transform Gas Phase Infra Red Spectroscopy was performed on a Magna System 750 IR using Omnic 7.1 software. The cell had a 10 cm path length with KBr windows. 32 scans were performed. The cell was flushed with argon and the area around the cell was flushed with N_2 gas until the CO_2 absorbance was at a minimum. This spectrum was used as a background. Acquisition of the spectrum of the reaction gases were handled similarly; the area around the cell was flushed with N_2 gas until the CO_2 absorbance was at a minimum. From this the aforementioned background spectra was subtracted.

Statistical Analysis

The diameters of 85-200 particles were measured from several TEM images for every sample, and are reported in the text as mean ± standard deviation. For repetitive experiments at identical water concentrations, the data sets were treated to ANalysis Of VAriation (ANOVA).

The count of the number of particles measured, their average diameter and standard deviations are reported for each sample. ANOVA (single factor) was conducted on sets of samples at the same concentration giving an F value. F-critical is the value above which the null hypothesis (that the data sets are from the same probability distribution) is rejected at $\alpha = 0.05$.

SI. Table 1: Statistical analysis of particle diameter within concentration groups.

[H_2O] (ppm)		Count	Average (nm)	St. Dev. (nm)	F	F-critical
101	A	158	5.58	0.50	23.9	2.6
	B	147	5.52	0.44		
	C	85	5.06	0.46		
	D	120	5.59	0.59		
181	A	141	4.68	0.65	6.2	2.6
	B	133	4.67	0.59		
	C	112	4.92	0.56		
	D	126	4.84	0.40		
234	A	134	3.11	0.51	490.2	3.9
	B	134	4.54	0.55		
479	A	181	4.23	0.59	449.7	3.9
	B	145	3.01	0.42		
657	A	96	2.54	0.49	276.0	3.0
	B	133	2.42	0.39		
	C	154	3.53	0.43		
1073	A	150	3.47	0.45	242.1	3.9
	B	198	2.80	0.36		
1590	A	134	2.47	0.40	30.8	3.9
	B	128	2.20	0.38		

ANOVA (single factor) was then performed between groups and a Tukey Post Test to examine the statistical differences between pairs of groups. Prism 5.0 software was employed.

Table App. A- 2: Analysis between concentration groups

One Way ANOVA between groups

P value	< 0.0001
Are means signif. different (*i.e.,* P < 0.05)?	Yes

Tukey's Multiple Comparison Test

Water concentration (ppm) groups	Mean Difference	Significant? *i.e.,* P < 0.05?
101 vs 181	0.66	No
101 vs 234	1.613	Yes
101 vs 479	1.818	Yes
101 vs 657	2.608	Yes
101 vs 1073	2.303	Yes
101 vs 1590	3.103	Yes
181 vs 234	0.9525	No
181 vs 479	1.158	No
181 vs 657	1.948	Yes
181 vs 1073	1.643	Yes
181 vs 1590	2.443	Yes
234 vs 479	0.205	No
234 vs 657	0.995	No
234 vs 1073	0.69	No
234 vs 1590	1.49	No
479 vs 657	0.79	No
479 vs 1073	0.485	No
479 vs 1590	1.285	No
657 vs 1073	-0.305	No
657 vs 1590	0.495	No
1073 vs 1590	0.8	No

1 X. W. Teng and H. Yang, *Journal of Materials Chemistry*, 2004, **14**, 774-779.

2 T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. Bin Na, *Journal of the American Chemical Society*, 2001, **123**, 12798-12801.