Supporting Information

Formation of Colloidal Nanocrystal Clusters of Iron Oxide by Controlled Ligand Stripping

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Table S1 Detailed experimental information and corresponding products

Ligand stripping agent	**"LS" agent volume/mL**	**OA /mL**	**ODE /mL**	**$Fe(CO)_5$ /mL**	**3D structure**	**TEM images**
Blank	0	2	10	0.2	Nanosphere	Fig. 1a, Fig. S1
PEG 400	0.1	2	10	0.2	Dimer	Fig. 1b, Fig. 2a
TEG	0.01	2	10	0.2	Dimer/ Oligomer	Fig. 3a
TEG	0.02	2	10	0.2	Oligomer	Fig. 3b
TEG	0.03	2	10	0.2	Oligomer	Fig. 3c
TEG	0.05	2	10	0.2	Oligomer	Fig. 3d
TEG	0.1	2	10	0.2	Oligomer	Fig. 1c, 2b
TEG	0.3	2	10	0.2	Oligomer/ Cluster	Fig. 3e
DEG	0.1	2	10	0.2	Cluster	Fig. 1d, 2c, Fig. S2
EG	0.1	2	10	0.2	Cluster	Fig. S5b

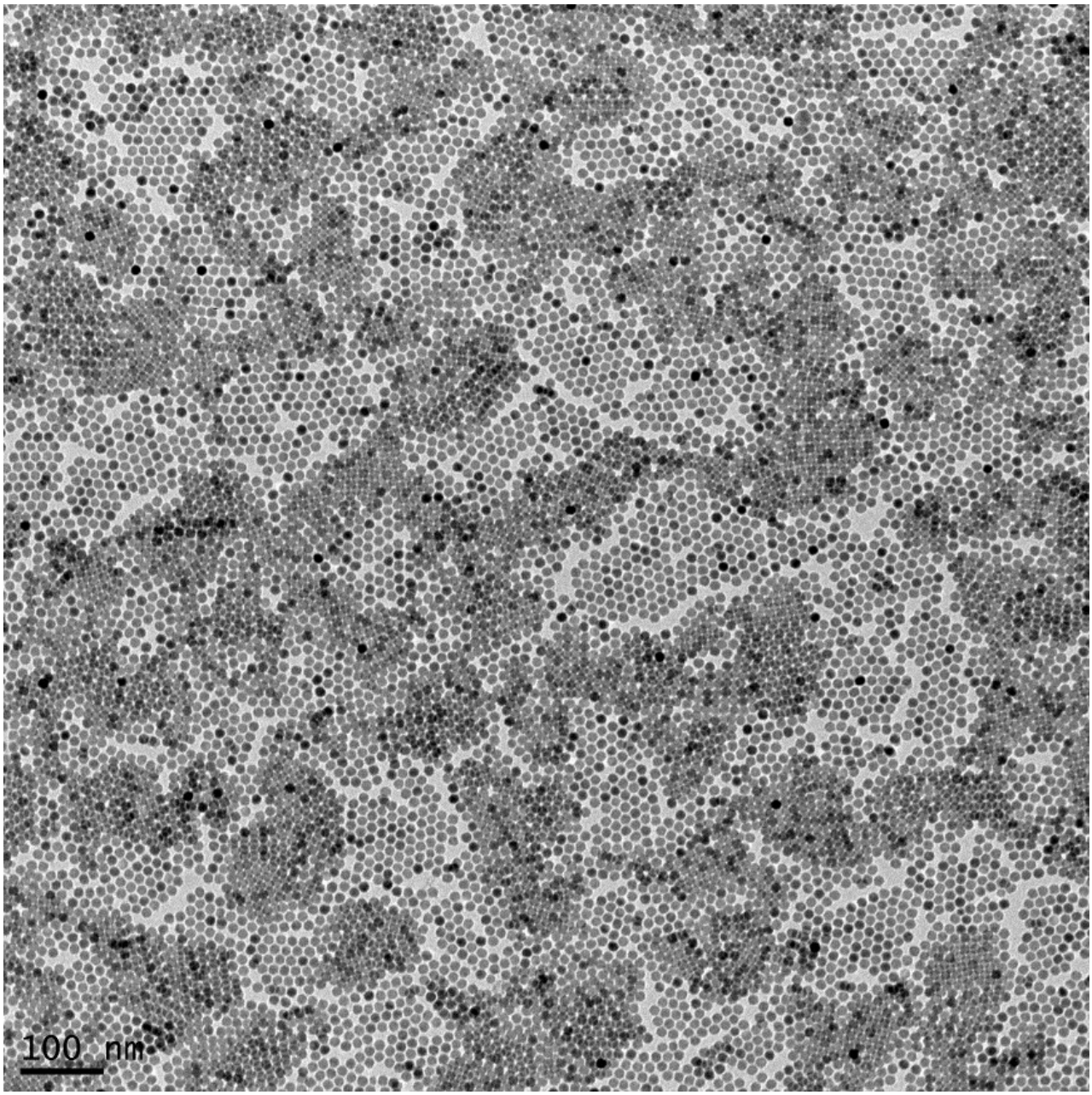
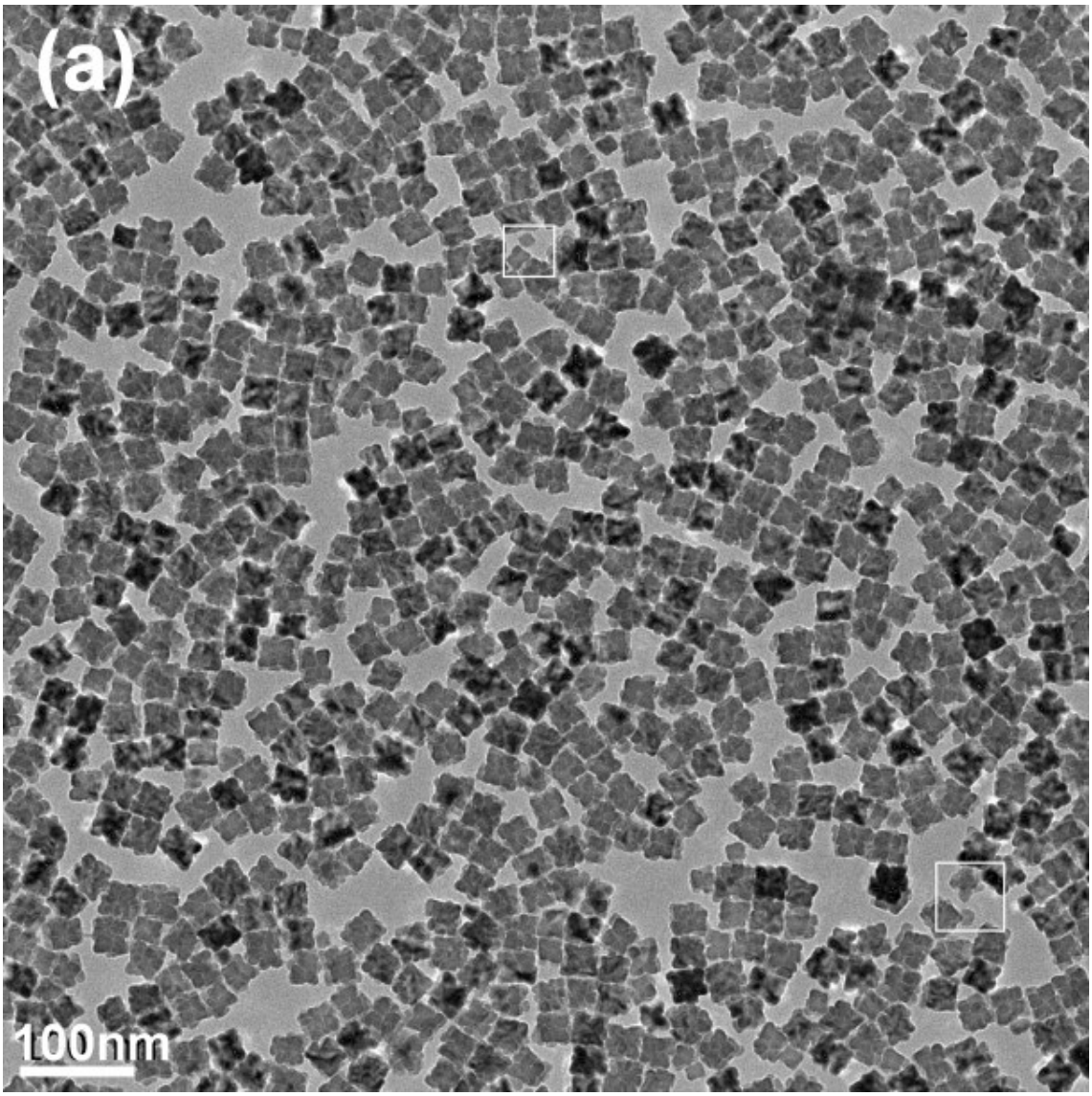


Fig. S1 TEM images of blank sample without any diol added.



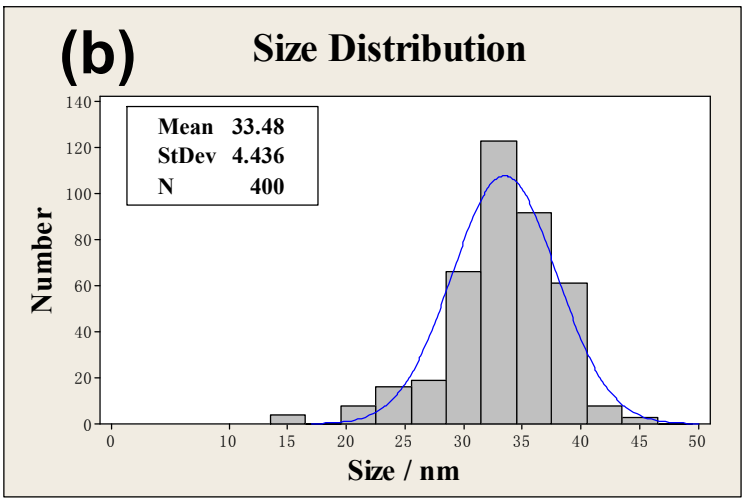


Fig. S2 (a) Large scale TEM images of 40nm iron oxide clusters using DEG as ligand stripping agent. White squares remark some monomers and oligomers. (b) Size distribution of iron oxide clusters.

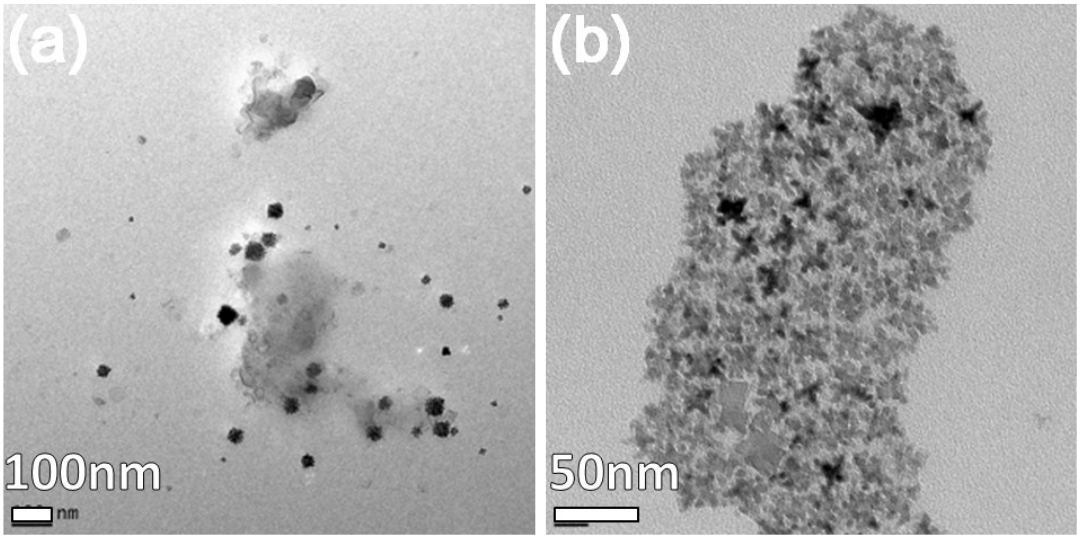


Fig. S3 TEM images of iron oxide clusters formed using DEG as ligand stripping agent at 295 °C: (a) immediately after solution turned black; (b) after reacting for 1 min. The TEM image of the product after reacting for 1 h can be found in Fig. S2.

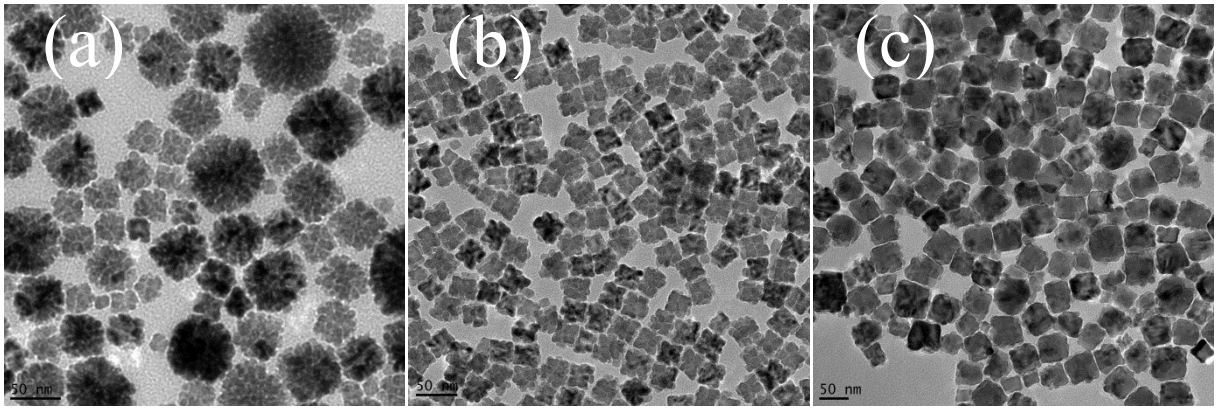


Fig. S4 TEM images of iron oxide clusters formed at (a)295°C 10min+240 °C 60min, (b) 295°C 10min+240 °C 180min and (c) 295°C 90min.

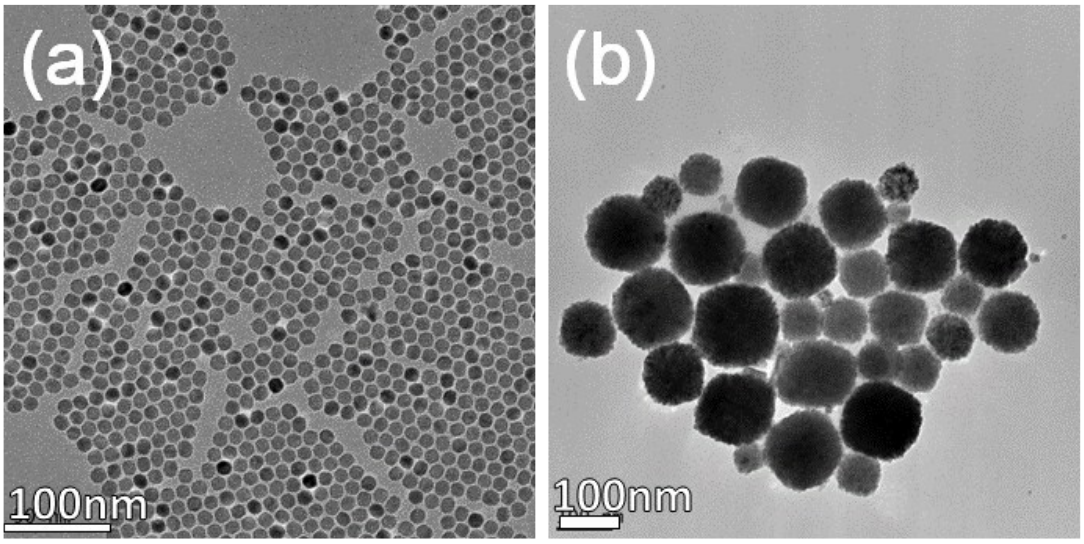


Fig. S5 TEM images of (a) diol are added after the solution turns black at 295^{o}C; (b) iron oxide clusters using EG as ligand stripping agent.

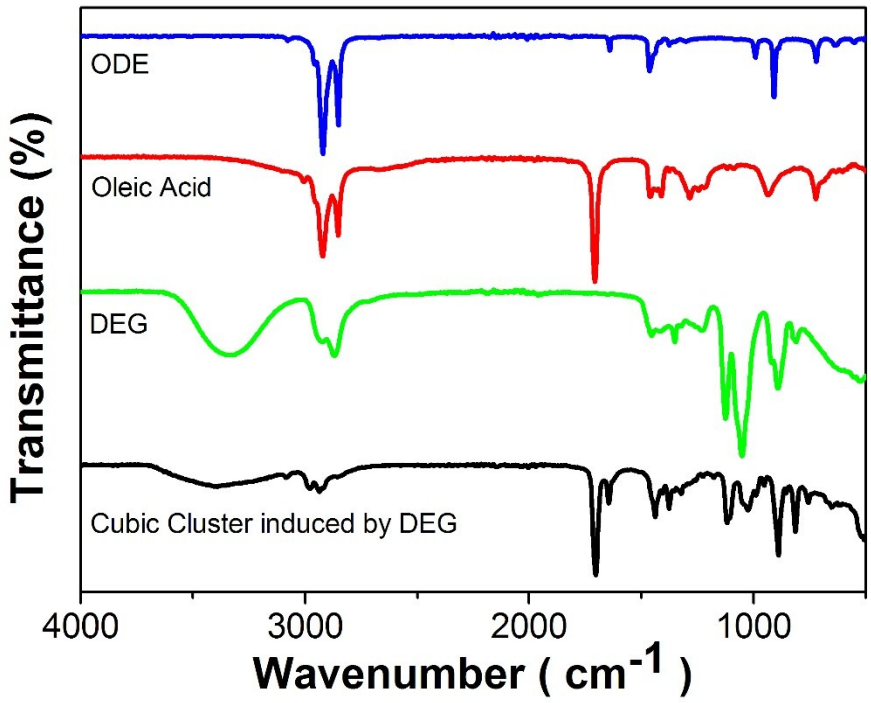


Fig. S6 Fourier transform infrared (FTIR) spectra of ODE, OA, DEG and cubic clusters induced by DEG. The presence of OA on the surface of cubic clusters is confirmed by the characteristic peak of carboxyl group at around 1700 cm^{-1}. The OH stretch positioned at around 3340 cm^{-1} and the double C-O stretch at 1125 cm^{-1} and 1062 cm^{-1} further confirmed the binding of DEG on the cubic clusters. The FTIR spectra were measured on a Bruker Alpha FT-IR spectrometer.

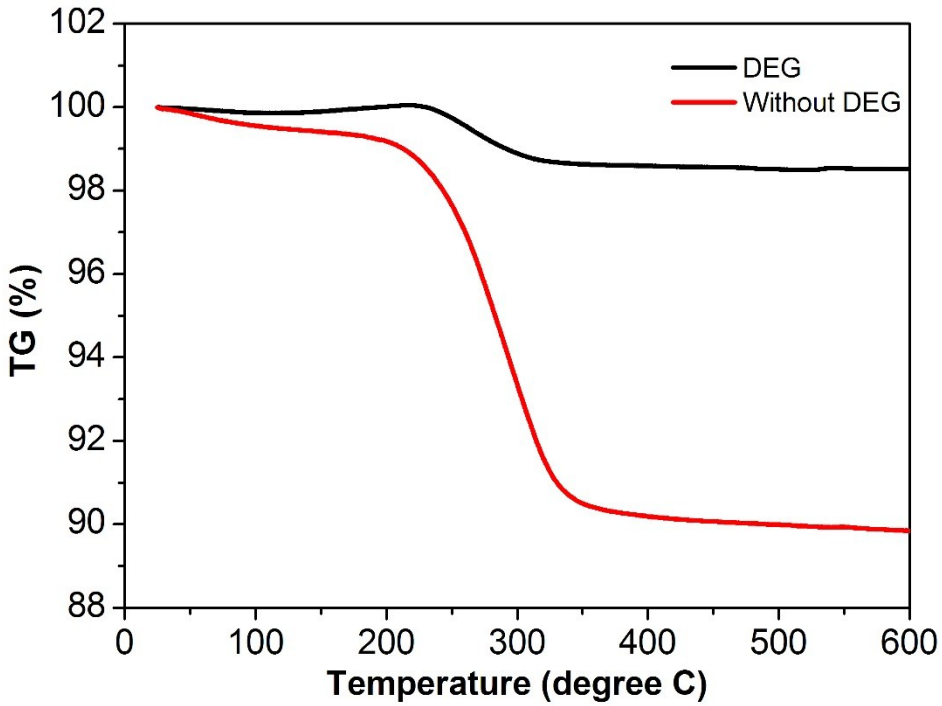


Fig. S7 Thermogravimetric analysis (TGA) of the spherical nanoparticles prepared without stripping ligands and the cubic clusters synthesized using DEG as the stripping ligand. The spherical nanoparticles prepared in the absence of DEG showed a weight loss of ~10% compared to a weight loss of ~2% for the DEG induced cubic clusters. The difference in weight loss percentage can be attributed partly to the large molecular weight difference between OA (282.47 g/mol) and DEG (106.12 g/mol), and partly to the relatively weaker binding of DEG than OA to the surface of iron oxide. Both factors lead to the decrease in total weight percent of the capping ligands in the products. This result also confirms the stripping effect of oleic acid by diols. The initial rise in the weight of the cubic clusters is due to additional oxidation of the clusters: as the clusters are much larger in size, their oxidation in the solution becomes more difficult so that the iron oxide might contain Fe_3O_4 phase which can be further oxidized when heated in air. The TGA was performed on a Seiko 220 TG/DTA.

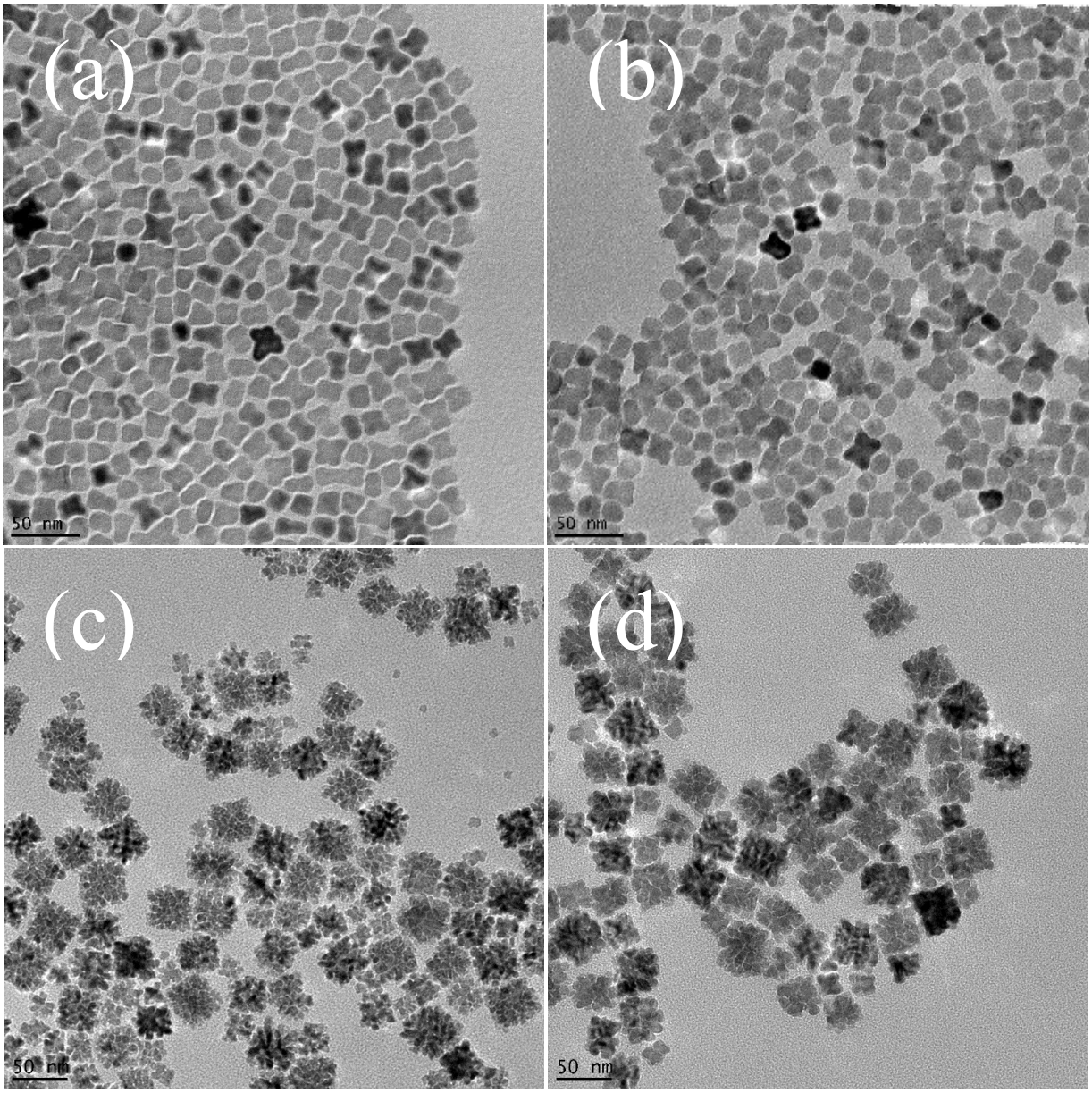


Fig. S8 TEM images of iron oxide oligomers before (a) and after (b) oxidation. TEM images of iron oxide clusters before (c) and after (d) oxidation.

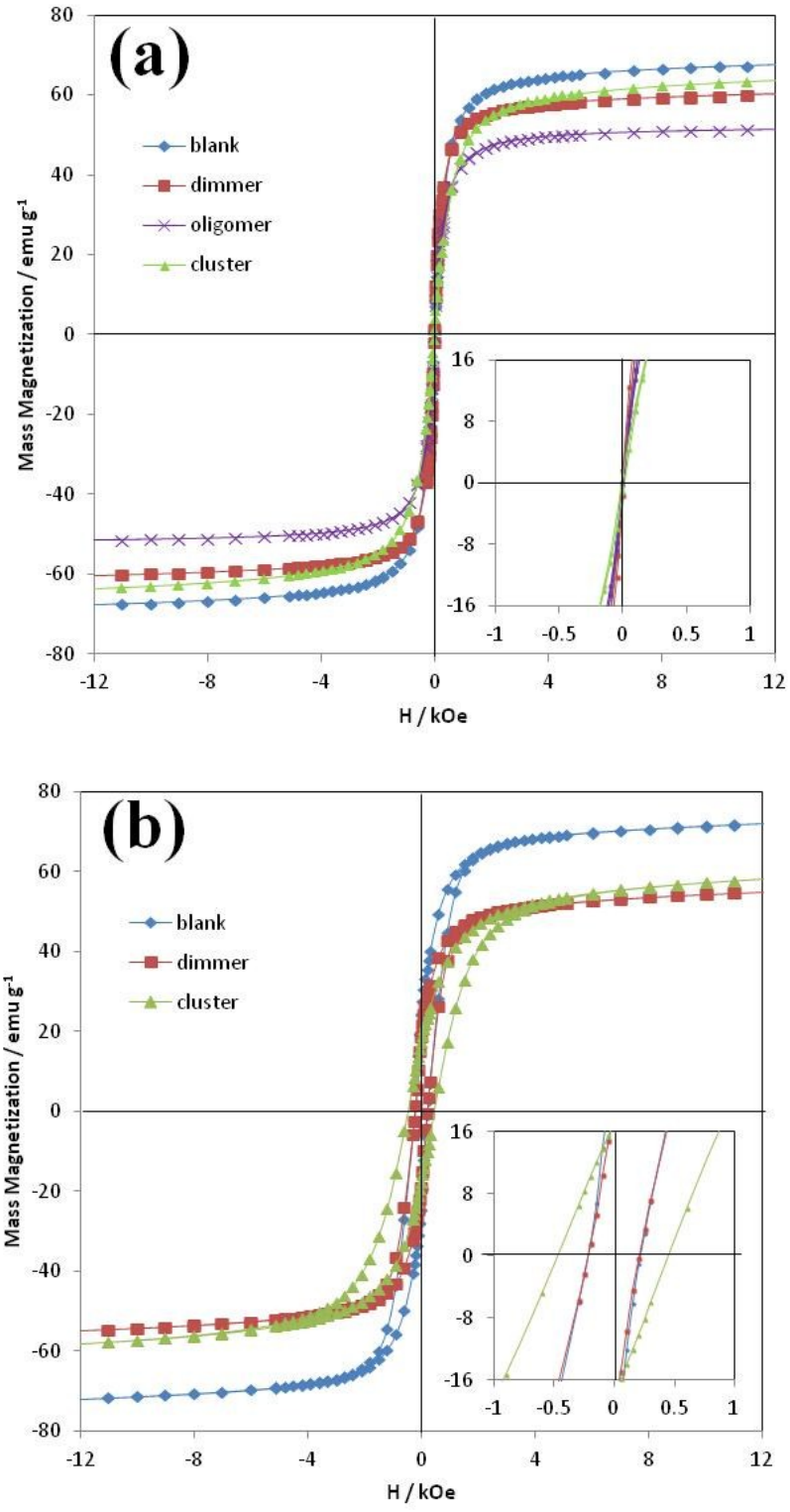


Fig. S9 Magnetization as a function of field for iron oxide nanoaggregates at a temperature of a) 300K and b) 5K. The insert shows the enlarged partial hysteresis curves for iron oxide nanoaggregates.