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

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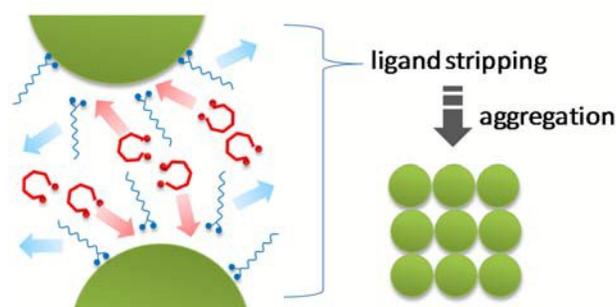
**We report a "ligand stripping" method for the creation of secondary structures of colloidal nanocrystals. Using iron oxide as an example, we demonstrate that the use of diols as "stripping agents" allows controllable removal of the original capping ligands and induce aggregation of nanocrystals into well-defined clusters.**

Colloidal nanocrystals with controlled size and shape are of great interest for researchers from a wide range of disciplines, including materials science, chemistry, physics and engineering.<sup>1</sup> Significant progress has been made in the development of robust synthesis protocols which allow precise control over their composition, size, shape, surface properties and uniformity.<sup>2</sup> Recently, the focus of synthetic efforts has been devoted to the creation of colloidal nanocrystals clusters (CNCs), the secondary structures of colloidal nanocrystals, which show great potential for the development of advanced materials with novel functions.<sup>3</sup> Basically, there are two strategies for the preparation of CNCs:<sup>4</sup> (1) one-step processes which integrate the synthesis of nanocrystals and their aggregation into clusters in a single step;<sup>5</sup> and (2) multi-step processes which first generate nanocrystals with desired size, shape and surface functionality, and then assemble them into clusters of designed degree of aggregation in followed steps such as solvent evaporation, electrostatic attraction, or interfacial tension.<sup>6</sup> Generally, one step processes are more efficient in producing CNC structures, but realizing fine control over size distribution of the final products remains a challenge.

Peng et al. reported a limited ligand protection (LLP) method to produce complex 3D CNC nanostructures, such as  $\text{In}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{MnO}$  and  $\text{ZnO}$  crystalline nanoflowers.<sup>7</sup> The key is to maintain an appropriate concentration of capping ligands,

which is not enough to protect the primary nanocrystals against aggregation but sufficient to stabilize the resulting 3D nanostructures. Although conceptually elegant, we find it difficult to extend LLP method to many other systems especially in the cases where the ligands are involved in the production of monomers required for nanoparticle formation. For example, in the classic synthesis of superparamagnetic iron oxide ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles, monodisperse particles are produced by thermal decomposition of  $\text{Fe}(\text{CO})_5$  in the presence of a capping ligand of oleic acid (OA).<sup>8</sup> Changing the relative concentration of OA led to variation in the particle size but not their aggregation state. Lowering the oleic acid amount did not result in maghemite nanoflowers or any other aggregates, instead, only smaller spherical maghemite nanocrystals were produced.<sup>9</sup> In this case, OA acts not only as a capping ligand that ensures the colloidal stability of the nanoparticles, but also participates in the reaction with  $\text{Fe}(\text{CO})_5$  for the production of iron-oleic acid metal complex which is the needed precursor for nanoparticle growth. In this regard, a more effective and general strategy is preferred to decrease their colloidal stability and induce the formation of secondary structures.

Herein we demonstrate a "ligand stripping" method that enables precisely controlled aggregation of nanocrystals and produces a series of complex 3D nanostructures with well-defined morphologies. The key strategy involves the



**Scheme 1** Schematic illustration of the "ligand stripping" method.

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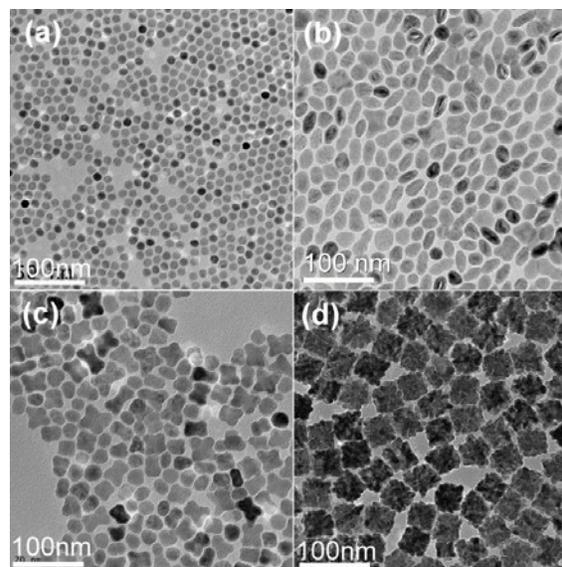
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destabilization of colloidal nanocrystals by replacing the original capping ligand with a stripping agent. The stripping agent binds to the surface of nanocrystals weakly, thus induces their aggregation into nanocrystal clusters. Using iron oxide as an example, we demonstrate that the use of diols as "stripping agents" can controllably remove the original capping ligands (OA) and induce aggregation of nanocrystals into clusters of defined shapes. The degree of aggregation can be controlled using diols with different stripping power. In this paper, we use  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$  including diethylene glycol (DEG) ( $n=2$ ), tetraethylene glycol (TEG) ( $n=4$ ) and polyethylene glycol 400 (PEG 400) ( $n\approx 8$ ) as "ligand stripping" agents. We show that a higher degree of aggregation can be readily achieved by either using diol of lower molecular weight or simply increasing the diol concentration.

The iron oxide CNCs were synthesized by modifying a previously established procedure by Hyeon et al.<sup>8</sup> In a typical synthesis of cubic clusters, 0.2 mL of  $\text{Fe}(\text{CO})_5$  (1.52 mmol) was added to a mixture containing 0.1 mL of DEG (1.11 mmol), 10 mL of ODE and 2 mL of oleic acid (6.41 mmol) at 110 °C. The resulting mixture was heated up to 295 °C. According to Hyeon et al., the initial reaction involves decomposition of  $\text{Fe}(\text{CO})_5$  and then reaction with oleic acid to form iron-oleic acid complex. The sudden change of the solution color from clear light yellow to black represents the burst nucleation of FeO nanocrystals. After the solution turned black, the solution was kept at that temperature for 1 h. All the heating processes took place under vigorous stirring in an argon atmosphere. The resulting black solution was cooled to 200 °C, oxidized by bubbling air into the solution for 1 h at 200 °C, and then cooled down to room temperature. Finally, iron oxide cubic nanoclusters were collected by centrifugation and washed with toluene/ethanol. Iron oxide dimers and oligomers were synthesized by using PEG 400 and TEG instead of DEG, respectively (ESI,† Table S1).

Spherical maghemite nanocrystals of 12 in diameter were formed without the addition of any diol additives into the  $\text{Fe}(\text{CO})_5/\text{OA}/\text{ODE}$  solution (Fig. 1a), which is consistent with the previous report by Hyeon et al.<sup>8</sup> When 0.1 mL PEG 400 was introduced, most of the products show elongated nanostructure and some show apparent dimer structure (Fig. 1b). If 0.1 mL TEG was added instead of PEG 400, most products were composed of several nanoparticles which were termed as "oligomers" in this work (Fig. 1c). And if DEG was applied instead, monodisperse 40 nm sized cubic nanoclusters were formed (Fig. 1d). There were dozens of original particles in each cluster which indicate the degree of aggregation increases dramatically. If diols of the same volume were used as ligand stripping agents, those molecules with less EG repeating units showed stronger ability in causing aggregation. Figure 1 indicates that both the yield and the morphology uniformity of clusters increased with stripping ligands containing less EG repeating units. In particular, with DEG as the ligand stripping agent, uniform cubic clusters with yield near 100% could be obtained (Fig. S2a). The presence of a small number of NCs and oligomers (marked by white squares in Fig. S2a) suggests that they are probably the building blocks



**Fig. 1** TEM images of iron oxide aggregates prepared by using different diols as ligand stripping agents: (a) sphere nanoparticles without diol added; (b) dimers induced by PEG 400; (c) oligomers induced by TEG; (d) cubic clusters induced by DEG.

of the larger clusters.<sup>2</sup>

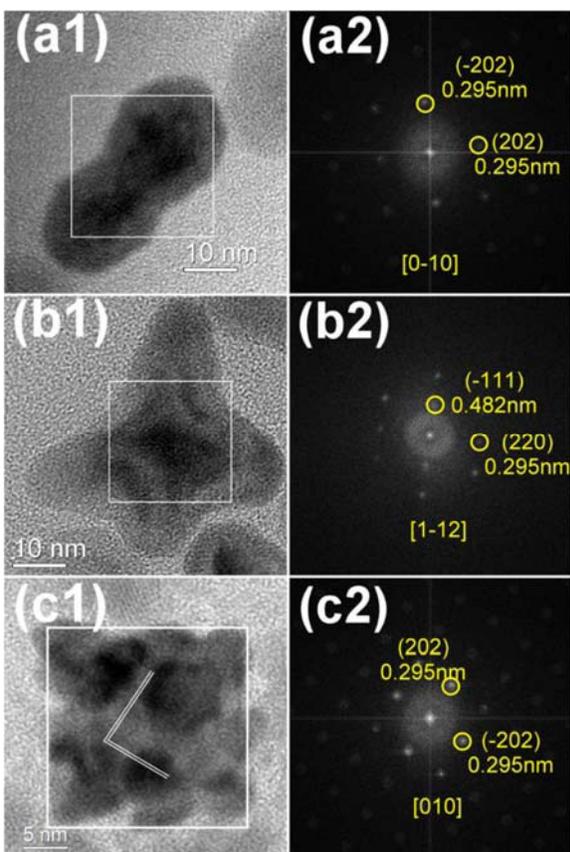
We have followed the evolution of cubic CNCs by TEM imaging. In the early stage after the solution was heated to 295 °C, the solution was still clear and light yellow. Mainly amorphous complexes together with some nanocrystals and small nanocrystal clusters could be observed (Fig. S3a). At this stage, amorphous complex precursor has not been fully decomposed. Within one minute after the solution turned black, clusters with size  $\sim 40$  nm became the principal product (Fig. S3b). After that, the overall size of clusters did not change much with reaction time prolonging. In another word, the formation and aggregation processes of nanocrystals happened in a very short period of time. By comparing Fig. S3b with Fig. 1d, we can find that during the later growth stage, the cubic shape of the clusters became clearer and the clusters appeared to be more compact and the size distribution became narrower. In addition, the density of the iron oxide clusters can be further finely tuned by controlling the aging temperature and time (Fig. S4). In brief, higher temperature and longer aging time result in more compact structures due to the fusion of nanocrystals within clusters.

It is worth mentioning that, the ligand stripping agent has to be added into the reaction system before the solution turns black. As the burst of nucleation and subsequent growth of nanocrystals completes within minutes, the addition of stripping ligands afterwards did not cause immediate aggregation and the product appeared to be still single spherical nanocrystals (Fig. S5a). This is because the full grown nanocrystals have relatively low surface energy and they have less tendency to aggregate. It is also necessary to point out that the size of the primary particles decreased as the degree of aggregation raised. These observations clearly indicate that

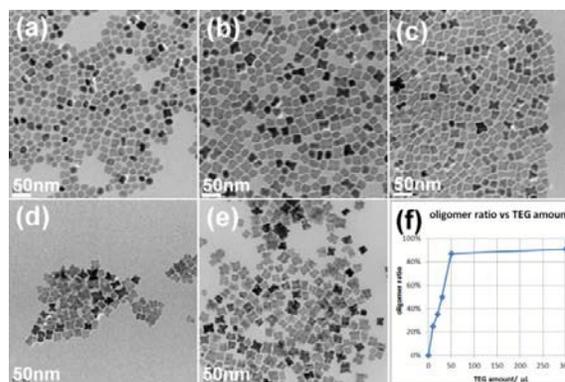
the stripping agents interact with the nanocrystals at the early stage of their formation, with stronger interaction for smaller diols. This is confirmed by adding ethylene glycol (EG) to the reaction, where larger clusters about 100 nm were produced. Careful inspection shows that the primary particles are extremely small, only a few nanometers in size. As the boiling point of EG is only 195°C, as opposed to DEG and TEG which are 245 °C and 330 °C, respectively, the aggregation of the nanocrystals could not be well controlled so that the resultant CNCs were not uniform (Fig. S5b).

Detailed crystal structures of iron oxide dimers, oligomers and clusters were studied (Fig. 2). HRTEM imaging of iron oxide shows continuous lattice fringes for all types of the CNCs, indicating single crystallinity which was further confirmed by corresponding FFT patterns of the square area. Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) has an inverse spinel structure and belongs to the cubic crystallographic system (space group  $O_h^{-7}$ -Fd3m), with 40 atoms (eight Fe<sub>2</sub>O<sub>3</sub> units) per unit cell with lattice parameters  $a = b = c = 8.347 \text{ \AA}$  (JCPDS No. 39-1346).<sup>10</sup>

In addition to the stripping power of the diols, the degree of aggregation could also be controlled by their concentration in the reaction. Here we chose TEG as an example to show such dependence (Fig. 3). When the least amount of 0.01mL TEG was used, most of the products were single particle or dimer,



**Fig. 2** HRTEM images of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> aggregates: (a1) dimers induced by PEG 400; (b1) oligomers induced by TEG; (c1) cubic clusters induced by DEG. Images of a2-c2 are corresponding FFT patterns of the square areas.



**Fig. 3** TEM images of iron oxide aggregates made by different amounts of TEG: (a) 0.01 mL; (b) 0.02 mL; (c) 0.03 mL; (d) 0.05 mL; (e) 0.3 mL. And (f) shows the relationship between the oligomer ratio and the TEG amount.

and oligomer ratio was rather low. When TEG amount increased, the single particle and dimer ratio kept decreasing and oligomer ratio increasing. Extremely low amount TEG resulted in single spherical and dimer like particles while extremely high amount TEG led to cube-like clusters.

The stripping of OA by diols from the nanocrystal surface occurs at the early stage of nanocrystal growth. At the beginning of the reaction, as the oleate is already part of the precursors and the total amount of OA (6.41 mmol) is significantly more than diols (1.11 mmol), the nucleation and growth of FeO nanocrystals are dominated by the presence of OA so that the reaction proceeds in a way similar to the standard synthesis (without diols), although the diols may act as co-ligands to limit the growth of primary nanocrystals. The decomposition of iron-oleate complex supports the growth of nanocrystals; while at the same time significantly reduces the concentration of OA in the system as the decomposition products evaporate, making it possible for diols to attack the surface of nanocrystals and kick off the attached OA. On the other hand, the adhesion of diols to the surface of oxide nanocrystals is considerably weak at high temperatures, resulting in reduced surface coverage of ligands and therefore destabilization of the colloidal nanocrystals. The coexistence of OA and DEG on the surface of the cubic clusters was confirmed by Fourier transform infrared (FTIR) analysis (Fig. S6), and the reduced coverage of capping ligands on the surface of the nanocrystal clusters was clearly revealed by thermogravimetric analysis (TGA, Fig. S7). Finally, upon aggregation, the primary nanocrystals bind to each other. Although further verification is needed, we believe the binding of primary nanocrystals most likely proceeded through the well-known oriented attachment mechanism as each resulting cluster is a single crystal.<sup>11</sup> It is necessary to point out that the oxidation of FeO CNCs by bubbling air at 200°C did not significantly alter their cluster structure and overall morphology (Fig. S8).

The bulkiness of the diol molecules is believed to play an important role in determining their diffusion rate in solution and thus their ability in attacking OA molecules on the

nanocrystal surface. Even if the concentrations of added diols were kept the same, diols with larger molecular weight still showed lower aggregation ability. For example, although the quantity of –OH groups of 0.3 mL PEG is 1.5 times as that of 0.1 mL DEG, the final products were still oligomers (Fig. 3e), the aggregation degree of which was much lower than clusters produced by DEG (Fig. 1d).

The magnetization hysteresis loops of the iron oxide at 300 and 5 K are shown in Fig. S9. The saturation magnetizations ( $M_s$ ) of iron oxide single nanoparticles, dimers, oligomers and clusters at 300 K were measured at 67.6, 60.1, 51.4 and 63.7 emu/g, respectively. All samples possess typical superparamagnetic features at room temperature. However, the magnetization versus field curve exhibits a ferromagnetic behavior at 5 K. The saturation magnetizations ( $M_s$ ) of iron oxide single nanoparticles, dimers and clusters were 72.0, 54.9 and 58.2 emu/g, and the coercivity values ( $H_c$ ) were 200, 200 and 430 Oe, respectively. According to reference, bulk magnetite and maghemite have the highest saturation magnetizations ( $M_s$ ) among the iron oxides (92–100 emu/g and 60–80 emu/g, respectively).<sup>12</sup>

In summary, an effective "ligand stripping" approach has been developed for the growth of colloidal nanocrystal clusters. Taking iron oxide as an example, we demonstrate that using diols as "stripping agents" it is possible to controllably remove the original capping ligands (OA) and induce aggregation of nanocrystals into well-defined clusters, oligomers and dimers. The degree of aggregation can be controlled by using diols with different stripping power or controlling the concentration of diols. We believe that this "ligand stripping" method represents a general approach for the creation of secondary structures of colloidal nanocrystals. These complex crystalline nanostructures described herein offer unique nanoarchitectures for constructing novel functional nanoscale devices.

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## Notes and references

- 1 C. B. Murray, C. R. Kagan and M. G. Bawendi, *Ann. Rev. Mater. Sci.*, 2000, **30**, 545.
- 2 Y. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664.
- 3 (a) J. Ge, Y. Hu, M. Biasini, W. P. Beyermann and Y. Yin, *Angew. Chem. Int. Ed.*, 2007, **46**, 4342; (b) J. P. Ge, Y. X. Hu and Y. D. Yin, *Angew. Chem. Int. Ed.*, 2007, **46**, 7428; (c) R. Fernandes, M. Li, E. Dujardin, S. Mann and A. G. Kanaras, *Chem. Comm.*, 2010, **46**, 9270; (d) D. Baranov, L. Manna and A. G. Kanaras, *J. Mater. Chem.*, 2011, **21**, 16694; (e) A. G. Kanaras, C. Sönnichsen, H. Liu and A. P. Alivisatos, *Nano Lett.*, 2005, **5**, 2164.
- 4 Z. D. Lu and Y. D. Yin, *Chem. Soc. Rev.*, 2012, **41**, 6874.

- 5 (a) Y. Zhu, W. Zhao, H. Chen and J. Shi, *J. Phy. Chem. C*, 2007, **111**, 5281; (b) S. Xuan, F. Wang, Y.-X. J. Wang, J. C. Yu and K. C.-F. Leung, *J. Mater. Chem.*, 2010, **20**, 5086; (c) X.-L. Fang, C. Chen, M.-S. Jin, Q. Kuang, Z.-X. Xie, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, *J. Mater. Chem.*, 2009, **19**, 6154; (d) H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen and Y. D. Li, *Angew. Chem. Int. Ed.*, 2005, **44**, 2782; (e) X. F. Yang, J. X. Fu, C. J. Jin, J. A. Chen, C. L. Liang, M. M. Wu and W. Z. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 14279; (f) J. Liu, Z. Sun, Y. Deng, Y. Zou, C. Li, X. Guo, L. Xiong, Y. Gao, F. Li and D. Zhao, *Angew. Chem. Int. Ed.*, 2009, **48**, 5875; (g) X. Hu, J. Gong, L. Zhang and J. C. Yu, *Adv. Mater.*, 2008, **20**, 4845; (h) J. Geng, Y. Lv, D. J. Lu and J. J. Zhu, *Nanotechnology*, 2006, **17**, 2614.
- 6 (a) A. Corma, P. Atienzar, H. Garcia and J.-Y. Chane-Ching, *Nat. Mater.*, 2004, **3**, 394; (b) D. E. Gómez, I. Pastoriza-Santos and P. Mulvaney, *Small*, 2005, **1**, 238; (c) Y. Lin, H. Skaiff, T. Emrick, A. Dinsmore and T. Russell, *Science*, 2003, **299**, 226.
- 7 (a) A. Narayanaswamy, H. Xu, N. Pradhan and X. Peng, *Angew. Chem. Int. Ed.*, 2006, **45**, 5361; (b) A. Narayanaswamy, H. Xu, N. Pradhan, M. Kim and X. Peng, *J. Am. Chem. Soc.*, 2006, **128**, 10310.
- 8 T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. Bin Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798.
- 9 K. Woo, J. Hong, S. Choi, H. W. Lee, J. P. Ahn, C. S. Kim and S. W. Lee, *Chem. Mater.*, 2004, **16**, 2814.
- 10 P. Mäkie, G. Westin, P. Persson and L. Österlund, *J. Phys. Chem. A*, 2011, **115**, 8948.
- 11 (a) D. Li, M. H. Nielsen, J. R. Lee, C. Frandsen, J. F. Banfield and J. J. De Yoreo, *Science*, 2012, **336**, 1014; (b) Q. Zhang, S.-J. Liu and S.-H. Yu, *J. Mater. Chem.*, 2009, **19**, 191; (c) M. Niederberger and H. Cölfen, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3271.
- 12 M. Cornell and U. Schwertmann, *The Iron Oxides, VCH: New York*, 1996, 117.

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