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Continuous Phase Transformation in Nanocube Assemblies

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The phase behavior of 3D assemblies of nanocubes in a ligand-rich solution upon solvent evaporation was experimentally investigated. Using small angle x-ray scattering and electron microscopy, we observed a continuous phase transformation of assemblies between a simple cubic and a rhombohedral structure with a variable angle depending on ligand thickness. We established a quantitative relationship between the particle shape evolution from cubes to quasi-spheres and the lattice distortion during the transformation with a pathway exhibiting the highest known packing.

The phase behavior of self-assembled molecularly-stabilized and mediated spherical nanocolloids has been an active area of research [1-3]. Recent advances in the fabrication of anisotropic shaped particles allow for an exploration of geometrical effects in their condensed phase [4, 5]. On nanoscale, the packing behavior of ligand-tethered objects, such as cubes [6] and polyhedrons [7, 8], can deviate significantly from the pure geometrical predictions due to the contribution of soft molecular shells via modulation of particle shape and interparticle interactions. The resulting interplay between geometrical effects and shell properties provides a conceptually new parameter for nanocolloid assembly. Furthermore, free ligands in a solution can also play crucial roles for assembly of condensed states. For instance, ligand excess favored the ordering of 2D spherical colloidal arrays [9], whereas induced a phase separation for particles with different shapes [10].

In addition to assembly of static systems, an investigation of reorganization in systems built from reconfigurable components is imperative for smart and stimuli-responsive materials. Recently several studies reported transformations in systems containing molecular decorated reconfigurable objects, such as length-switchable rods assemblies [11] and molecularly stimulated 3D nanoparticle arrays [12]. From a fundamental perspective, the relationship between a structurally evolving single component and the resulting structural response of the whole system is not well understood, partially due to limited experimental realizations. Here, we adopted dodecanethiol (DT) ligated palladium nanocubes (NC) as a model for investigation of a phase behavior of NCs 3D assembly during the system reconfiguration process. We observed a continuous structural transformation of NCs assemblies in a ligand-rich solution during solvent evaporation. The changes were attributed to the evolution of particle shape from a cube to a quasi-sphere.

The studied system consists of well-defined palladium cubes with edge of 10.6 ± 0.9 nm (Fig. 1a). NCs were synthesized in an aqueous solution by a modified procedure [13] using polyvinylpyrrolidone (PVP) capping and subsequently replaced by DT ligand (inset, Fig. 1b) with thickness ~ 1.7 nm [14]. High-resolution transmission electron microscopy (TEM) reveals a face centered cubic (FCC)-type single crystal of NC (inset, Fig. 1a). We conducted the synchrotron-based small-angle X-ray scattering (SAXS, NSLS X-9A beamline, $\lambda = 0.7867$ Å) measurements of NCs dispersed in aqueous solution (Fig. 1b). The fit (Irena package [15]) of an angular averaged SAXS profile yields a spherical particle which volume corresponds to a cube

with 10.9 nm edge length, that is in agreements with TEM results. We induced assembly of DT coated NCs by placing them into slightly poor solvent, toluene (40 μ l) at \sim 5% of solid content. The effect of free ligands on the assembly was studied by adding 10 μ l DT into the solution. The solution was then transferred into capillary, in which in-situ SAXS measurements were conducted.

The structural evolution of the NC assemblies with gradual solvent evaporation resulted in the time-dependent development of the SAXS patterns and the corresponding structure factors $S(q)$, as shown in Figure 2a. $S(q)$ is obtained as $I_a(q)/I_p(q)$, where $I_a(q)$ and $I_p(q)$ are background corrected SAXS profiles measured from aggregate and free particles, respectively, and peak positions in the $S(q)$ are determined by Lorentzian fitting. We denote q_1 , q_2 and q_3 as the positions of the strongest peaks at 0.0444 \AA^{-1} , 0.0628 \AA^{-1} , and 0.0888 \AA^{-1} , respectively, for the sample at the initial state (C_{L1}). The sequence of measurements, C_{Ln} ($1 \leq n \leq 6$), corresponds to a sample at 0, 24, 58, 98, 221, and 500 hours of evaporation duration at \sim 370 K, with a solution fully evaporated for C_{L6} .

Based on $S(q)$ analysis we indexed the initial state C_{L1} as a simple cubic (SC) structure (Fig. 2a). Such SC structure has been previously shown for assemblies of nanocubes [16]. Upon solvent evaporation, SAXS reveals two major structural changes: (i) q_1 , corresponding to (100) plane, shifts towards smaller q from C_{L2} to C_{L6} and (ii) the peak position ratio, q_2/q_1 decreases. Moreover, the second peak, nominally arising from SC (110) plane, gradually merges into the (100) peak and becomes its shoulder peak. These observations indicate a phase transformation upon solvent evaporation. The NC assembly reversibly transforms into the original SC structure, C_{L1} , from the dried state C_{L6} by adding solvent, as indicated by $S(q)$ for C_{L7} . To investigate the determining factors for the phase evolution, we conducted two control experiments. We first employed TEM to verify a structural stability of the NCs during the solvent evaporation. Figures 2b and 2c show NCs of similar sizes, shapes and packing at C_{L1} and at C_{L7} , respectively. Second, analogous experiments without free DT in the solution (denoted as C_{LF} series, Fig. 2d) show the stable SC phase for C_{LF1} , C_{LF2} , and C_{LF3} , obtained after 0, 58, and 500 hours of evaporation, respectively. Therefore, we conclude that the evaporation-assisted phase transformation is due to the ligand excess, although the local concentration of ligand in the cubes proximity might differ significantly from an average solution value.

The continuous structural evolution can be described as a gradual distortion of a SC lattice in the [111] direction, which is an angle-variable rhombohedral structure (RS). With angle α change from 90° to 60° , RS depicts a continuous phase transformation from SC to FCC. This type of transformation has been observed in arsenic atomic system [17] and porous silica film[18]. The reduced position of diffraction peak (hkl) for a RS can be expressed as $q(hkl)/q(100) = [(h^2 + l^2 + 2k^2) * \sin^2\alpha + 2(hk + kl + lh) * (\cos^2\alpha - \cos\alpha)]^{-1/2} * \sin^{-1}\alpha$, and the calculated values for $q(110)/q(100)$, $q(200)/q(100)$, and $q(210)/q(100)$ against α are plotted in Fig. 3a (solid lines). The planes (100), (110), (200) and (210) of SC phase evolve respectively into (111), (200), (222) and (311) of FCC phase when α decreases to 60° . One feature of the RS model is that the $q(110)$ approaches the $q(100)$ gradually with α decrease, which resembles the observed q_2/q_1 evolution for the C_{Ln} . We used experimental values of q_2/q_1 for $q(110)/q(100)$ in RS model to determine α , then, we mapped each C_{Ln} and C_{LFn} on the $q(110)/q(100)$ line in Figure 3a (black symbols). Using obtained α , we plotted q_3/q_1 values (Fig. 3a, red symbols). While for all C_{LF} systems, $\alpha \sim 90^\circ$ (Fig. 4d(1)), for C_L system, α decrease from 88.2° at C_{L1} to 74.9° at C_{L6} (Fig. 4d(2)) indicates that a full evolution toward FCC phase (Fig. 4d(3)) is not completed. The change of a lattice constant, a , can be estimated for the RS as $a = d(100) * \sin\alpha * (1 - 3\cos^2\alpha + 2\cos^3\alpha)^{-1/2}$, where $d(100) = 2\pi/q_1$ (Fig. 3b). During solvent evaporation a slightly decreases to 13.8 nm at C_{L2} from 14.2 nm at C_{L1} , possibly due to chain rearrangements, and, then it continuously increases, reaching 18.3 nm at C_{L6} .

Based on shape considerations, nano-cubes favor SC phase [16], while FCC packing is preferable for spheres. Thus, we suggest that the α - variable RS phase transformation is related to the system's attempt to accommodate a changing particle shape from cube to quasi-sphere due to a ligand adsorption. The shape evolution results from cohesive interactions between adsorbed and NC-attached DT molecules, and stronger NC-DT van der Waals (vdW) attraction compared to DT-DT. The convex growth of DT crown-like layer leads to the quasi-spherical shape transformation of NC and satisfies the requirement for surface energy minimization [19, 20]. Figure 3c shows the monotonous increase of α with $x = D_{cc} / L_{pe}$, where D_{cc} is a nearest-neighbor NC center-to-center distance, and L_{pe} is an effective NC edge length. For RS $D_{cc} = a$, and $L_{pe} = 13.3$ nm accounting for DT molecules interpenetration [14]. The values of $x=1$, $\alpha = 90^\circ$ and $x=\sqrt{3}$, $\alpha = 60^\circ$ respectively corresponds to cubes and spheres. For our system we observed a

variation of x varies from 1 to ~ 1.37 , with related α change from 90° to 74.9° , indicating an incomplete transition from cubes to spheres. A “superball” model [21] with object shape defined by $|x|^{2p} + |y|^{2p} + |z|^{2p} \leq 1$, where x , y , and z are Cartesian coordinates, was introduced to describe the sphere to cube evolution with deformation parameter p change from 1 to ∞ (Fig. 4c).

In the framework of the superball model the relationship between a particle shape and a lattice structural response can be established. Interestingly, the densest proposed [21] packing C_1 ($p > 1$) corresponds to a RS with the lattice vectors (L_v) defined as $\mathbf{e}_1 = -2(s + 2^{-1/2p}) \mathbf{i} + 2s \mathbf{j} + 2s \mathbf{k}$, $\mathbf{e}_2 = -2s \mathbf{i} + 2s \mathbf{j} + 2(s + 2^{-1/2p}) \mathbf{k}$, $\mathbf{e}_3 = -2s \mathbf{i} + 2(s + 2^{-1/2p}) \mathbf{j} + 2s \mathbf{k}$, where \mathbf{i} , \mathbf{j} , \mathbf{k} are unit vectors along x , y and z directions, and s is the smallest positive root of the equation $(s + 2^{-1/2p})^{2p} + 2s^{2p} - 1 = 0$. The L_v construction relates α and p , as $\alpha(p) = \arccos[\mathbf{e}_i \cdot \mathbf{e}_j / (|\mathbf{e}_i| |\mathbf{e}_j|)]$, $i, j = 1, 2, 3, (i \neq j)$. Conversely, p is only defined by α as well. The proposed RS mechanism for a lattice transformation is in accord with a local requirement for a particle “sliding” without substantial rotation, which is limited by a particle cusp for $p \neq 1$. We plotted the calculated values of $1/p$ as a function of α (Fig. 4b, red solid line) and mapped (red circles) a corresponding $1/p$ values, from 0 to 0.4, for each experimental α (Fig 3c). Figure 4a illustrates the phase transformation in 3D and its 2D analog from SC to FCC via RS, as induced by evolution of cubes to spheres with shape defined by the superball model. Our measurements shows that the transformation is accompanied by $\sim 40\%$ decrease of a correlation length, ξ , reflecting an order diminishment. The Williamson-Hall (WH) slope [22], a relative measure of a strain-induced average lattice distortion, increases nearly 50 times for corresponding $1/p$ change from 0 to 0.4, indicating a strain growth, a possible origin of ξ decrease. We note, a decreased local mobility of NCs due to the solvent evaporation can be responsible for the incomplete RS to FCC transformation and the strain increase. A full evolution to spheres is hindered when ligand shell increase: convex DT layer growth is decreased, and the adsorption of DT molecules on NC is diminished due to the reduction of vdW interaction.

The shape-induced phase transition is advantageous considering packing efficiency and interparticle interactions. To evaluate a favorable packing, we calculated volume fractions, $\phi(p)$, occupied by particles in RS and SC phases, as $\phi_{RS}(p) = V_{sb}(p)/V_{RS}(p)$ and $\phi_{SC}(p) = V_{sb}(p)/V_{SC}(p)$, respectively, where V_{sb} is the volume of superball [21], and, $V_{RS}(p) =$

$\mathbf{e}_1 \times \mathbf{e}_2 \cdot \mathbf{e}_3$ and $V_{SC}(p) = \mathbf{e}_1 \times \mathbf{e}_2 \cdot \mathbf{e}_3 |_{p=\infty} = 8$ are the unit cell volumes of RS and SC, respectively. The calculated ϕ_{RS} and ϕ_{SC} (Fig.4b, black solid and dashed lines) show that the difference in ϕ between RS and SC for $1/p < 0.05$ is very small, however, it quickly increases for $1/p > 0.12$. This indicates that RS offers a denser packing than SC for rounded particles, which justifies the SC to RS transition with $1/p$ increase, while ϕ_{RS} also exhibits the densest known packing of rounded cubes [21]. The higher packing of RS compared to SC is intuitively easy to understand: by allowing for an α -dependent cube “sliding” RS provides offset for the highest points on the convex surfaces of adjacent rounded cubes. The recent theoretical work [23] shows that rounded cubes can pack in a less dense cubatic phase for about $1/p > 0$, however, such degree of roundness is not realized in our system. From the interaction point, we consider solely the van der Waals (vdW) forces between NCs. Because of their short range character, only interaction between adjacent particles (W_a) is included [16]. When $1/p$ increases from 0 to 0.12, W_a decreases quickly from $\sim 14 k_B T$ to $\sim 4 k_B T$, and $W_a \sim k_B T$ for $1/p > 0.25$. Therefore, for a small $1/p$ (cube-like) a face-to-face SC arrangement of ligand coated NC is also favorable from vdW consideration, since a center-to-center distance is minimized. When particle shape evolves toward a quasi-sphere with $1/p$ increase, vdW interactions become less significant, and a RS transformation is favorable.

In summary, we investigated the relationship between nano-particle shape, ligand shell and the emergent phase behavior of nano-cube assemblies. The observed RS phase transformation was attributed to the evolution of particle’s shape from a cube to a quasi-sphere due to the ligand adsorption with the densest known pathway.

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- [1] B. A. Korgel, and D. Fitzmaurice, Phys. Rev. Lett. **80**, 3531 (1998).
- [2] H. M. Xiong, D. van der Lelie, and O. Gang, Phys. Rev. Lett. **102**, 015504 (2009).
- [3] D. Pontoni *et al.*, Phys. Rev. Lett. **102**, 016101 (2009).
- [4] A. Donev *et al.*, Phys. Rev. Lett. **92**, 255506 (2004).
- [5] K. Liu *et al.*, Science **329**, 197 (2010).

- [6] X. Zhang, Z. L. Zhang, and S. C. Glotzer, *J. Phys. Chem. C* **111**, 4132 (2007).
- [7] R. P. A. Dullens *et al.*, *Phys. Rev. Lett.* **96**, 028304 (2006).
- [8] M. R. Jones *et al.*, *Nat Mater* **9**, 913 (2010).
- [9] S. Narayanan, J. Wang, and X. M. Lin, *Phys. Rev. Lett.* **93**, 135503 (2004).
- [10] T. Ming *et al.*, *Angew. Chem. Int. Edit* **47**, 9685 (2008).
- [11] T. D. Nguyen, and S. C. Glotzer, *Acs Nano* **4**, 2585 (2010).
- [12] M. M. Maye *et al.*, *Nat Nanotechnol* **5**, 116 (2010).
- [13] B. Lim *et al.*, *Adv.Funct. Mater* **19**, 189 (2009).
- [14] L. Motte, F. Billoudet, and M. P. Pileni, *J. Phys. Chem.* **99**, 16425 (1995).
- [15] J. Ilavsky, and P. R. Jemian, *J Appl Crystallogr* **42**, 347 (2009).
- [16] S. Yamamuro, and K. Sumiyama, *Chem. Phys. Lett* **418**, 166 (2006).
- [17] T. Kikegawa, and H. Iwasaki, *J. Phys. Soc. Jpn.* **56**, 3417 (1987).
- [18] B. W. Eggiman, M. P. Tate, and H. W. Hillhouse, *Chem Mater* **18**, 723 (2006).
- [19] F. B.-W. P.G. de Gennes, D. Quere, *Capillarity and Wetting Phenomena Drops, Bubbles, Pearls, Waves* (Springer, New York, 2003), p. p 153 (Chapter 7).
- [20] A. Checco, O. Gang, and B. M. Ocko, *Phys. Rev. Lett.* **96**, 056104 (2006).
- [21] Y. Jiao, F. H. Stillinger, and S. Torquato, *Physical Review E* **79**, 041309 (2009).
- [22] G. K. Williamson, and W. H. Hall, *Acta Metall Mater* **1**, 22 (1953).
- [23] R. D. Batten, F. H. Stillinger, and S. Torquato, *Physical Review E* **81**, 061105 (2010).

Figure Captions

FIG. 1 (a) The TEM image of PVP stabilized Pd nanocubes and (inset) HRTEM image of a Pd cube (b) SAXS scattering profile obtained from free NC in a solution (open circles), fit with Irena2 package (line), and (inset) schematic of a DT-functionalized nanocube, as discussed in the text.

FIG. 2 (a) Evolution of the 2D SAXS patterns and $S(q)$ of assembled nanocubes upon evaporation of ligand-rich solution. The TEM images of nanocubes obtained in the states C_{L1} (b) and C_{L7} (c). (d) $S(q)$ for different states of NC assembly in a ligand-free solution.

FIG. 3 (a) Calculated ratios of diffraction peak positions for shown planes in SC and FCC phases, and their dependence on α in RS model (lines). Estimated α for assembled phase for different states, from experimental q_2/q_1 ratio (black symbols), and q_3/q_1 values (red symbols) for obtained α . The same black and red symbols correspond to the same sample states. (b) The dependence of a on a system state. (c) The dependence of α on nearest-neighbor NC center-to-center distance (D_{cc}) normalized by effective particle edge length (L_{pe}).

FIG. 4 (a) 3D and 2D illustration of a phase transformation from SC to FCC via RS phase due to evolution of effective particle shape from cube to sphere using superball model for shown p values. (b) Calculated $1/p$ (red solid line) and ϕ for RS (black solid line) and SC (black dashed line) as a function of α . The black and red symbols correspond to the experimental data, obtained as discussed in the text. (c) Calculated particle shapes as for shown p values. (d) Schematics of the transformation of SC to FCC lattice via RC phase (NC are represented by white spheres).

Fig. 1

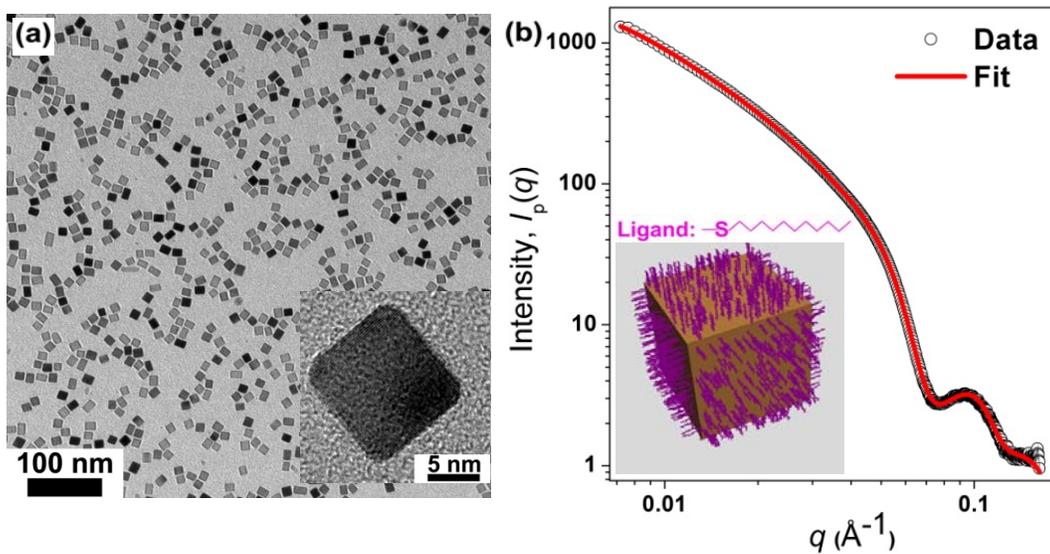


Fig. 2

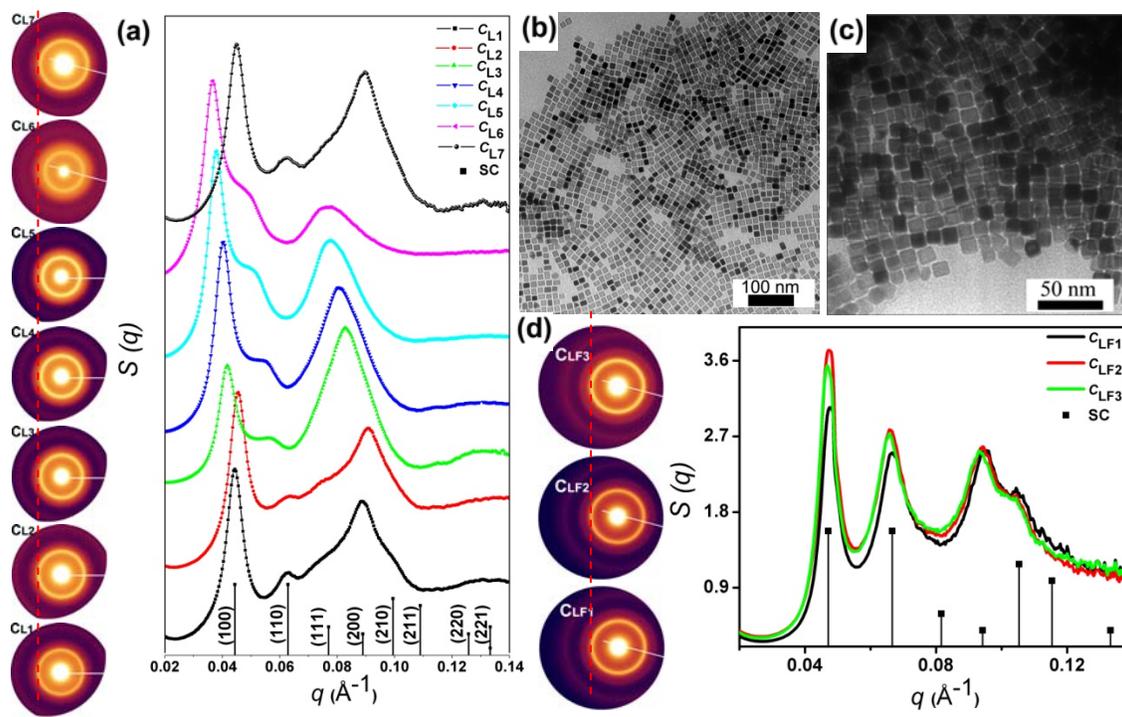


Fig. 3

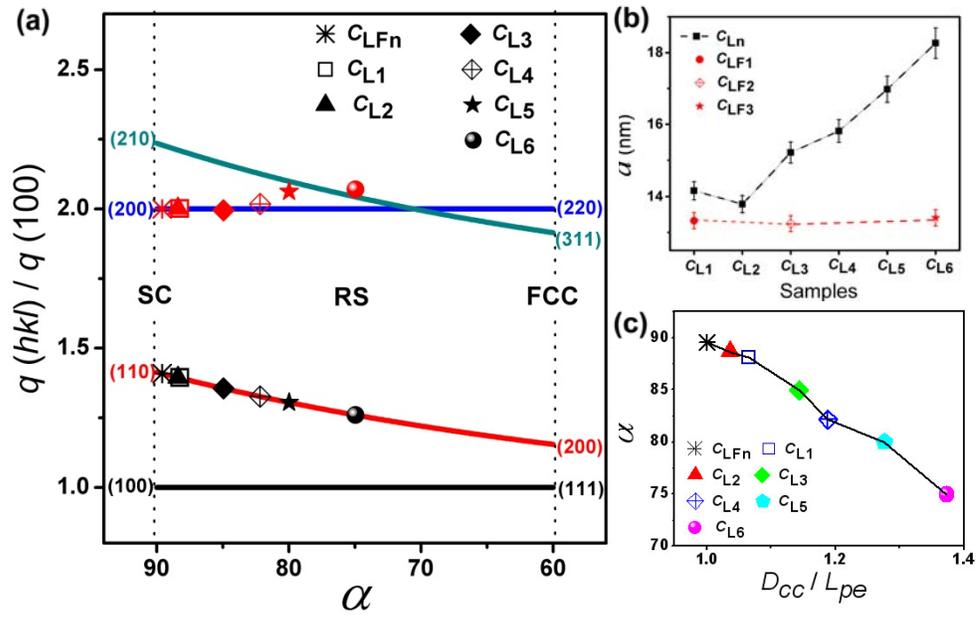


Fig. 4

