[6] E. S. Kikkinides, A. K. Stubos, K. P. Tzevelekos, A. C. Mitropoulos, N. Kanellopoulos, *Adsorption and Its Applications in Industry and Environmental Protection*, Vol. I: *Applications in Industry*, **1999**, *120*, 687.
[7] J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem. Int. Ed.* **1999**, *38*, 56.
[8] K. W. Gallis, J. T. Araujo, K. J. Duff, J. G. Moore, C. C. Landry, *Adv. Mater.* **1999**, *11*, 1452.
[9] G. Büchel, K. K. Unger, A. Matsumoto, K. Tsutsumi, *Adv. Mater.* **1998**, *10*, 1036.
[10] J. V. Sanders, *Nature* **1964**, *204*, 1151.
[11] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.
[12] O. D. Velev, E. W. Kaler, *Adv. Mater.* **2000**, *12*, 531.
[13] H. Miguez, F. Meseguer, C. Lopez, A. Mifsud, J. S. Moya, L. Vazquez, *Langmuir* **1997**, *13*, 6009.
[14] G. S. Attard, J. C. Glyde, C. G. Goltner, *Nature* **1995**, *378*, 366.

Polyhedral Shapes of Cobalt Nanocrystals and Their Effect on Ordered Nanocrystal Assembly**

By *Zhong L. Wang*,* *Zurong Dai*, and *Shouheng Sun*

Controlled assembly of monodispersive nanocrystals (NCs) has been a key issue in fabricating functional nanodevices. A relatively simple and new approach to NC assembly is to use structurally stabilized monodispersive NCs as building blocks, which can self-assemble into 2D and 3D structures.[1] This general approach to nanocrystal arrays has been applied to a variety of nanocrystalline materials, including Ag,[2,3] Au,[4–6] Co,[7,8] FePt,[9] α-Fe_2O_3,[10] CoO,[11] and CdSe.[12] Extensive investigations in NC assemblies have revealed that the symmetry of the observed superlattices is influenced by the NC size, NC shape, and relative dimensions of the NC core and the organic capping.[13]

It was recently demonstrated that a chemically prepared assembly of ferromagnetic FePt NCs as small as 4 nm can support high-density magnetic transitions at room temperature.[9] The key challenges in this self-assembly method are to control the defects of the self-assembly to ensure an ordered structure, and to prepare an assembly with uniform thickness and large lateral dimension. These two technical concerns are closely related to the NC shapes. It has been demonstrated that, in the Ag NC system, the NC shapes play a crucial role in determining the structure of the NC arrays.[1] In this paper, we report a detailed transmission electron microscopy analysis of the shapes of the 11 nm Co NCs and their effect on the Co NC superlattice assembly. We find that these Co NCs have anisotropic polyhedral shapes. The self-assembly of the NCs and the defect structures in the NC arrays are governed by these anisotropic shapes.

Cobalt NCs were prepared from solution-phase reduction of cobalt chloride in the presence of stabilizing agents.[8] The NCs are encapsulated by the oleic acid. The NCs can be dispersed readily in hexane solvent. A droplet of the solution was deposited on an ultra-thin carbon film. The solvent was allowed to evaporate slowly at room temperature. The structure, shapes and the NC superlattices of these Co NCs were analyzed using a JEOL 4000 EX high-resolution transmission electron microscope (HRTEM).

The X-ray diffraction (XRD) studies have shown that each of the as-prepared Co NCs has the β-Mn structure[14] (ε-Co phase, space group $P4_132$)[15] with a cubic unit cell of 20 atoms and 6.097 Å on a side. Figure 1 shows an electron diffraction pattern recorded from a Co NC assembly. This diffraction pattern is consistent with the XRD data reported previously with the most intense diffraction peaks appearing as {221}, {310}, and {311}.[8] The three rings were enclosed by the objective aperture of the HRTEM, thus the atomic-scale lattice images are dominated by the interference among the three beams and the central transmitted {000} beam.

Figure 2a shows an ordered self-assembly of the Co NCs, which exhibits long-range translation order. The packing of

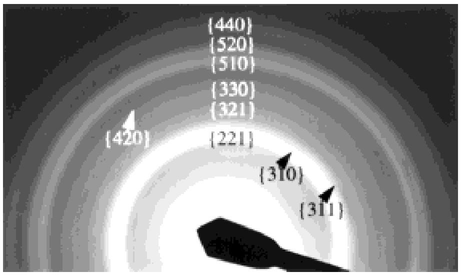

Fig. 1. Electron diffraction pattern recorded from the as-synthesized Co nanocrystals, which matches well to the intensities and indexes for the β-Mn structure.

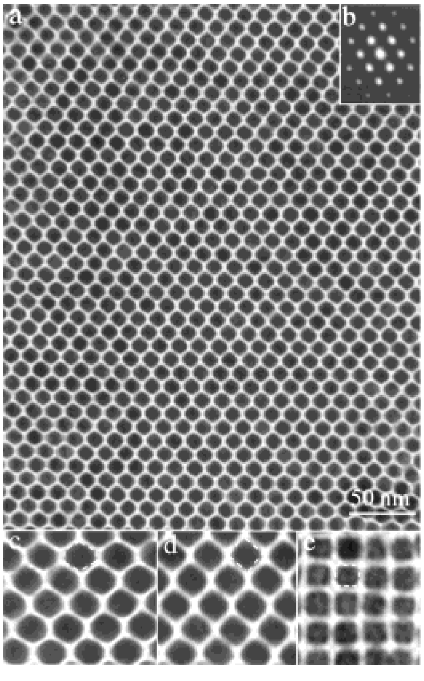

Fig. 2. a) Self-assembly of the 11 nm Co NCs. The thickness of the stacking is ~3 nanocrystals. b) A low-angle electron diffraction pattern recorded from the area showing the symmetry of the self-assembly. c)–e) Three typical local structures introduced by the anisotropy shape of the NCs.

---

[*] Prof. Z. L. Wang, Dr. Z. Dai
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245 (USA)
Email: zhong.wang@mse.gatech.edu

Dr. S. Sun
IBM T. J. Watson Research Center
Yorktown Heights
New York 10598 (USA)

[**] Research was supported by the US National Science Foundation (DMR-9733160).

these shaped Co NCs is rather different from the spherical ones reported previously[8] and is complicated by the existence of the polyhedral shapes of the NCs. A low-angle electron diffraction pattern recorded from the region (Fig. 2b) disproves the six-fold symmetry of the array. Three typical structures of the self-assembly are displayed in Figures 2c–e. From these enlarged images, it is apparent that three types of shapes, square-like, hexagon-like and square exist in the assembly. These different shapes of NCs result in the breaking of the normal six-fold symmetry in the superlattice assembly.

The unique feature of the Co NC shapes is easily seen in the HRTEM images (Fig. 3). From XRD studies of the Co NC assembly, it is known that the (221) and (310) diffraction peaks are the most intense in the diffraction pattern. This means that in the HRTEM experiment, the interference among the (221), (310) and the central transmitted beams is dominated. By matching the interplanar distances and plane-to-plane angles through the Fourier transform of the images, the NC facets can be directly linked to the {221} and {310} planes. The (221) and (310) reflection rings are almost inseparable in the electron diffraction pattern, but the angles among them are critical in identifying the facets. From the images shown in Figures 3a and b, where the electron beam is parallel to $[62\bar{5}]$, the NCs are partially enclosed by the $\pm(2\bar{1}2)$, $\pm(122)$ and $\pm(\bar{1}30)$ facets. When the electron beam is parallel to [001] (Fig. 3c), the $(\overline{31}0)$ and $(1\bar{3}0)$ facets are imaged edge-on. Along the [120] direction (Fig. 3d), the $(2\overline{12})$ and $(2\bar{1}2)$ facets are imaged edge-on. These HRTEM images recorded from three different NC orientations are used to reconstruct the NC 3D shapes.

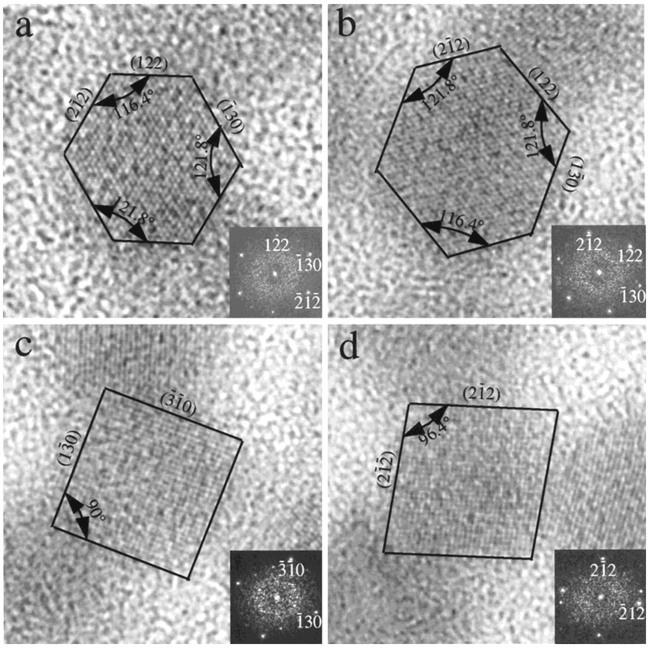

Fig. 3. Typical HRTEM images of the Co nanocrystals oriented along a,b) $[62\bar{2}]$, c) [001], and d) [120], showing the {221} and {310} facets. The insets are the Fourier transforms of the corresponding images.

Figure 4a shows a polyhedral model of the NC enclosed by $\pm(2\bar{1}2)$, $\pm(122)$, $\pm(\bar{1}30)$, $\pm(310)$, $\pm(2\overline{12})$, and $\pm(12\bar{2})$ facets. The structure can be simply constructed from a square-based rod defined by the $\pm(\bar{1}30)$ and $\pm(310)$ facets, which is cut by the $(2\bar{1}2)$, (122), $(\bar{2}12)$, and $(\overline{12}2)$ facets at the top and by the $(\bar{2}1\bar{2})$, $(\overline{122})$, $(2\overline{12})$, and $(12\bar{2})$ facets at the bottom. The projected shapes of the polyhedron along $[62\bar{5}]$, [120], and [001] are given in Figures 4b, c, and d, respectively. These projections match well with the NC shapes observed in the images displayed in Figure 4.

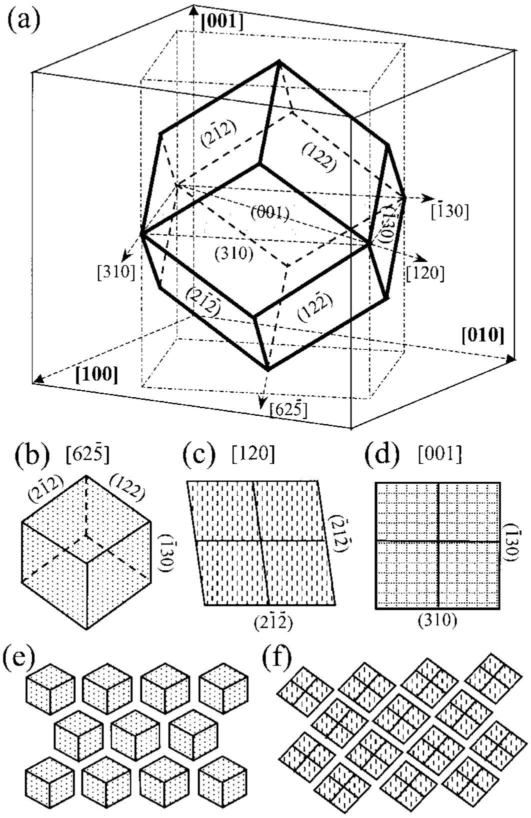

Fig. 4. a) Three-dimensional polyhedral shape of the Co nanocrystals constructed using the information provided by HRTEM images. b)–d) The projected shapes of the polyhedral model along $[62\bar{5}]$, [120], and [001], respectively. e,f) Monolayer close-packing of the polyhedra oriented in $[62\bar{5}]$ and [120], respectively.

If one takes the model given in Figure 4b and packs the NCs on a 2D surface, the assembly shown in Figure 4e is obtained. This model is constructed following the principle of the face-to-face for the same type of facets. For example, the $(\bar{1}30)$ face for one particle is against the $(1\bar{3}0)$ face of the other, and the $(2\bar{1}2)$/(122) face is to the $(\bar{2}1\bar{2})$/$(\overline{122})$. This configuration is observed in Figure 2c. If one uses the model given in Figure 4c to form a 2D close packing, the configuration given in Figure 4f is constructed, which is just the assembly observed in Figure 2d, where the NCs prefer to orient along [120]. If the polyhedrons are aligned parallel to [001] (see Fig. 4d), each NC appears as a square in the image and their assembly forms a square packing (Fig. 2e). Therefore, the three typical self-assemblies presented in Figures 2d–e result from the ordered orientations of the Co NCs due to their anisotropic shapes.

The NC shape effect on the assembly was first observed in the Ag NC system, in which the NC shape is dominated by the truncated octahedron, resulting in two popular defects, twins and stacking faults.[2] These types of defects are also observed in the present Co NC system, as shown in Figure 5a and b. The stacking faults can be either intrinsic or extrinsic. On one hand, the NCs can be assembled in a face-to-face manner for the same type of crystallographic planes. Alternatively, the $(\bar{1}30)$ facet of one particle can face the $(2\bar{1}2)$ facet of the other particle, resulting in a rotation of the orientation of the NCs and leading to the formation of twins in the NC assembly.[16] If the rotation occurs in only one column in the assembly, a stacking fault is created (Fig. 5c).

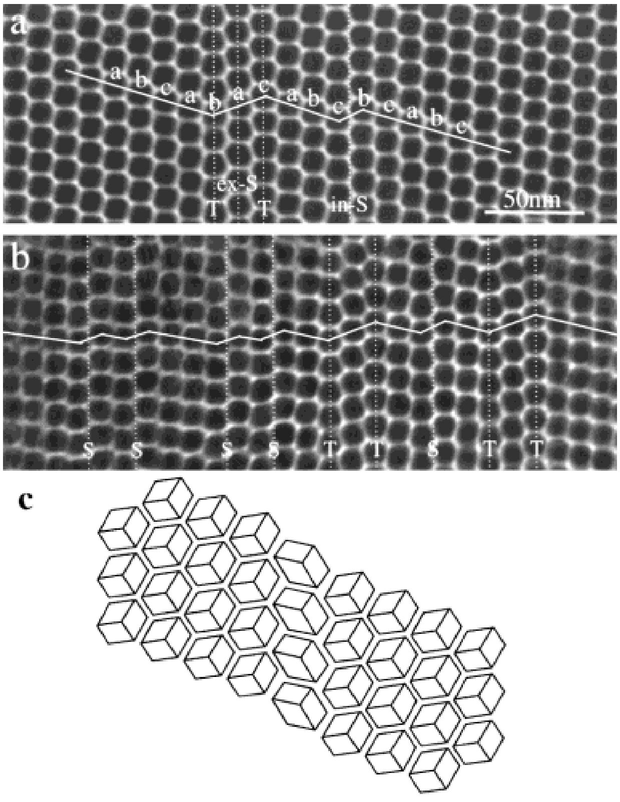

Fig. 5. a,b) Stacking fault (S) and twin (T) structures observed in the self-assemblies of Co NCs. c) Structure model of the stacking fault.

Figure 6 shows the co-existence of twins, stacking faults as well as a partial dislocation in the self-assembly. The “strain” induced by the dislocations and defects result in relative misalignments among the NCs. These stacking faults and twins totally disturb the local ordering of the self-assembly.

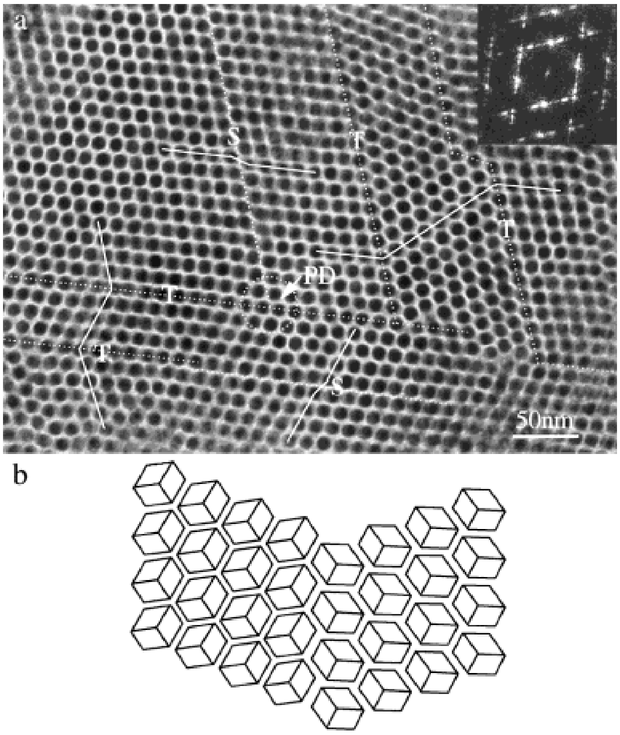

Fig. 6. a) Co-existence of stacking faults (S), twins (T), and partial dislocations (PD) in the self-assembly of the Co NCs. The inset is a Fourier transform of the corresponding image. b) Structure model of the twins.

In summary, we have shown that the chemically synthesized 11 nm Co NCs with a cubic β-Mn type structure have polyhedral shapes defined by the {221} and {310} faces. The self-assembled Co NC array preserves a long-range translation order but shows a short-range orientation order due to the NC shapes. This NC assembly follows a principle of face-to-face stacking. Twins and stacking faults are created in the assembly due to the mismatched faces of the adjacent NCs. These defects introduced in magnetic NC assembly will be a primary concern in future ultra-high density magnetic data storage media and nanoelectronic devices. A precise understanding of the assembly mechanism and the role played by the NC shape is essential for the fabrication of defect-free magnetic NC arrayed network.

Recieved: June 16, 2000

---

[1] For reviews see: Z. L. Wang, *Adv. Mater.* **1998**, *10*, 13. Z. L. Wang, *J. Phys. Chem. B* **2000**, *104*, 1153.

[2] S. A. Harfenist, Z. L. Wang, R. L. Whetten, I. Vezmar, M. M. Alvarez, *J. Phys. Chem. B* **1996**, *100*, 13 904.

[3] P. C. Ohara, J. R. Heath, W. M. Gelbart, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1078.

[4] R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. L. Wang, C. C. Cleveland, W. D. Luedtke, U. Landman, *Adv. Mater.* **1996**, *8*, 429.

[5] R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney, R. G. Osifchin, *Science* **1996**, *273*, 1690.

[6] C. J. Kiely, J. Fink, M. Brust, D. Bethell, D. J. Schiffrin, *Nature* **1998**, *396*, 444.

[7] C. Petit, A. Taleb, M. P. Pileni, *Adv. Mater.* **1998**, *10*, 259.

[8] S. Sun, C. B. Murray, *J. Appl, Phys.* **1999**, *85*, 4325.

[9] S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* **2000**, *287*, 1989.

[10] M. D. Bentzon, J. Van Wonterghem, S. Morup, A. Thölen, C. J. W. Koch, *Philos. Mag. B* **1989**, *60*, 169.

[11] J. S. Yin, Z. L. Wang, *Phys. Rev. Lett.* **1997**, *79*, 2570.

[12] C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **1995**, *270*, 1335.

[13] R. L. Whetten, M. N. Shafigullin, J. T. Khoury, T. G. Schaaff, I. Vezmar, M. M. Alvarez, A. Wilkinson, *Acc. Chem. Res.* **1999**, *32*, 397.

[14] C. B. Shoemaker, D. P. Shoemaker, T. E. Hopkins, S. Yidepit, *Acta Crystallogr. B* **1978**, *34*, 3573.

[15] D. Dinega, M. G. Bawendi, *Angew Chem. Int. Ed.* **1999**, *38*, 1788.

[16] Z. L. Wang, *Mater. Characterization* **1999**, *42*, 101.