

# Self-Assembled Superlattices of Size- and Shape-Selected Nanocrystals: Interdigitative and Gear Molecular Assembling Models

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Size and shape selected nanocrystals behave as fundamental building blocks that can be used to construct nanocrystal assembled superlattices. This is a new state of materials that has orders in atomistic and nanocrystal length-scales. The nanocrystals are passivated with organic molecules (call thiolates) that not only protect them from coalescing but act as the molecular bonds for forming the superlattice structure. The interparticle distance is adjustable, possibly resulting in tunable electric, optical, and transport properties. In this article, nanocrystal superlattices (NCSs) constructed by truncated octahedral Ag particles are studied to illustrate the bundling and interdigitation of the passivation thiolates in forming the directional molecular bonds in NCSs. The  $\{111\}_s$  facets observed in the NCSs suggest the key roles played by the molecular bonding energy in forming the surfaces of NCSs. The formation of twins in the NCSs supports the "gear" assembling model of the nanocrystals. The gear assembling is likely to have higher energy than the interdigitative assembling.

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## INTRODUCTION

Nanophase and nanoparticle materials, as a component of nanotechnology in the 21st century, have attracted a great deal of attention in the technical community. The unique properties of nanophase materials are determined not only by their intrinsic atomistic-scale structure, but also by the interparticle interaction. The role played by particle size is comparable, in some cases, to the particle chemical composition, adding another flexible parameter for designing and controlling their behavior. Nanoparticles possess physical and chemical functions specificity and selectivity; thus they can be ideal building blocks for two- and three-dimensional cluster self-assembled superlattice structures, in which the particles behave as well-defined molecular matter and they are arranged with long-range translational and even orientational order.

A number of researchers have successfully fabricated *self-assembly passivated nanocrystal superlattices* (NCSs) or *nanocrystal arrays* (NCA) of metal, semiconductor, and oxide clusters [1-8], which are a new form of materials with fundamental interests and technological importance. Self-assembled arrays involve self-organization into monolayers, thin films, and superlattices of size-selected nanoclusters encapsulated in protective compact organic coating. By changing the length of the molecular chains, quantum transitions and insulator to conductor transition could be introduced, resulting in tunable electronic, optical, and transport properties [9].

Following the author's previous review on NCS [10], this article reviews our current research effort in characterizing nanocrystal self-assembled materials. The focus is on the interparticle molecular bonds and the mechanism for creating defects in NCSs. In-

terdigitative and “gear” assembling models will be shown as the two fundamental assembling configurations of the passivating molecules.

### THREE-DIMENSIONAL SELF-ASSEMBLING OF NANOCRYSTALS

NCSs are characterized by unprecedented size-uniformity and translation and even orientation order, created through a multi-stage processing strategy involving self-

assembly, annealing, etching of defects, reversible passivation by self-assembled monolayers, and macroscopic separation by size of the resulting assemblies [2, 3]. Particles that can be self-assembled usually have sizes smaller than 10nm; it is in this size range that many exciting and unusual physical properties are enhanced. The nanocrystals are passivated by a monolayer of long-chain organic molecules, such as SR, where  $R = n-C_nH_{2n+1}$ ,  $n = 4, 6, 8, 12 \dots$ , called thiolates. The thiolate serves not only as the protection for the particles to avoid direct

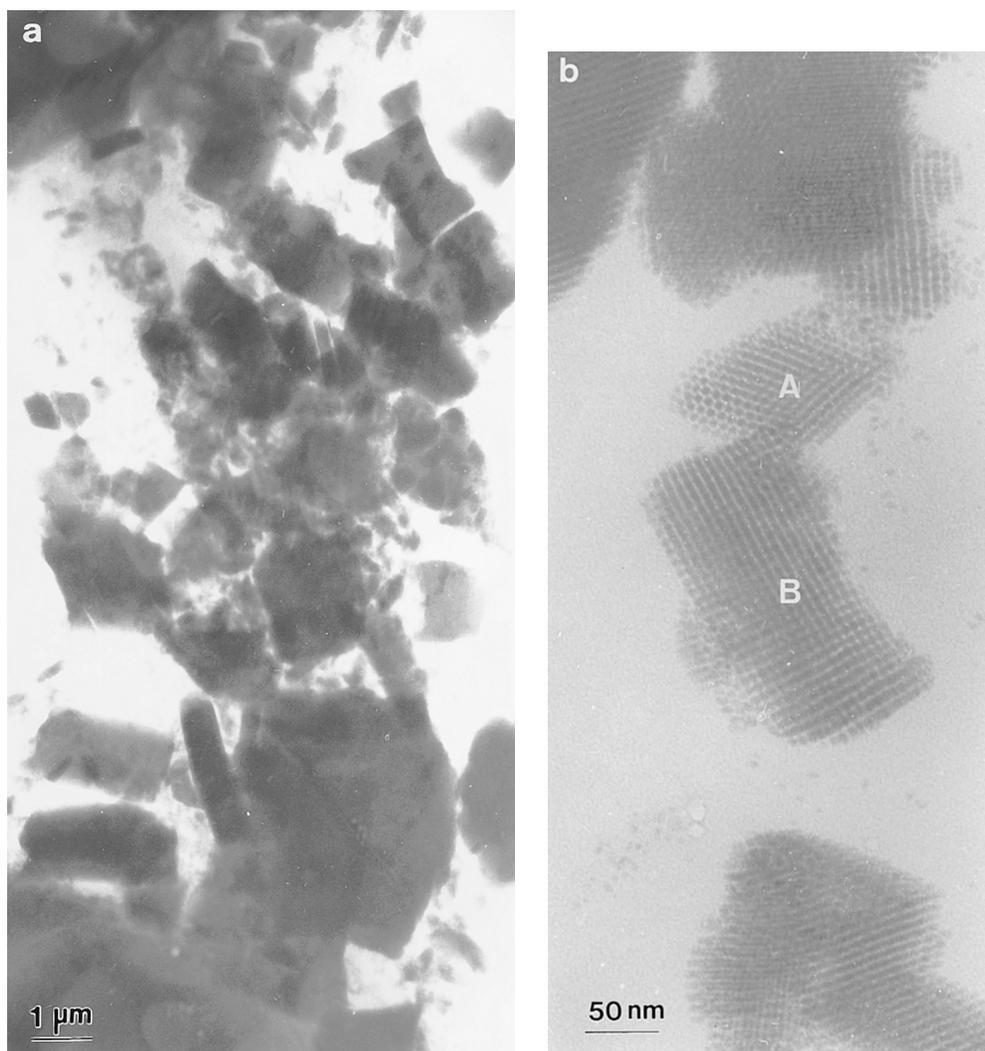


FIG. 1. (a) Low magnification and (b) high magnification TEM images of three-dimensional superlattices assembled by Ag nanocrystals. The NCSs have a *fcc* lattice. The nanocrystals were synthesized by an aerosol method [3].

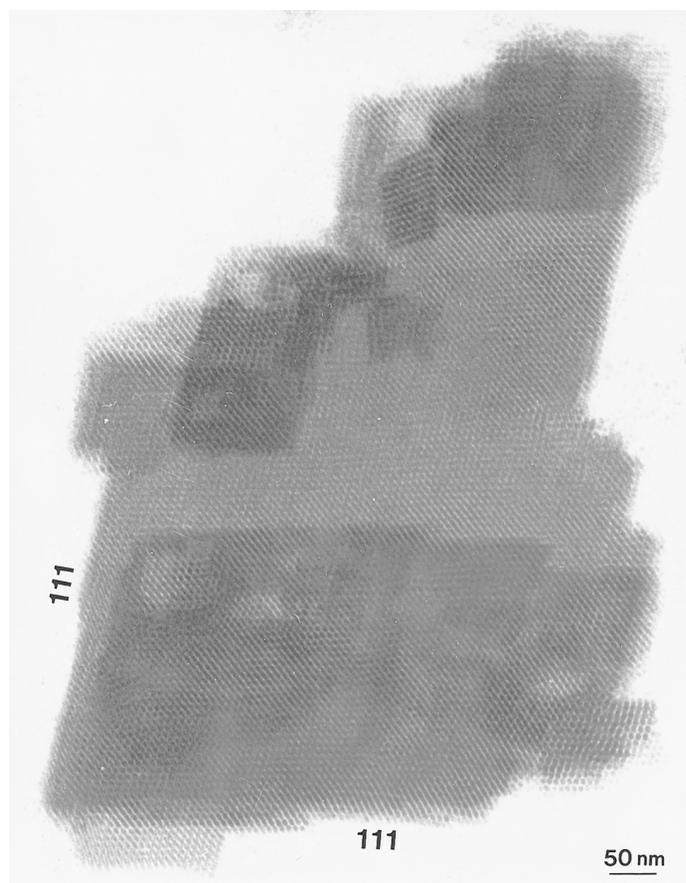


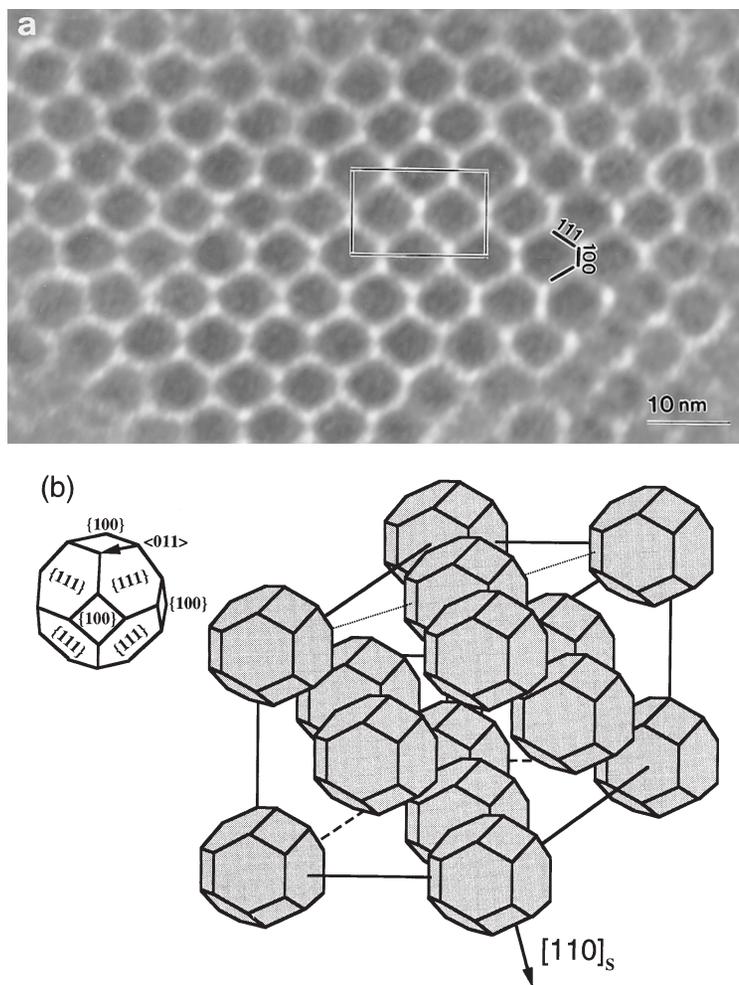
FIG. 2. TEM image of  $\{111\}_s$  faceted nanocrystal superlattices assembled by Ag nanocrystals. The NCS is oriented along  $[110]_s$ , the preferred orientation of this type of NCSs.

contact between the particles with a consequence of coalescing, but also provides a means for interparticle bonding.

Three-dimensional assembling of nanocrystals can form large size bulk crystalline materials. Shown in Fig. 1a is a TEM image of powder NCSs, whose sizes can be larger than  $5\text{--}10\mu\text{m}$ . A high magnification image of the NCSs (Fig. 1b) reveals the array lattices formed by the nanocrystals, where each dark dot is a row of nanocrystals. The crystallography of the nanocrystal assembly can be directly determined by the image, where the crystal A is oriented along the  $[110]_s$  of the face-centered cubic (*fcc*) [the subscript *s* stands for the superstructure of the NCS], and the crystal B is oriented along  $[100]_s$  of the *fcc*. The 3-D structure of the NCS is *fcc*. It is also noticed that

the NCSs have faceted shape and the preferred faces are  $\{111\}_s$  and  $\{100\}_s$ .

The faceted structure of the NCSs is clearly shown in the image given in Fig. 2, in which the  $\{111\}_s$  faces of this *fcc* structured Ag NCS are unambiguously presented. It is well known that the  $\{111\}$  faces in *fcc* are the most densely packed plane, resulting in the lowest surface energy. This atomistic scale structural principle also holds in nanocrystal assembling, showing the strong intermolecular interaction (via van der Waals force) among the surface passivated molecules as well as between the nanocrystals. Therefore, the nanocrystals actually behave like molecular matter and their assembling is not only a geometrical matching (see the next section), but also a bonding energy governed structure.



**FIG. 3.** (a)  $[110]_s$  TEM image of a 3-D  $fcc$  assembled Ag nanocrystal superlattice. The nanocrystals are truncated octahedra and they have orientational symmetry. (b) The 3-D  $fcc$  self-assembling model of the NCS (the specimen was provided by Drs. S. A. Harfenist and R. L. Whetten).

### INTERDIGITATION OF MOLECULAR BONDS IN NANOCRYSTAL SELF-ASSEMBLING

If the nanocrystals can be taken as the building blocks, their 3-D assembling is unavoidably affected by the particle shape. In this section, the self-assembling of truncated octahedral Ag nanocrystals is taken as an example to illustrate the roles played by the particle shape in NCSs [2, 10]. Our main goal is to illustrate the formation of directional, interparticle molecular bonds by the thiolates.

Figure 3a is a TEM image recorded from an Ag NCS deposited on a carbon sub-

strate. The Ag nanocrystals have a truncated octahedral shape and they are oriented along the  $[110]$  of the Ag atomic lattice in the image, along which four  $\{111\}$  and two  $\{100\}$  facets are imaged edge-on. The unit cell of the NCS is also oriented along  $[110]_s$  of  $fcc$ . Therefore, the orientation relationship between the Ag particles and the nanocrystal lattice is  $[110] \parallel [110]_s$  and  $[001] \parallel [110]_s$ . Accordingly, a structure model for the NCS is built (Fig. 3b) in which the nanocrystals are oriented following an assembling principle of *face-to-face* [10]. The orientational order is observed for the first time in this NCS system.

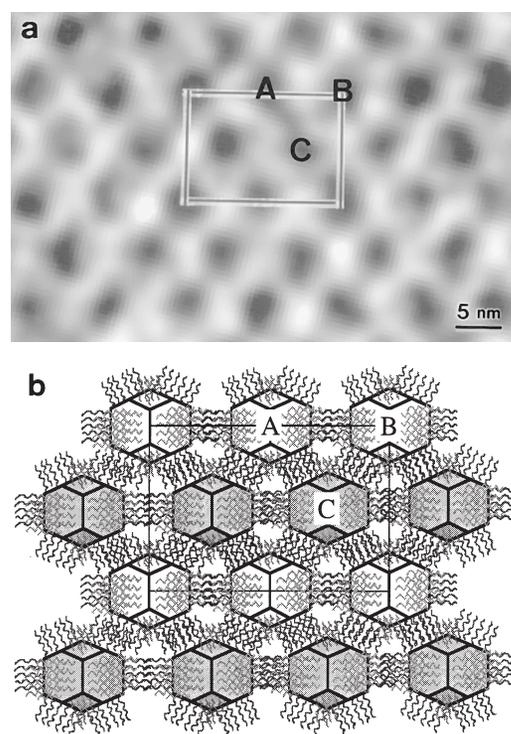
A careful examination of the image

shown in Fig. 3a indicates there are some white spots in the image, corresponding to open channels formed by the thiolate molecules. This suggests that the thiolates are tethered on the faces of the nanocrystals and they are likely to be erected on the surface. The shortest distance between the face-to-face {100} facets of the two adjacent particles is only 1.5–2 nm, almost equal to the 1.5 nm chain length of the thiolate molecules used for passivating the Ag nanocrystals. Therefore, the thiolate molecules tethered on the facets of the nanocrystals are likely to interpenetrate, forming the *interdigitative bonds*. This model is supported by the image contrast displayed in Fig. 3a. A direct observation of the thiolates can be provided by the energy-filtered TEM (EF-TEM) [11].

The EF-TEM relies on the principle of electron energy-loss spectroscopy (EELS) and the images (or diffraction patterns) are formed by electrons with specific energy-losses [12]. If the electrons which have excited the carbon K ionization edge are selected for forming the image, the image contrast is approximately proportional to the thickness projected carbon atoms in the specimen, providing a direct chemical map of carbon. The thiolate molecules are composed of mainly carbon, thus the EF-TEM of the carbon K edge can give the distribution of the thiolates around the nanocrystals. For this analysis, Ag NCSs are deposited on an amorphous  $\text{SiO}_x$  substrate and the effects from the substrate can be removed by processing the experimental images acquired pre- and post-edge.

The EF-TEM was performed for the Ag NCS oriented along  $[110]_s$ , which is the optimum orientation for imaging thiolate distribution between the particles. The EF-TEM image acquired using the carbon K edge from a Ag NCS gives an interesting contrast feature (Fig. 4a). The projected carbon density between the particles shows a contrast pattern that is the strongest between the A and B types of particles, while the contrast is lower between the A and C or B and C types of particles. To interpret this phenomenon, we first construct the

$[110]_s$  projection of the NCS based on the 3-D model given in Fig. 3b, and the result is shown in Fig. 4b. From the structural point of view, the molecular bonds tend to parallelly align the facets on which they are tethered. For the nanocrystals A and B assembled by facing the  $[100]$  faces, in addition to the carbon density contributed by the interdigitated thiolates passivated on the  $[100]$  facets (which are edge-on while viewed along  $[110]_s$ ), the thiolates passivated on the four  $[111]$  planes (not edge-on) also contribute to the projected carbon density although the  $[111]$  faces are at an angle with the projection direction. Therefore, the projected density of the thiolate molecules between particles A and B is expected to be higher than that between A and C (or B and



**FIG. 4.** (a) Energy filtered TEM image of the *fcc* structured Ag NCS recorded using the electrons after exciting the carbon K ionization edge, showing the distribution of the thiolates molecules around the nanocrystals. The orientation of the NCS is  $[110]_s$  and the 3-D self-assembling model is given in Fig. 3b. (b) A model of thiolate distribution on the surfaces of Ag nanocrystals, which supports the interdigitative molecular bonding in the NCS.

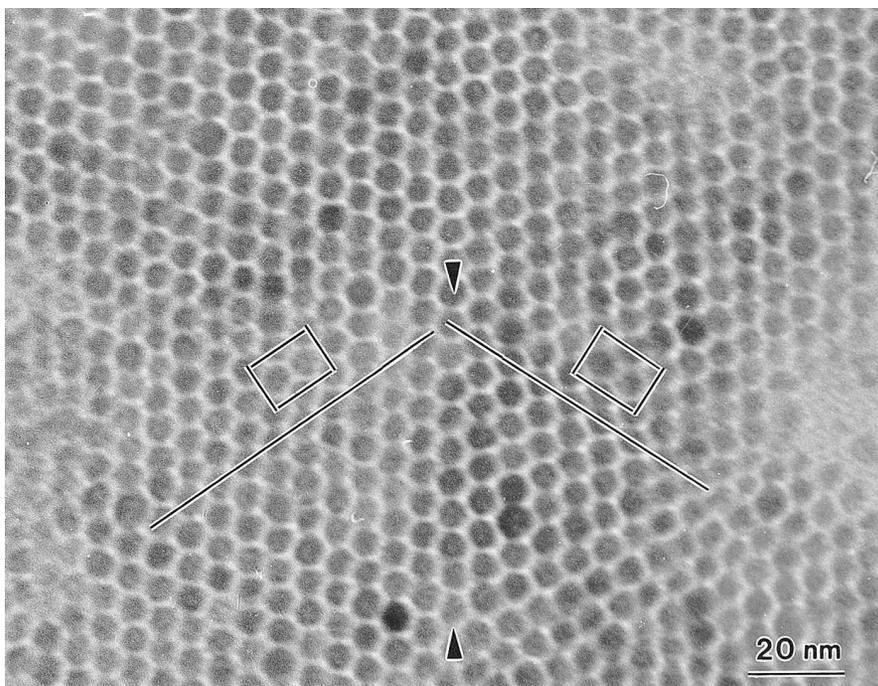


FIG. 5. TEM image of an *fcc* Ag NCS with twinned structure, where the unit cells are indicated on both sides of the twin plane. There is a slight glide parallel to the twin plane.

C) if the size of  $\{111\}$  faces is the same as the fact of  $\{100\}$  as well as the density of the thiolate passivation is the same on both  $\{111\}$  and  $\{100\}$ . Considering that the resolution of the EF-TEM is on the order of  $\sim 2\text{nm}$ , the channels formed by the bundled thiolates may not be resolved in this type of images.

#### THE “GEAR” MODEL OF NANOCRYSTAL SELF-ASSEMBLY AND TWIN STRUCTURE

As reported previously, NCS has many aspects analogous to the atomic level structure, and it can have a variety of defect structures [10]. One of the common defects is a twin (Fig. 5). In this *fcc* structured NCS of Ag nanocrystals dominated by truncated octahedra, the twin and stacking planes are  $\{111\}_s$ , as indicated by arrowheads. To understand this structure, two principles need to be observed in reference to the theoretical calculation of Luedtke and Landman [13]. First, from the geometrical point of view, the NCSs are assembled by aligning the nanocrystals *face-to-face*. Thus, the  $\{111\}$

facets can be interconnected naturally with either the  $\{111\}$  facets of the  $\{100\}$  facets, the latter, if possible, results in a rotation of the superlattice, possibly leading to the formation of a  $\{111\}_s$  twin. Secondly, the thiolates are bundled on the facets of the Ag nanocrystals, the assembling of the nanocrystals can be achieved by a “gear” model, in which the bundled thiolates are the “teeth” of the gear and the two nanocrystals are assembled simply by filling the space, resulting in a rotation in the particle orientation. This type of assembling is simply a geometrical matching between the nanocrystals, while the van der Waals molecular interaction dominates the bundling of the thiolates belonging to the same particle. The twin model is thus given in Fig. 6, in which the two  $\{111\}_s$  planes of the NCSs forming the twin has an angle of  $109.4^\circ$ , in agreement with the experimental image (Fig. 5), while the  $\{111\}$  faces of the nanocrystals on the left hand side is not exactly parallel to the  $\{100\}$  faces of those on the right-hand side. This again suggests the erected bundling of the thiolates on the nanocrystal surfaces.

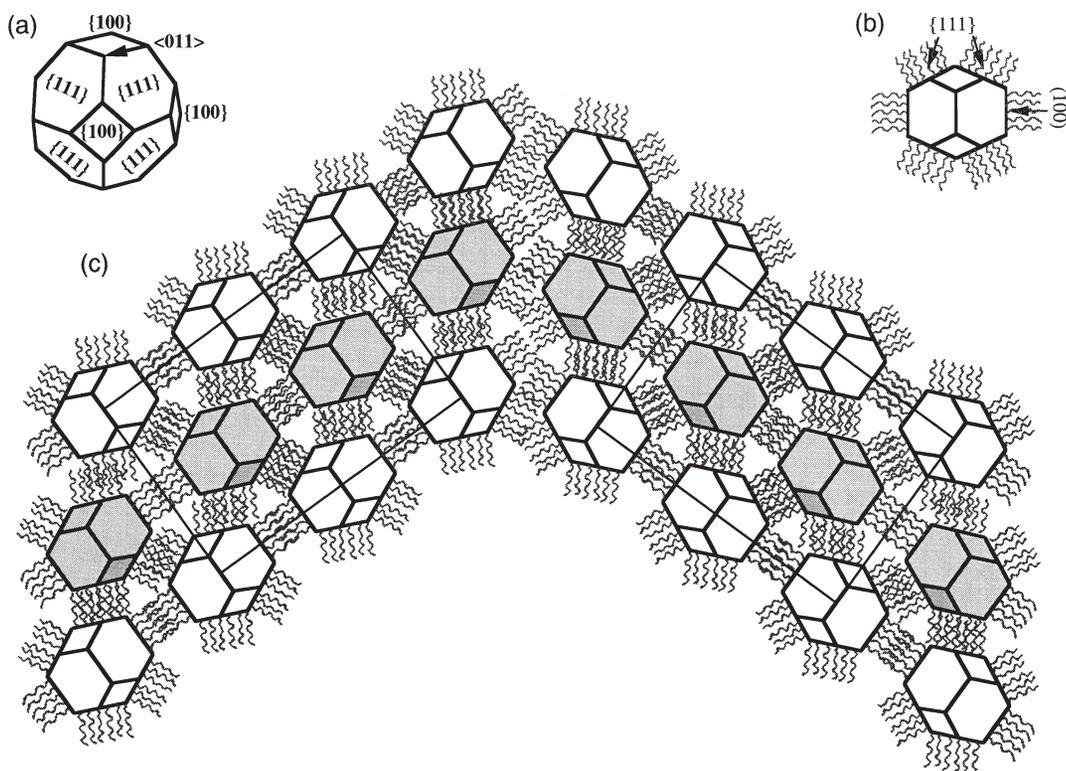


FIG. 6. (a-c) A "gear" assembling model of the bundled thiulates for forming the twin structure in NCS.

### SELF-ASSEMBLING OF MAGNETIC NANOCRYSTALS

Patterned magnetic nanocrystals are of vital interest both scientifically and technologically because of their potential applications in information storage, color imaging, bioprocessing, magnetic refrigeration, and ferrofluids. In ultra-compact information storage, for example, the size of the domain determines the limit of storage density while the sharpness of the domain boundaries is closely related to the media noise. This issue is critically important in the 300 Gbit/in<sup>2</sup> information storage predicted for the 21st century [14]. The noise reduction can be achieved by the segregation of a non-magnetic phase at the grain boundaries, thus the media are composed of at least two materials. The self-assembly passivated nanocrystal superlattice is a potential candidate for solving this problem, in which the passivated surfactant serves not only as an isolation layer but also as a pro-

tection layer for the nano-magnets. Shown below is an example of self-assembling of CoO tetrahedral nanocrystals.

Cobalt oxide nanocrystals were synthesized by chemical decomposition of  $\text{Co}_2(\text{CO})_8$  in toluene under oxygen atmosphere. Sodium bis(2-ethylhexyl) sulfosuccinate ( $\text{C}_{20}\text{H}_{37}\text{O}_2\text{SNa}$ , in short, Na(AOT)) was added as a surface active agent, forming an ordered monolayer passivation (called the thiolate) over the nanocrystal surface. The particle size was controlled by adjusting the wt.% ratio between the precursor and Na(AOT). The as-prepared solution contained Co and CoO nanoparticles, and pure CoO nanoparticles were separated using a technique reported by Yin and Wang [8, 15].

Figure 7 shows a bright-field TEM image of the as-formed NCAs on an amorphous carbon film, in which the well-ordered nanocrystal arrays are seen with translational order. It is striking that all of the nanocrystals shown here have a narrow size distribution. The particles are in the size range of

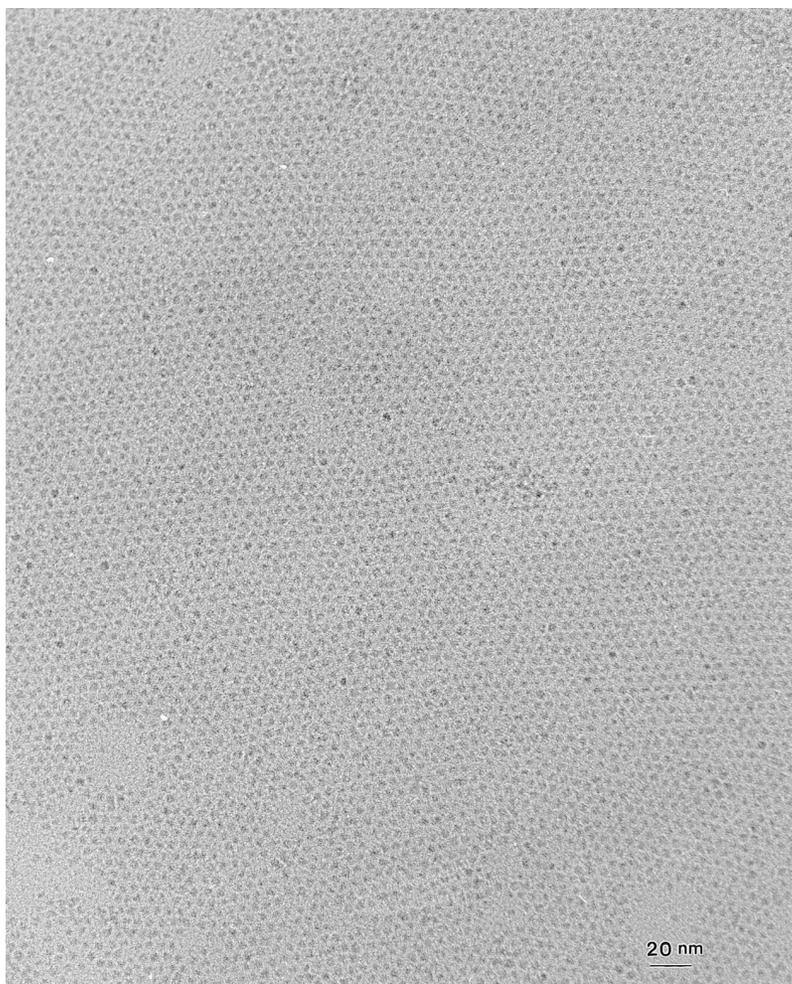


FIG. 7 TEM image showing the self-assembled monolayer of tetrahedral CoO nanocrystals (specimen provided by Dr. J. S. Yin).

4–5 nm. The nanocrystal structure has been identified as CoO with the NaCl structure [8]. More importantly, the particle shapes are dominated by tetrahedra. This is the first example of illustrating the ordered self-assembling of tetrahedral nanocrystals. Recently tetrahedra Ag nanocrystals have also been prepared and their assembling has been studied [16].

The strength of the chain molecule is in the order of 0.1 eV, comparable to the kinetic energy of atom thermal vibration. A key question here is about the stability and the phase transformation behavior of the weakly bonded NCA since the melting point of nanoparticles is much lower than that of the bulk. Considering the even

lower melting point of the passivating organic molecules, the stability of the superlattices (not only the structure of nanocrystals but also the “crystallinity” of the superlattice) above ambient temperature is a serious concern because the NCS is likely to be used in the areas such as microelectronics and data storage. The in-situ behavior of monolayer self-assembled NCAs of cobalt oxide nanoparticles has been observed using TEM [17]. The results proved the high stability of a monolayer assembling to temperatures as high as 600°C, while the multilayer assembly coalesced at 250°C. The substrate exhibited strong adhesive effect on the stability of the nanocrystals, but reaction between nanocrystals and

the carbon substrate occurred at temperatures  $\sim 400^\circ\text{C}$ .

## CONCLUSION

In this article, nanocrystal superlattices (NCSs) constructed by truncated octahedral Ag particles are studied to illustrate the bundling and interdigitation of the passivation thiolates in forming the directional molecular bonds in NCSs. The thiolates are bundled and tethered on the faces of the nanocrystals, and tend to align the nanocrystal face-to-face in forming the NCSs. This configuration is favorable geometrically and energetically. The  $\{111\}_s$  facets observed in the NCSs show the key role played by the molecular bonding energy in forming the surface of NCSs. This result suggests that the intermolecular interaction energy is likely to be much higher than the phonon energy ( $\sim 0.1$  eV). The formation of twins in the NCSs supports the "gear" assembling model of the nanocrystals. The gear assembling is likely to have higher energy than the interdigitative assembling. The NCSs of truncated octahedral Ag particles is an ideal system for observing these models.

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