

Self-assembly PbSe Nanoparticles into Nanorings

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ABSTRACT

In this presentation, we report the self-assembly of monolayer and multilayer nanorings of PbSe nanoparticles. PbSe nanoparticles were synthesized by using a high temperature precipitation method. The nanoparticles are about 5 nm and appeared as truncated octahedral enclosed by the {100} and {111} crystal facets of fcc structure. The large area monodisperse self-assembly nanoarrays were obtained by dropping the high concentration solution of PbSe nanoparticles on the carbon grid. The nanoparticles are hexagonal close packed and oriented randomly in the nanoarrays. By diluting the solution for large area self-assembly, self-assembly of monolayer and multilayer nanorings can be achieved. The nanoring formation is determined by hydrodynamics, surface effects, and interaction between the nanoparticles and carbon grid.

INTRODUCTION

PbSe is one of the promising materials for the thermoelectric cooling and power generating device [1]. Its nanoparticles can potentially improve the thermoelectric properties by increasing the Seebeck coefficient due to the altered electronic density of states, or making use of compositionally modulated materials that would block phonons while transmitting electrons [2-4]. Nanometer-scale rings formed from assemblies of colloidal particles and individual molecules are potentially useful superstructures [5,6]. The foreseen application in nanoelectronics and nanodevices drives us to study ring-like superstructure formation for functional nanoparticles [6,7]. In this paper, we present a successful synthesis of monodisperse PbSe nanocrystals and their self-assembly into monolayer and multilayer nanorings.

EXPERIMENTAL

The colloidal PbSe nanocrystals were synthesized using a high temperature co-precipitation approach in an organic solution [8-10]. Typically, lead acetate (Aldrich, 99.99%) was dissolved in diphenyl ether (Aldrich, 99+%) along with oleic acid (Aldrich, 90%) as a stabilizing agent. The mixture was heated up to 180°C under flowing argon gas with constant stirring. Then trioctylphosphine (TOP) (Aldrich, 90%) with pre-dissolved Se metal (Aldrich, 99.999%) (1M) was injected in using a syringe, and the system was maintained at 180°C for 10 minutes under an argon atmosphere. The resulting PbSe

colloids were then cooled down to room temperature and subsequently precipitated by adding a polar alcohol solvent, e.g. ethanol, and centrifugation. The nanocrystals were re-dispersed in a proper non-polar solvent such as octane. The particle size of PbSe ranged from ~5 nm to 10 nm. To further narrow the size distribution, a size-selection treatment was performed using the solvent-nonsolvent pair of octane and octanol [10]. The resulting monodisperse PbSe suspension (95wt% octane + 5wt% octanol) was then further diluted and dropped onto a carbon grid for self-assembling nanorings. Transmission electron microscopy (TEM) observation was performed on JEOL 2010 equipped with energy dispersive spectrometry (EDS).

RESULTS AND DISCUSSION

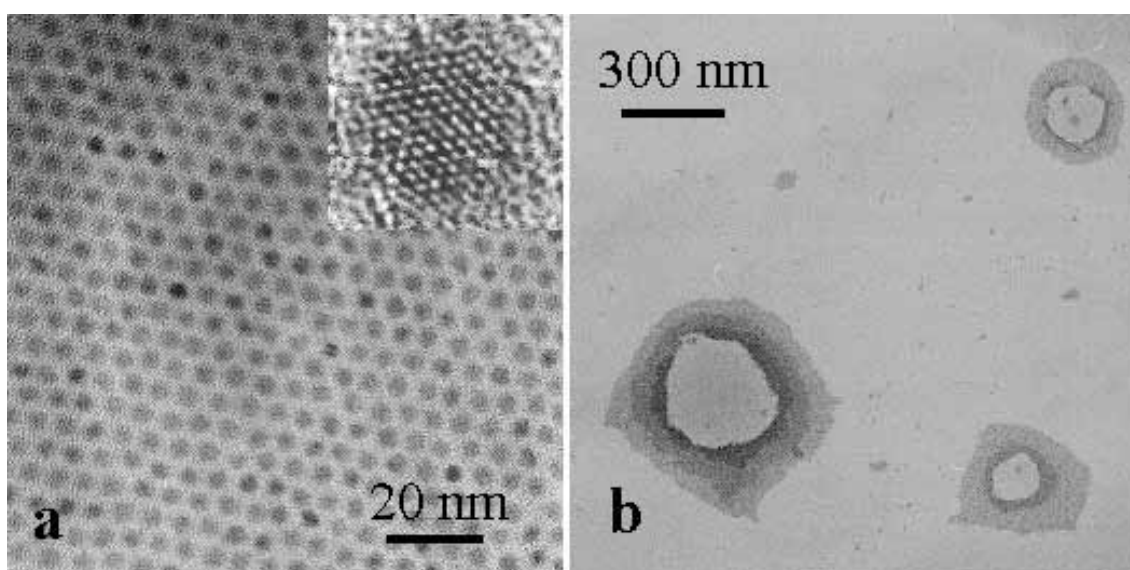


Figure 1. TEM images of (a) monodisperse PbSe nanocrystals and (b) nanorings of PbSe nanocrystals with different sizes. The inset is a HREM image of $\langle 110 \rangle$ oriented nanocrystal.

After the size selection, monodisperse PbSe nanocrystals can be seen by dropping the solution on the carbon grid as shown in Fig.1(a), in which PbSe nanocrystals have hexagonal close packing. The size of the nanocrystals is about 5 nm. By high resolution electron microscopy (HREM) investigation, most PbSe nanocrystals are typical truncated octahedral nanoparticles as shown in the inset of Fig.1(a). The $\{111\}$ and $\{100\}$ facets can be clearly seen from $\langle 110 \rangle$ HREM image of the PbSe nanocrystal. The nanorings can be obtained by placing one droplet of diluted colloidal suspension of monodisperse PbSe nanocrystals on a carbon grids. Fig.1(b) is a low magnification TEM micrograph showing nanorings with different sizes of PbSe nanocrystals. The diameters of nanorings ranged from several ten nanometers to several hundred nanometers. Few nanocrystals exist inside and outside the ring compared to the micron sized rings.

Fig.2(a) shows a monolayer nanoring of PbSe nanocrystals. The diameter of the ring is about 120 nm and the thickness of the annular wall is about 40 nm. The

nanocrystals still pack in order in the nanoring. Fig.2(b) is a submonolayer nanoring of PbSe nanocrystals. The diameter of the nanoring is about 300 nm and the annular thickness of the wall is about 100 nm. Some nanocrystals of the second layer occupy the 2-fold saddle and 3-fold hollow sites of the first layer array and form a superlattice and ring structure packing towards the inner rim of the ring [11].

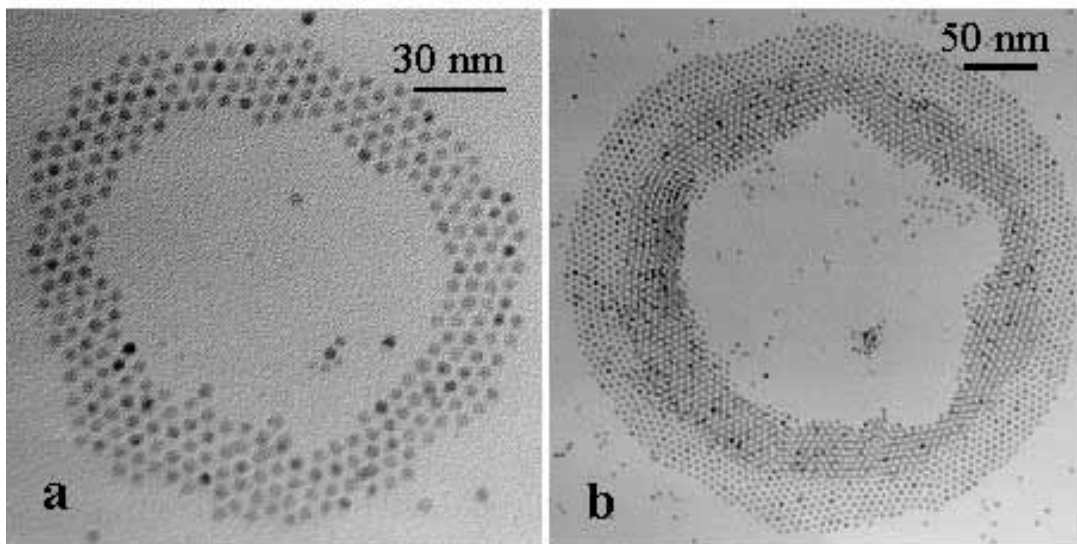


Figure 2. TEM images of (a) monolayer nanoring and (b) sub-monolayer nanoring of PbSe nanocrystals.

Multilayer nanorings were first achieved as shown in Fig.3(a). The size of the nanoring is about 200 nm and the wall of the ring is about 80 nm. The first three layers are clearly identified by arrows 1, 2, and 3. The nanoring becomes darker towards the inner rim, which implies that a multilayer packing ring was formed. Fig.3(b) shows a ring with a size of two micrometers containing two small nanorings inside and one nanoring outside. Note that all nanorings tangentially contact with the big ring and there are few nanocrystals spreading inside the nanorings compared to the micron sized ring.

The formation of rings is the result of a complex process determined by hydrodynamics, surface effects, and interaction between nanocrystals and substrates [5,12]. We deduced that when the PbSe nanocrystal solution was dropped on the carbon grid, the liquid thin film was formed. As the liquid thin film thickness reached critical value, holes opened in order to restore the film to its equilibrium thickness. The holes nucleated and grew bigger due to evaporation-driven instability [5]. The advance of the growing hole rims in the solvent film stopped when the radial force outwards was no longer sufficient to overcome the frictional effects of the nanocrystals which had been collected in the rim. For multilayer nanorings, the local concentration of the solvent caused the nanocrystals to pack as three dimensional arrays. As the hole grew bigger, the radial force pushed the multilayer arrays outwards and formed multilayer ring packing. Most of the nanorings formed individually and separately in our experiment, however, micron size rings were sometimes observed containing nanorings as shown in Fig.3(b).

We deduced that the driving radial force for the advancing rim of liquid thin film for nanorings is bigger than that of micron sized rings, which pushed most nanocrystals to the rims of nanorings. This is the reason that we see less nanocrystals inside nanorings

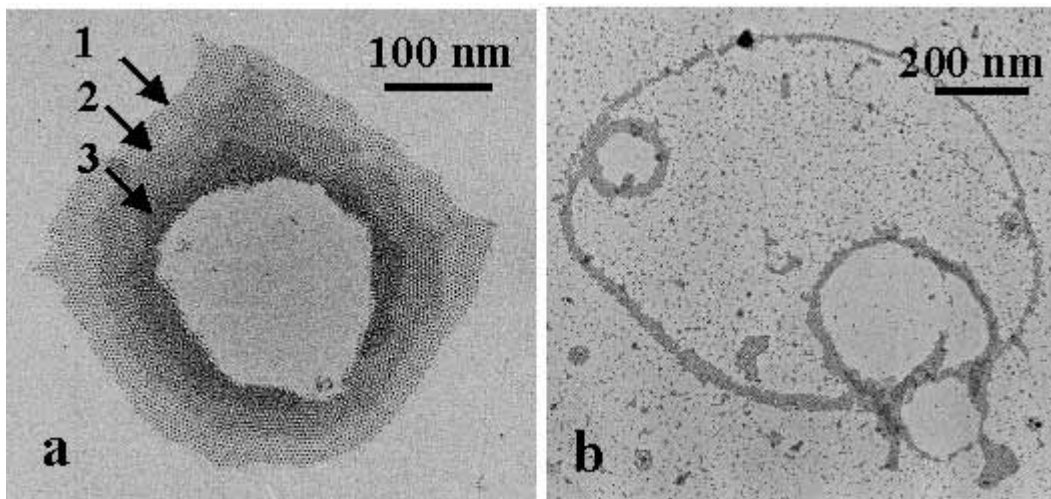


Figure 3. TEM images of (a) multilayer nanoring self-assembly and (b) rings with tangent contacts.

than micron sized rings. As the rims of nanorings contacted with the micron sized rings, they were stopped by the wall of the micron sized ring and formed tangent contacts.

Below is the lateral friction and outward thickening forces [5]:

$$F=2\pi r^2 S[(t_e t_{hole})^2-1] \Phi R_{pin} K$$

r is particle size and S is spreading coefficient. Φ is concentration of solution, t_e is equilibrium thickness, t_{hole} is thickness of forming nanoholes, R_{pin} is ring size, and K is friction coefficient. For a specific particle size r , solvent and substrate (for a fixed set of value for S , t_e and t_{hole}), the ring size R_{pin} from the equation is expected to vary inversely with concentration Φ . Furthermore, the ring size can be tuned up by controlling the concentration.

CONCLUSIONS

Truncated octahedral PbSe nanocrystals enclosed by the {100} and {111} crystal facets of fcc structure were synthesized using a high temperature precipitation approach in an organic solution. The large area monodisperse self-assembly nanoarrays were obtained by dropping the high concentration solution of PbSe nanoparticles on the carbon grid. The nanoparticles are hexagonal close packed and oriented randomly in the nanoarrays. By controlling the concentration of nanoparticles, self-assembly of monolayer and multilayer nanorings can be achieved. The nanoring formation is determined by hydrodynamics, surface effects, and interaction between the nanoparticles

and carbon grid. Nanoring formation is an interesting self-assembly phenomenon and has a potential for future fabrication of nanodevices.

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