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Supercrystal structures of polyhedral PbS nanocrystals

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ABSTRACT

The construction of supercrystals with non-spherical building blocks has attracted increasing attention due to their potential applications in the fabrication of novel devices. In this study, we report the large-scale preparation of dimension-controllable supercrystals of polyhedral PbS nanocrystals through a solvent-evaporation approach. Because of the capillary flow of the drying droplet on the substrate, nanocrystals self-assemble into three distinct types of supercrystals on specific regions of the substrate during the solvent evaporation: two-dimensional supercrystals appear in the central region; three-dimensional faceted supercrystals and three-dimensional bulk supercrystals are found near the edge of the substrate. Moreover, the formation of superlattice structure of each type of supercrystals can be tuned by changing the shape of building blocks. The influences of experimental factors on self-assembly are investigated as well. We anticipate that our research can provide some new insights into the construction of supercrystals with novel structures and large sizes.

1. Introduction

Self-assembly is an important “bottom up” method to fabricate new materials with attractive properties. During the last decade, the self-assembly of colloidal microspheres have been studied intensely in order to fabricate photonic crystals which have unique ability to control the propagation and spontaneous emission of electromagnetic waves[1,2]. In addition, since Murray et al. found that CdSe nanocrystals (NCs) could self-assemble into three-dimensional (3D) supercrystals (SCs) in 1995 [3], the construction of ordered assembly of NCs has attracted intensive interests due to their novel collective properties and potential applications in the field of device fabrication at a practical scale [4,5]. More often than not, the building blocks of these photonic crystals and supercrystals have a spherical shape, and either hexagonal close-packing (hcp) or face-centered cubic close-packing (fcp) is generated, limiting the diversity of the assembly structure.

Recently, with the advancement of synthetical techniques to control the size and shape of NC [6,7], SCs with abundant lattice structures have been developed, using NCs with various shapes and sizes of tens of nanometers, including Au nanorods [8], faceted pentagonal silver nanorods [9], and copper sulfide nanodisks [10], etc. Among all the candidates for building SCs, regular polyhedrons have attracted much attention for their facility to self-assemble into ordered structures, benefiting from their similar shape with spheres, while the anisotropy of the shape provides enormous possibilities to generate SCs with various lattice structures. Recently, ordered superlattices of faceted magnetic NCs [11] and gold NCs [12,13] were generated from shape-segregated self-assemblies, and two-dimensional (2D) superlattices of cuboctahedral and octahedral Ag NCs were obtained using the Langmuir–Blodgett technique [14]. Simple cubic SCs of PbTe [15] and Pd [16] nanocubes were fabricated, respectively. By using octahedra as building blocks, various SCs were observed upon solvent evaporation in the case of In_2O_3 [17], Au [18], and Fe_3O_4 [19] NCs. Long-range ordered 3D close-packed Ag SCs were obtained by controlling the volume of starting materials [20], and 3D SCs of octahedral MnO were crystallized in a oversaturated solution method [21]. In addition, Wang et al. observed the self-assembly of PbS truncated octahedron crystals in the synthesized process in the solution [22]. However, SCs with large sizes and specific dimensionalities are still need to be developed for further application. Moreover, investigation is still needed to further explore the relationship between the physical characters (such as size and shape) of the building blocks and the corresponding assembly structures.

The self-assembly of NC driven by solvent evaporation is often influenced by the flow of the solvent. As have been reported by Deegan et al. [23], when a drop of dispersion is cast onto the substrate with a non-zero contact angle, the contact line of the drying drop is pinned to its initial position. Since the liquid starts to evaporate from the edge, evaporative loss will be replenished by liquid from the interior, and the outward flow will carry the dispersed solids to the edge. As a result, the distribution of solids gets higher from the central region of the substrate to the edge. Then, since the drop has a tendency to maintain a constant shape which is determined by the Young’s condition, the drop will shrink and leave a ring named “coffee ring” on the edge of the substrate. Recently,

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the phenomenon of capillary flow has been employed to construct novel structures in several cases [8,24,25], which also inspires us to construct SCs with various structures by controlling the solvent evaporation process.

In this paper, we observed the formation of 2D and 3D SCs of PbS polyhedrons on silicon substrates. Because of the capillary flow of a drying drop, SCs with different dimensionalities and superlattice structures emerged on specific regions of the substrate. The general observation was as follows: 2D SCs appeared in the central region and formed by the self-assembly of polyhedral PbS NCs with the inducement of the substrate; 3D SCs were found in the edge region in the form of polygonal colloidal crystals and coffee ring. Stacking modes of the SCs were discussed in detail based on scanning electron microscope (SEM) measurements. We found that the structure of SCs was greatly affected by the shape rather than size of the building block. Influence factors which are responsible for the formation of SCs were also discussed.

2. Materials and methods

2.1. Synthesis of PbS NCs

The synthesis and characterization of PbS NCs have been reported in our previous work [26]. In a typical synthesis of PbS octahedra, 1 mL of thioacetamide (TAA) solution (0.5 M) was added into 21 mL of the aqueous mixture of hexadecyl trimethyl ammonium bromide (CTAB), acetic acid (HAc) and $Pb(Ac)_2$ at room temperature, and the final concentrations of CTAB, HAc, $Pb(Ac)_2$ and TAA were 5.7 mM, 91.0 mM, 22.7 mM and 22.7 mM, respectively. Then the mixture was heated to 80 °C for 24 h. The uniformity and purity of the NCs were improved by density gradient centrifugation, and then the sediments were redispersed into a CTAB solution with a specific concentration. The final concentration of the NCs in the dispersion was about 2.1 nM (the detailed calculation of NC concentration is presented in the supporting information). Octahedra with smaller size and truncated octahedra were obtained by increasing the concentration of TAA to 31.3 mM and 62.5 mM, respectively.

2.2. Self-assembly of PbS NCs

Suspensions of highly monodisperse PbS NCs in CTAB solutions with specific concentrations were used as building blocks and silicon wafers were used as substrates of the self-assemblies of PbS NCs. The Si wafers were pretreated with H_2O_2 and H_2SO_4 in order to generate a hydrophilic surface. In a typical self-assembly process, a piece of Si wafer with the size of 1 cm × 1 cm was placed on the bottom of a little vial, then a drop of PbS suspension with a volume of 70 μL was introduced onto the top of the Si wafer. The PbS NCs were then precipitated and assembled while the water was evaporated at various rates. In the typical process, a cap was placed on the top of the vial, and water evaporated through the apertures between the vial and the cap. This would take a relatively long period and the assembly would not be finished in less than 24 h. To investigate the influence of solvent evaporation rate, two other processes were carried out as well: remove the cap, and let the solvent evaporate naturally at the room temperature or at 40 °C. The former process would finish in 5–6 h and the latter in about 1 h.

2.3. Characterization of PbS NCs and assemblies

The morphologies of the SCs were measured by the SEM. Images were obtained with a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) with a primary electron energy of 3 kV, and the samples were sputtered with a thin layer of Pt (with a thickness of about 5 nm) in advance to improve the conductivity. The crystalline structures of PbS NCs and SCs were detected using a Siemens D5005 X-ray diffractometer (XRD). Inductively Coupled Plasma (ICP) was carried out with Perkin Elmer Optimal 3300 DV analyzer to determine the concentration of the suspension. Size and size distribution measurements of the NCs were performed by dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern Instrument Ltd.).

3. Results and discussion

3.1. General view of SCs on the substrate

In our experiment, one drop (typically 70 μL) of PbS dispersion was cast onto a 1 cm × 1 cm silicon wafer and then slowly dried in a controlled way. The NC concentration in the dispersion is 2.1 nM

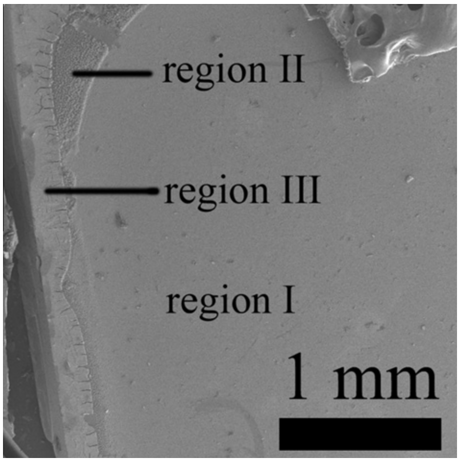

Fig. 2. Low-magnification SEM image of SCs on a corner of 1 cm × 1 cm silicon wafer. Region I–III are marked on the image.

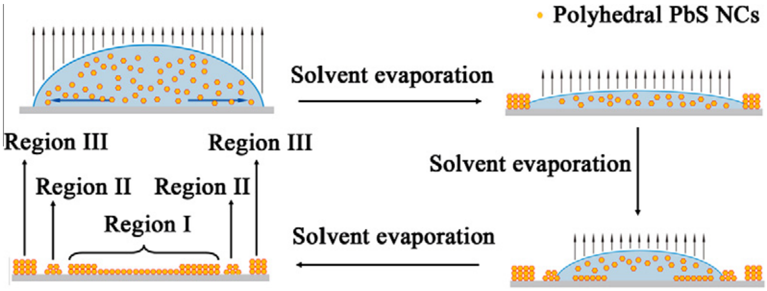

Fig. 1. Schematic illustration of the formation process of supercrystal on the substrate.