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Self-Organization of PbS into Quantum Dots Superlattices

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Abstract: Self-organization of PbS into quantum dots superlattices is demonstrated for the first time, and hexaplanar colloidal crystals 1-10μm in size made from PbS quantum dots 4nm in diameter are shown in Transmission Electron Microscope (TEM) micrograph, and the inner structures of the superlattices can be seen from the High Resolution Transmission Electron Microscope (HRTEM).

Keywords: Self-organization, quantum dots, PbS superlattices.

Ordered colloids or "colloidal crystals", which have long-range spatial order, have been investigated extensively, and still remain an active area of research[1]. Self-organization is a general phenomenon of colloidal dispersions where control over particle size and stabilization has been achieved. Self-organization requires only a hard-sphere repulsion, a controlled size distribution, the inherent Van der Waals attraction between particles, and a means of gently destabilizing the dispersion. The inherent tendency for monodisperse lyophobic colloids to self-organize provides a general route to new nanostructured materials. Size-selected nanocrystals behave like molecular matter that functions as ideal building blocks for two- and three-dimensional cluster self-organized superlattice structures. Well-defined ordered solids prepared from tailored nanocrystalline building blocks provide opportunities for optimizing properties of materials and offer possibilities for observing interesting and potentially useful new collective physical phenomena. This system contains ordering on two different length scales atomic level and nanocrystal-organization level; thus macroscopic properties of the nanocrystal superlattice is determined not only by the properties of each individual particle but also by the interaction among nanocrystals interconnected and isolated by a monolayer of thin organic molecules. Moreover, the length of the adsorbed molecules is a controllable parameter, rendering the ratio of particle size to interparticle distance adjustable[2], possibly resulting in novel tunable structural, optical[3], and transport properties[4,5,6]. PbS is a narrow band gap semiconductor that has a very large Bohr exciton radius about 18 nm. And it is believed that PbS is one of the very few materials that can show strong quantum confinement effect[7]. Nanocrystallites of PbS are ideal building blocks for the formation of quantum dot (QD) superlattice. And, it was demonstrated that the nanometer-scale

self-organization of semiconductor colloidal crystals is of high value in the engineering of nanodevices.

In this paper we demonstrate that superlattices of nanometer-sized QDs can be generated in solution as the "crystallization" of monodisperse colloids. There are four steps involved in the synthesis of the superlattices: (1) synthesis of ultrafine semiconductor crystallites encapsulated by a monolayer of organic surfactant to produce stable colloids; (2) size-selective precipitation to achieve crystallites with uniform diameters in the nanometer range; (3) formation of a superlattice of these coated particles on a solid substrate; and (4) displacement of the organic surfactant with a molecular interconnect that covalently bonds adjacent particles to each other without destroying the superlattice. Although this methodology was performed on semiconductor quantum dots it provides general procedures for the preparation and characterization of ordered structures of nanocrystallites from a variety of materials.

Experimental

A 10 mL solution of 1×10^{-3} M $PbCl_2$ was prepared, and to this was added a 10 mL solution of 2×10^{-3} M n-hexadecyl mercaptan, resulting in a turbid yellow solution. H_2S was then injected to the quickly stirred solution. Deep-yellow PbS colloids were achieved. Size-selective precipitation was carried out on the as-prepared PbS colloids as described in literature[8]. A copper grid coated with amorphous carbon film was dipped into the size-selected colloids for 3h, and then was transferred to a 10 mL solution of 1×10^{-3} M *p*-phenylenediamine for another 3h. Transmission Electron Microscope (TEM) and Selected Area Electron Diffraction (SAED) patterns were recorded on the sample-bearing copper grid, the High Resolution Transmission Electron Microscopy (HRTEM) was also employed to investigate the inner structure of the self-organized PbS quantum dots superlattices.

Results and Discussion

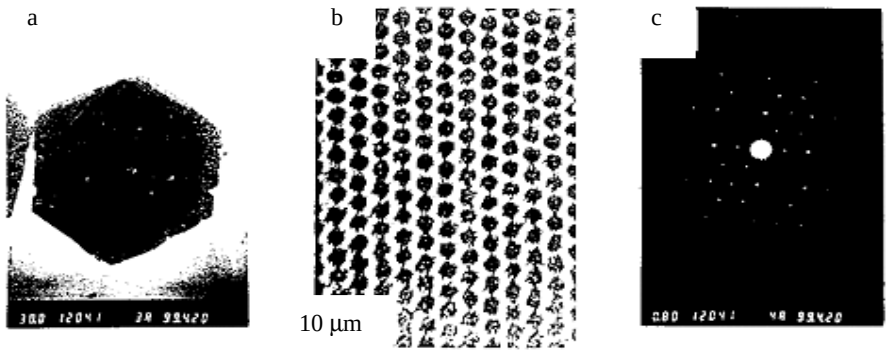
Hexaplanar colloidal crystals 1-10 μm in size made from PbS QDs 4 nm in diameter are shown in the TEM micrograph of **Figure 1** (a), and the SAED pattern is shown in **Figure 1** (c). From the graphs we can see that the PbS colloidal crystals are in near normal hexagonal close-packed shape, and the SAED pattern also shows this.

According to Gast[10] *et al.* and Thirumalai[11] *et al.*, hexagonal close-packed structure of colloidal crystals is extremely difficult to obtain because this structure is metastable and tends to transition to cubic (fcc or bcc) structures. But in our case, even after weeks, the colloidal crystals remain the original shapes. From the HRTEM micrograph (**Figure 1** (b)) we can see that the quantum dots are well orderly arranged and in a hexagonal close-packed network.

There are two things that deserve to mention here. The first is the importance of the size-selective procedure. From our experiments and the work of other researchers (*e.g.* see Ref.8 and 12) we find out that PbS nanocrystallites with a narrow-size-distribution is extremely difficult to prepare due to the tendency to aggregate induced by the huge

surface energy. When the polydispersity in size remains at some extent, there will be no self-organization pattern emerging. And it is not hard to think out one picture that many balls with various radii pack together disorderly. So the size-selective procedure must be repeated several times until a strong decrease in the average particle size and its distribution is observed. When the polydispersity in size is small enough, self-organization can be observed. The second thing is the importance of the molecular coupler (*i.e. p*-phenylenediamine). We have found that unlinked arrays were not very stable. They can be destroyed by high-energy electron beam of the TEM. However, it is possible to covalently link the clusters to each other using double-ended molecular coupler without destroying the planar array. In addition to physically bonding the clusters to each other, the molecular coupler also serves as " molecular wires" and provides controlled electronic coupling between adjacent particles.

Figure 1 (a) TEM, (b) HRTEM and (c) SAED of PbS self-organized quantum dots superlattices.



Conclusion

In conclusion, we have developed a novel method for self-organization of planar colloidal crystals. Colloidal self-organization with nanocrystallites is not restricted to semiconductor QDs[12]. Manipulation of insulating, semiconducting, magnetic, and metallic materials into superlattices as demonstrated for PbS QDs in the present paper should be readily accomplished after control over size distributions and stabilization have been established. The rational design of novel and potentially useful superlattice structures with a variety of nanometer-sized building blocks should then be possible.

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