

Thin Films and Coatings

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Nanocrystal orientation and superlattice array in Pbs-oleic acid thin films: The role of crystal habit and organic fibrils

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With regard to the materials science aspects of nanocolloid structural chemistry, this study is of great interest in the attempt to answer two of the major topics being hotly debated. The first concerns the principles of the ordering of self-assembled films and the driving forces for this kind of self-assembly [1,2]. The second topic concerns itself with the optimisation of physical properties of such systems containing confined and isolated but nevertheless interconnected structures [3].

For the self-assembly processes of ligand capped nanoparticles a complex set of events should be taken into account, such as the attraction between the surface charges of the inorganic nanoparticles and a significant contribution from van der Waals forces between the organic surface chains which are further assisted by capillary forces evolving during the drying processes and steric effects caused by the shape of the individual nanoparticles. As soon as a structure has been established by the self assembly process, further ordering may be assumed to be prevented by fibrillation of the organic surfactant. By careful analysis of high-resolution bright field images it was found that the nanoparticles are interconnected by organic fibrils of oleic acid which are partially mineralised by PbS. These inorganic bridges on an atomic level together with organic fibrils are responsible for keeping the orientation of the nanoparticles fixed thus preventing the system from adopting a disordered or arbitrary arrangement. Recently, we were able to determine the 3D structure of a PbS - oleic acid superassembly showing an intermediate character between a high and low orientational ordering of nanoparticles, respectively [4]. In this system, the truncated octahedrally shaped PbS nanocrystals are stabilized by organic molecules and assembled into an fcc superlattice with long-range "translational" order, while still maintaining their preferable crystallographic orientation limited to shorter ranges. This situation is reminiscent of a special type of colloidal crystal classified as "mesocrystals" which represent superstructures of nanoparticles with certain mutual orientation relations

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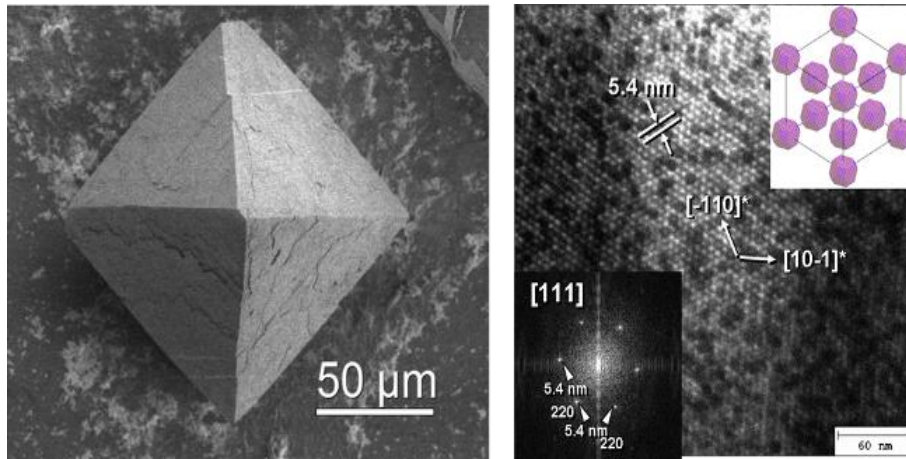


Figure 1.