Nanoparticles with different functionalities and their periodic structures

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Research Achievements: We work on synthesis of different types of nanoparticles with controllable size, shape and composition and understanding their fundamental properties. Nanoparticles display size-dependent electronic structure and could be used as the building blocks for electronic and optoelectronic devices including solar cells, photodetectors, and field-effect transistors; as well as in catalysis and biomedicine. Organization of uniform objects into periodic structures is found in many natural systems, such as atomic and molecular solids, opals, bacterial colonies, etc. In contrast to random mixtures, the ordered nanoparticle arrays provide precise uniformity of packing and rigorous control of the interparticle distances. The ability to assemble "artificial atoms" into ordered structures is expected to create novel class of "artificial solids", that are, nowadays, one of the most exciting materials. The interparticle spacing in nanoparticle superlattices is determined by the length of capping ligands and the type of superlattice. Interparticle spacing is a crucial parameter that dramatically affects electronic and optical properties of nanoparticle solids. Periodic structures can be obtained in a form of films by evaporation of colloidal solution or in a form of perfectly faceted colloidal crystals by technique called "controllable oversaturation" (Figure 1, inset). To date there was no clear understanding in the difference between three-dimensional films and colloidal crystals in terms of their lattice structure and interparticle spacing and how different the behavior of highly organized superlattices from their glassy analogues. We have performed systematic study on nanoparticles solids with no long range order, periodic nanoparticle films and colloidal crystals by time resolved small angle X-Ray scattering (SAXS). At the example of 7 nm PbS nanoparticles we have shown that both periodic films and colloidal crystals have the same face centered cubic structures, however they differ in terms of degree of ordering and interparticle spacing (Figure 1). Thus colloidal crystals demonstrated ~28% smaller interparticle spacing and almost no variation in sample to sample in degree of ordering as compared to periodic films. Moderate thermal annealing of both periodic structures at temperatures below the boiling temperature of capping ligands has let further irreversible shrinkage of crystalline lattice from 1.4 nm up to 0.9 nm without sintering of individual PbS nanoparticles. SAXS study performed for structures assembled from a variety of other nanoparticles (eg CdSe, Fe_xO_y, PbSe, etc) confirmed the better ordering and smaller interparticle spacing for colloidal crystals. In addition to that we have studied mechanical properties of colloidal crystals and effect of different capping ligands on the mechanical stability.

Electronic properties of semiconductor nanoparticles can be also altered by creation of hybrid structures at the level of individual nanoparticles. We explore the synthesis, optical and electronic properties of hybrid Au/PbS nanoparticles. We synthesized multicomponent nanostructures with metallic Au core and semiconducting PbS shells. In Au-PbS core-shells, we observed enhancement of the absorption cross section due to synergistic coupling between plasmon and exciton in the core and shell, correspondingly. Field-effect devices with channels assembled from arrays of Au-PbS core-shell nanostructures demonstrate strong p-type doping that we attributed to the formation of an intra-particle charge transfer complex.

Another example of hybrid structures at nanoscale is self-assembly of different types of nanoparticles that is amazingly simple and powerful technique in material design. In addition to periodic lattices isostructural to crystalline lattices we have found quasi-crystalline phase assembled from gold and iron oxide nanoparticles.

The surface of nanoparticles is extremely important for any type of applications, especially for catalysis and biomedicine. At the example of magnetic nanoparticles we have developed an approach based on chemiluminesence catalyzed by surface atoms to characterize the chemical activity of surface atoms and total stability of nanoparticles in aqueous media. Hybrid dumbbell-like structures (eg $CoPt_3$/Au) were found to reveal very different catalytic behavior.

Future work: We will focus on manipulation of interpaticle spacing in self-assembled structures in order to create mini-bands that are very important for electronic and optoelectronic properties. We will explore in more details the possibility of formation of nanoparticle quiasicrsytals from different types of nanoparticles. We will try to achieve better control over nanoparticle crystallization in terms of localization of crystallization event, control over type and dimensions of periodic structures. Also we will further study catalytic and electrocatalitic properties of nanoparticles, including complex multicomponent hybrid particles, hollow nanoparticles and multicomponent arrays.

Publications:

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