Poster

END-TO-END ASSEMBLY OF SHAPE-CONTROLLED NANOCRYSTALS VIA A NANO-WELDING APPROACH.

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Controlled assemblies of colloidal nanocrystals (NCs) have recently attracted growing interest as a result of their potentially novel electronic, optical and magnetic properties, which might be different from those of a corresponding collection of individual non-coupled NCs or from the bulk solid.

By the literature the formation of one-, two- and three- dimensional assemblies of NCs with different type materials is known.[1-3] A large variety of approaches has been used for their obtaining, using biomolecules as linkers or inorganic templating agents as architectonic platforms for several NCs. One issue that has been mainly addressed in this field is the control of the interparticle distance in the assembly which allows the tuning of the properties of the NC superstructure. Our work is based on a variety of chemically directed chalcogenide-based NC assemblies. By taking advantage of easily processable solution-based reactions at low temperatures, different chalcogenide materials of various sizes and shapes have been assembled without the need of organic linkers giving rise to only inorganic NC-based superstructures with different branching degrees.

One general assembling strategy has been used for the organization of differently sized and shaped Type IV-VI semiconductor nanocrystals, independently of the nature of the chalcogenide atom (S^{2-}, Se^{2-} or Te^{2-}). The NCs utilized were CdSe@CdS asymmetric core@shell nanorods, CdSe nanorods and CdSe@CdTe tetrapods, all of them synthetized by a seeded growth approach.[4] The scope of our work consists in the formation of an inorganic heterojunction between nanocrystals by means of a previous selective nucleation of gold dots on the tips of the semiconductor nanostructures. Infact, state of the art of gold nanoparticles shows the role of the iodide (I^-) to fuse and assemble colloidal gold NCs in solution[5-6]. However, in our experiments, iodine (I_2) seems to have a comparable effect using the previously mentioned semiconductor-Au heterostructures. Actually, the presence of iodine, even in trace amounts, was found sufficient to glue together the Au domains that had nucleated at the tips of the NCs (nanorods or tetrapods) (see Scheme 1).
All reactions take place in relatively short times ($t \leq 30$min) and at room temperatures. The final size of the assembly can be controlled by the ratio between NCs and aggregator agent (I_2) in the solution. The selective nucleation of Au domains in just one or both tips of the chalcogenide crystals introduces preferential anchoring points that allow tuning the assembling freedom degree of the heterostructures. In this way zero-dimensional superstructures, i.e. flower-like (see Figure 1), can be obtained in solution by the reaction of I_2 with only one tip Au-decorated nanorods, while 1D, 2D or 3D superstructures are formed in solution when all tips of the semiconductor structures present an Au domain (see Figure1).
In summary, our work introduces a general approach for the assembly of cadmium chalcogenide semiconductor NCs by means of metallic gold junctions. It yields solely inorganic nanocrystalline assemblies, which are stable in organic solvents and hence should be easily processable for the fabrication of new devices[7, 8,9]. Charge carrier transport should be facilitated across such superstructure of Au-interlinked NCs, and in addition novel structures

with interesting mechanical properties and/or controlled porosity could be realized, which, in the case of TP assemblies, could also serve as "scaffolds".

References:

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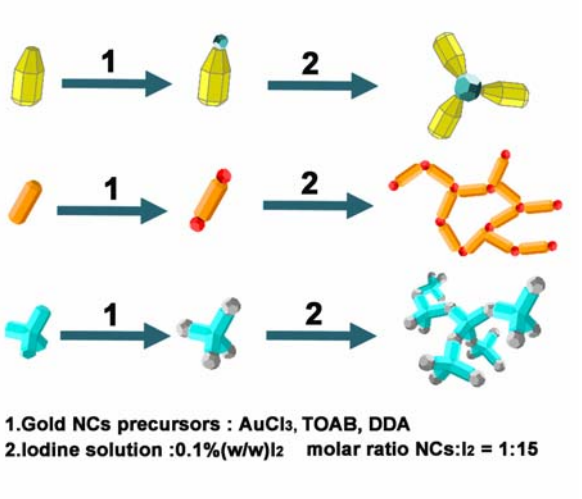
Figures:



Scheme 1. Assembly of bullet-, rod-, and tetrapod-shaped NCs mediated by coalescence of Au domains grown at their tips and then destabilized with the help of molecular iodine. The reactants for the gold growth are gold chloride ($AuCl_3$), tetraoctylammonium bromide (TOAB) and dodecylamine (DDA).

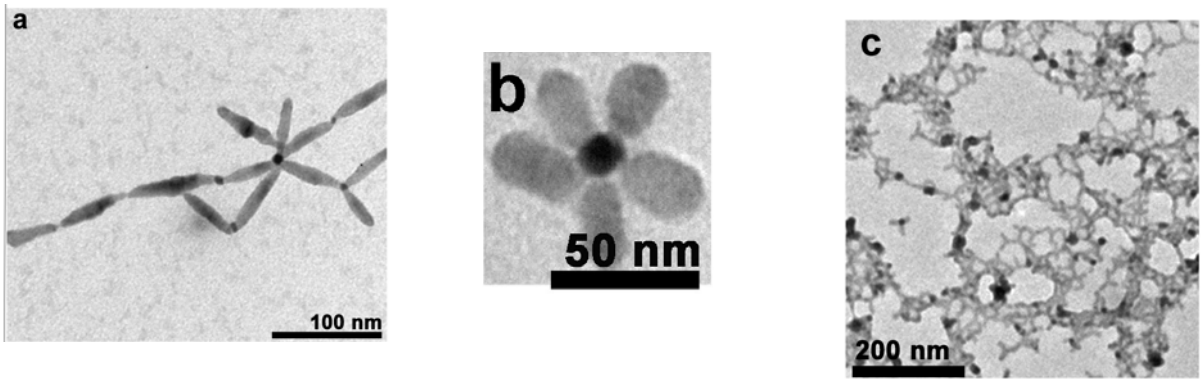


Figure 1. a) CdSe nanorods-based single structures formed at the initial steps of the assembly after reaction with I_2, b) CdSe@CdS core@shell rods decorated with one single Au tip after reaction with I_2, c) CdSe@CdTe tetrapods multibranched networks after reaction with I_2.