

Recent Developments in the Synthesis of Cd Chalcogenide Nanoparticles

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The synthesis of nanometer scale crystals with precisely defined shapes and sizes have potential applications to solar cells, miniaturized transistors, photonic devices, and biological imaging.¹⁻² Such crystals have size tunable optical properties, although the size distribution of a given ensemble of crystals must be relatively narrow to observe the size dependence.

Colloids may be prepared by the arrested precipitation of a supersaturated solution of the material of interest. However, large size distributions often result from these kinds of synthesis. This problem was often addressed by the use of structured solids like zeolites or templates like micellar solutions.³ More recently seeded vapor-liquid-solid deposition techniques have been used. Murray et al.⁴ discovered that Cd chalcogenide colloids synthesized through arrested precipitation can be relatively monodisperse without the use of a seed by careful control of the degree of supersaturation, and manipulation of the temperature. Alivisatos's group^{5,6} further developed this procedure and found that precursor concentration could determine the shape, rod or spherical, of the crystallites. They discovered that "fortuitous impurities" in their technical grade (90% purity) tri-*n*-octyl phosphine oxide (TOPO) were necessary to grow rod-shaped crystals. Using hexylphosphonic acid as a model impurity in 99% TOPO, they reproducibly grew monodisperse CdSe rods (figure 1). Peng and Peng⁷ proposed that different faces of the growing rod have different surface energies, consistent with an anisotropic wurtzite structure. The precursors preferentially extend a high energy face of the wurtzite phase to produce rods. They saw that in solutions with a low concentration of precursors spheres form, and higher concentrations lead to rods.

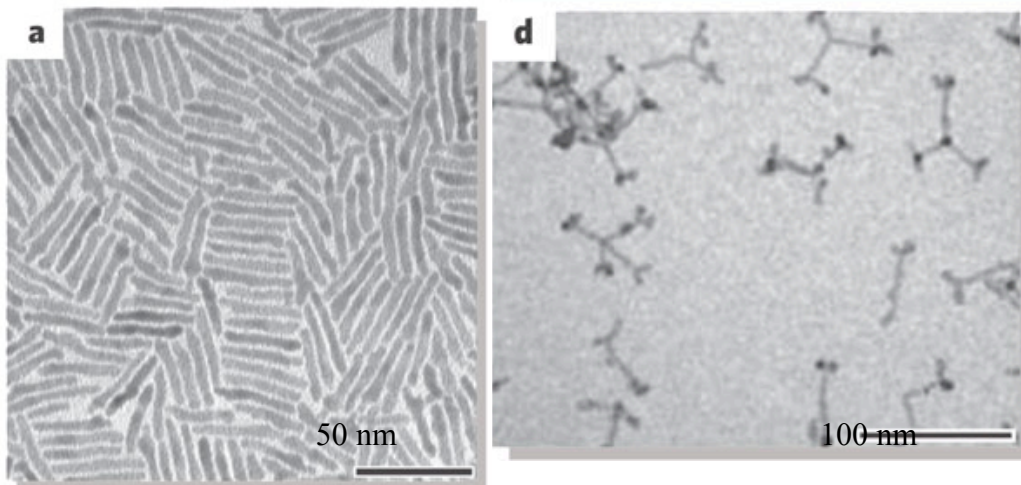


Figure 1: TEM images of rods and tetrapods. From references 1,9.

Manna et al⁸ observed the formation of CdTe and CdSe tetrapods (figure 1). They proposed that wurtzite-type arms grow from a zincblende-type core formed during the initial burst of nucleation. Shieh et al⁹ proposed that careful control of the degree of supersaturation after the initial nucleation event controls the amount of branching. Keeping the concentration low during nucleation, but moderate during growth by using sequential injections of precursor leads to slower growth and less branching.

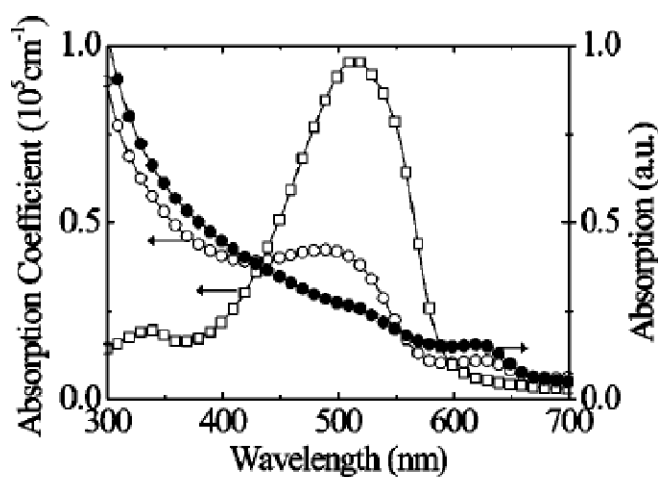


Figure 2: Comparison of absorption of an organic semiconductor film (poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylenevinylene)), open squares; CdSe tetrapods (50 x 5 nm arm dimension), filled circles; and a combination film, open circles. Note the enhanced absorption at both higher and lower wavelengths. From reference 10

The properties of these colloids make them a candidate for incorporation into thin film solar cells. They show broad absorption, coinciding with the sun's emission, and have better electron mobilities than most organic polymer semiconductors. Surface ligands confer solution processibility, which can be altered through ligand exchange. However, the efficiencies of solar cells made from these types of crystals still compare unfavorably with those of conventional silicon cells.¹⁰

References

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