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Synthesis and Structural Characterization of II-VI Semiconductor Nanocrystallites (Quantum Dots)

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Abstract. A methodology for the production of II-VI semiconductor nanocrystallites employing organometallic precursors has been developed. The rapid pyrolysis of reagents in a coordinating solvent provides temporally discrete nucleation. Subsequent controlled growth allows the production of macroscopic quantities of nanocrystallites with consistent structure, surface derivatization and a high degree of monodispersity. The samples produced are structurally characterized with a combination of X-ray and Electron Beam based techniques.

1. Introduction

The study of nanometer sized crystallites provides an opportunity to observe the evolution of material properties with size. The discrete nature of molecules and the collective behavior of materials must be unified in this intermediate size regime. Investigation of crystallite structure, in an appropriate model system, is required to distinguish novel properties truly inherent to the nanometer size regime from those associated with structural heterogeneities.

The preparation of a homologous series of samples, of a single material, spanning the size range of interest, presents formidable synthetic challenges. Each sample must display a high degree of monodispersity (size, shape, etc.) regularity in crystallite core structure, and a consistent surface derivatization (cap). These stringent sample requirements are met by drawing on lessons from classic colloid chemistry and organometallic synthesis.

The production of a series of monodisperse colloids depends on a temporally discrete nucleation event followed by controlled growth on the existing nuclei. Temporally discrete nucleation is attained by a rapid increase in the reagent concentrations resulting in an abrupt supersaturation which is relieved by the formation of nuclei and subsequent growth [1].

Dimethylcadmium [Me_2Cd] is chosen as the Cd source while Bis(trimethylsilyl)chalcogenides [TMS_2E E=S, Se, Te] or Trioctylphosphine selenides and tellurides [TOP=Se & TOP=Te] are selected as chalcogen sources. The use of TOP=Se & TOP=Te reagents is preferred due to their ease of preparation and stability. Me_2Cd and TMS_2E have been shown to undergo dealkylsilylation in a variety of solvents as a route to the production of bulk materials [2]. The utility of phosphine telluride as a source of neutral Te species has also been demonstrated [3]. Trioctylphoshine oxide [TOPO] is a robust high boiling point solvent. Mixed phosphine / phosphine oxide solutions have been found to be good solvents for the high temperature growth and annealing of CdSe crystallites [4].

Delivery of the reagent mixture, by syringe, into a hot reaction flask produces supersaturation followed by sudden homogeneous nucleation. The quantum size effect predicts an increase of the effective band gap in crystallites of decreasing size [5]. This "blue shift" of the optical absorption allows the growth of crystallites to be followed by UV-Vis spectroscopy.

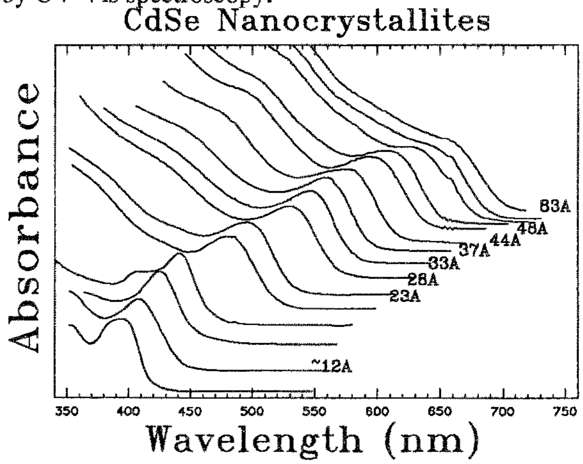

Fig.1. Plots of absorbance vs wavelength for a series of CdSe nanocrystallite samples show the expected "blue shift" with decreasing size.

The rate of crystallite growth shows a strong dependence on temperature and crystallite size. Lowering the reaction temperature from ~300^{O}C, for growth of the largest crystallites, to ~180^{O}C for the smallest crystallites allows slow, steady growth and low defect densities. Specific sizes are obtained by monitoring the optical absorbance and quenching the reaction when the desired optical features are observed. Quenching is achieved by lowering the temperature below 150^{O}C. The nanocrystallites are structurally characterized with the use of Transmission Electron Microscopy [TEM] and powder X-ray diffraction.

2. Synthesis

Preparation CdE Nanocrystallites:

Method (1): A 250 ml rb flask containing 40 g TOPO is connected to a Schlenk line and heated under vacuum to ~ 200^{O}C to remove all moisture and dissolved gases. The TOPO is then place under Ar and heated to 250^{O}C. Inside a glove box 2.78 mMoles of Me$_2$Cd (200 μl) is added to a vial containing 5 mls of TOP and stirred briefly. To a second vial containing a 5 mls of TOP, 2.78 mMoles of TMS$_2$E is added and stirred. The Me$_2$Cd and TMS$_2$E solution are combined and loaded into a 10 ml syringe. The contents of the syringe are then delivered in a single rapid injection to the rapidly stirring TOPO. The growth of the crystallites is monitored by UV-Vis spectroscopy and the reaction quenched when the desired optical absorption is observed.

Method (2): A second more convenient route to the production of CdSe and CdTe nanocrstallites utilizes TOP=Se and TOP=Te in place of the corresponding TMS$_2$E reagents. All remaining steps follow the procedure in method (1).

Isolation of CdE Crystallite Powders: Cooling the solution to ~60^{O}C and slowly diluting to 3X the initial volume with dry methanol results in the rapid flocculation of the CdE nanocrystallites. Further rinsing of the flocculate with methanol removes the excess TOPO and gives a free flowing powder. Cd metal and other byproducts of the reaction can be removed by redispersion of the powder in heptane and centrifugation to produce an optically clear supernatant and a metallic precipitate. The addition of excess of methanol to the filtered supernatant results in the recovery of a sample of reversibly flocculated crystallites. The crystallites capped with TOPO are now redispersible in a wide variety of solvents (alkanes, aromatics, THF, pyridines, amines, etc.).

3. Characterization

TEM: Studies of crystallites were carried out on an Akashi EM002B Transmission Electron Microscope. Statistical analysis of the images indicate standard deviations in particle diameter of between 5% and 8%. The smaller crystallites appear mostly spherical while the larger ones look slightly oblong. Faceting is poorly resolved. The use of the TEM in the "lattice imaging" mode allows resolution of the atom planes and columns. High magnification images detect stacking faults in the <002> hexagonal axis (see Fig.2). These stacking faults are the predominant form of planar disorder in the bulk.

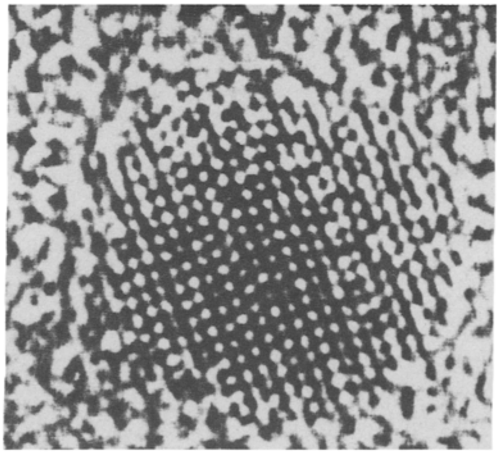

Fig. 2 A TEM image of a CdSe NC at 7 MX Magnification shows stacking faults along the <002> axis.

Powder X-ray Diffraction: X-ray diffraction studies were carried out with a Rigaku RU300 miniflex diffractometer operating in the Bragg geometry. Samples were prepared by pressing clean, dried powders into 0.5 inch diameter pellets.

Crystallites of CdE exhibit a predominantly hexagonal (wurtzite) crystal structure with the lattice spacing of the corresponding bulk materials (see Fig.3).

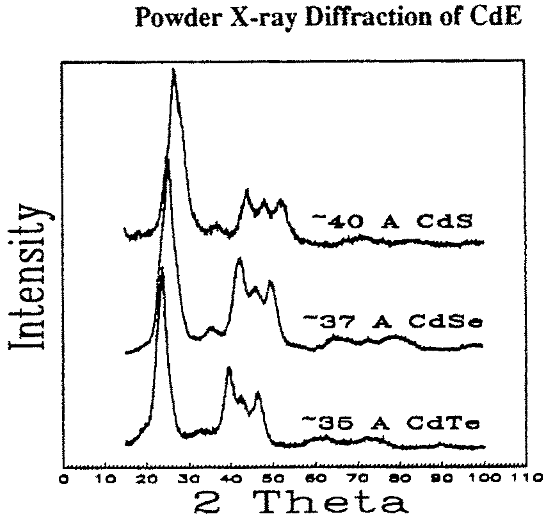

Fig. 3 Powder X-ray spectra of CdS, CdSe and CdTe samples exhibit wurtzite crystal structures.

CdSe samples from ~20 A to greater than 100 A in diameter show clear evidence of finite size broadening in all reflections. Excessive attenuation and broadening of the (102) and (103) reflections is characteristic of the presence of the stacking faults along the <002> axis observed in TEM experiments (see Fig.4). A combination of finite size and defect broadening of reflections results in a convolution of peaks in each diffraction feature. Direct observation of peak position and peak breadth are thus unreliable measures of lattice spacing and crystallite size. The use of computer simulations permits more detailed analysis of crystallite structure [4]. These simulations are consitent with single crystal CdSe particles displaying planar disorder equivalent to 1 or 2 stacking faults in the <002> axis. X-ray diffraction is largely insensitive to the surface imperfections observed in TEM.

The ~12A diameter species show a dramatic change in the powder diffraction features. These small particles possess too few atoms to clearly define a core crystal structure making the distinction between wurtzite and zinc blende classifications meaningless. The dramatic change in the diffraction pattern may indicate a significant surface reconstruction or contributions from surface capping groups.

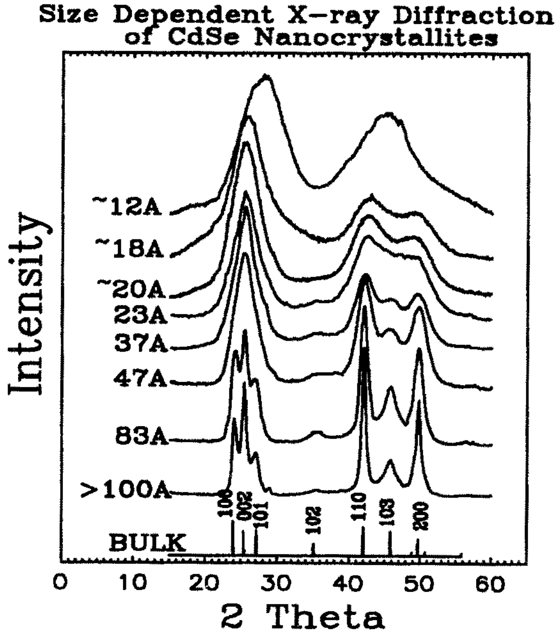

Fig. 4 X-ray powder diffraction studies of a series CdSe crystallites ~20 A to > 100 A in diameter display the wurtzite structure of the "bulk" while species ~12 A diameter show significant reconstruction.

4. Conclusion

The rapid pyrolysis of organometallic precursors in a coordinating solvent provides a simple "one pot" route to the production of macroscopic quantities of high quality II-VI semiconductor nanocrystallites with consistent surface passivation.

Characterization of the samples with TEM and X-ray diffraction show relatively monodisperse colloids of wurtzite II-VI particles structurally resembling fragments of the "BULK" until the smallest of sizes.

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