

Syntheses and Morphology Control of II-VI Group Nanocrystalline Semiconductors

Juewen Liu

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Nanomaterials are materials of several to one hundred nanometers in at least one of their dimensions.¹ Nanomaterials are currently a focus of study for their strongly size dependent properties which differ greatly from the corresponding bulk materials.² Nanocrystalline semiconductors are of special interest for their potential applications such as light-emitting diodes³ and biological labelings.^{4,5}

The synthesis of nanomaterial is a big challenge to material chemists. The properties of nanomaterials are size, size distribution and morphology dependent. A successful synthesis should be able to control all the above factors simultaneously. As any other crystal growth process, achieving supersaturation is the first step. After nucleation, the methods for controlling the growth of nanocrystalline are very important. The growth stage cannot be infinite, otherwise the size of the crystalline will be too large to be called "nano". Surfactants, micelles, polymers and zeolites can all be used as confining agent for nanocrystallites growth.⁶ Until early 1990s, no good methods have been developed to prepare nanocrystalline semiconductors with very narrow size distribution, although nanoscale can be reached.⁷

In 1993, Murray *et al*⁸ has developed the route of thermal decomposition of molecular precursors in hot coordination solvent to synthesize nanocrystalline cadmium chalcogenides. After size sorting, very narrow size distribution can be achieved (S.D. <5%). Katari *et al*⁹ have modified the approach by separating nucleation stage with growth stage and single size can be achieved without size sorting. Monomer concentration is found to be an important factor for controlling size distribution. At high monomer concentration, the sizes of nanocrystallites are focusing to a narrow range, while lower the monomer concentration will broaden size distribution. A diffusion controlled crystal growth mechanism has been proposed to explain the effect of monomer concentration.¹⁰

Morphology control has been achieved by adding HPA (hexylphosphonic acid) to TOPO to make bisurfactant solvent system.¹¹ A TEM picture of a rod morphology nanocrystalline CdSe is shown in fig1. HPA is a strong coordination reagent for Cd atoms. 20% HPA has been found to be the optimal concentration for nanorods to grow.¹² By thermal decomposition of single molecular precursor, Cd(S₂CNEt₂)₂ in HAD (hexadecylamine), nanorods, bipods, tripods and tetrapods can be prepared simply by varying the growth temperature.¹³ Again, the diffusion controlled mechanism has been proposed to explain the forming of nanorods. Three stages of growth have been identified by varying monomer concentration.¹⁴ At very high monomer concentration,

the growth is exclusively along the c-axis of wurtzite structure and the aspect ratio increases very fast during this stage. Lower the monomer concentration, the crystal will grow in all the three dimensions with no change in aspect ratio. At a certain monomer level, the volume of nanocrystallites stops changing while the aspect ratio decreases.

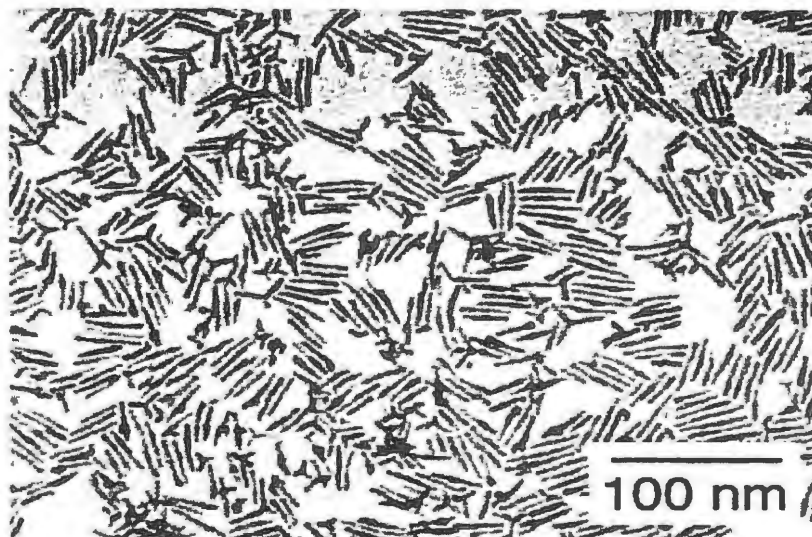


Fig1.

With the better understanding of reaction mechanism and kinetics of nanocrystalline growth, the essential of the size distribution and morphology control is found to be the concentration of cadmium HPA complex, which suggests that $\text{Cd}(\text{CH}_3)_2$ might not be necessary. CdO is used instead of $\text{Cd}(\text{CH}_3)_2$ as Cd source. A route towards green chemistry morphology controlled synthesis of cadmium chalcogenides has been developed.¹⁵

References

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