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Organometallic Synthesis of GaAs Crystallites Exhibiting Quantum Confinement

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The optical spectra of semiconductor crystallites whose dimension is comparable to the bulk exciton diameter show quantum confinement effects.¹⁻⁶ To date, experimental studies of nanometer-size crystallites have been restricted to II-VI and I-VII semiconductors, while III-V semiconductors, including one of the most important direct band gap semiconductors, GaAs, have not yet been studied in this form, because of the numerous difficulties encountered in their preparation. Compared to the I-VII and II-VI semiconductors, the III-Vs have a greater degree of covalent bonding, a less ionic lattice, and larger exciton diameters (the exciton diameter in GaAs is 190 Å, compared to 60 Å for CdS). For this reason, quantum size effects on the optical spectra have been predicted to be more pronounced in the III-V class of materials than in the II-VIs,⁷ and crystallites of GaAs are more likely to find application in optical devices than CdS clusters.^{8,9} In this paper we present the first documented preparation of relatively monodisperse, redissolvable, crystalline, nanometer-size particles of GaAs.^{10,11} The nanocrystals were prepared in polar organic solvents, using a reaction developed by Wells and co-workers.^{12,13}

GaCl₃ and As(SiMe₃)₃ react in hydrocarbons to give solid products, which on heating afford GaAs.¹³ Our X-ray diffraction experiments on the black GaAs powder prepared in this manner show that the domain size is 100 Å. We carried out the same reaction in quinoline. GaCl₃ (99.99%) was purchased from Aldrich, purified by sublimation, and stored in a dry box. Tris(trimethylsilyl)arsine was prepared according to literature methods,¹⁴ purified by vacuum distillation, and stored in a drybox at 0 °C. Proton NMR and infrared spectra matched the literature values.¹⁵ Quinoline was purchased from Aldrich and distilled immediately prior to use. Quinoline (25 mL) containing 6.5×10^{-3} mol of tris(trimethylsilyl)arsine was added to 6.5×10^{-3} mol of GaCl₃ in 25 mL of quinoline. The resulting mixture was heated at reflux (240 °C) for 3 days. A red powder was isolated by removal of the solvent, and the powder consisted of GaAs particles which are redissolvable in pyridine or quinoline. Flame annealing of the powder under vacuum at 450 °C improved the crystallinity of the particles, but resulted in loss of solubility.

The quinoline-soluble GaAs particles have been studied by

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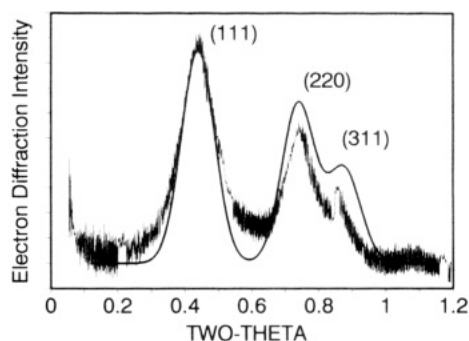
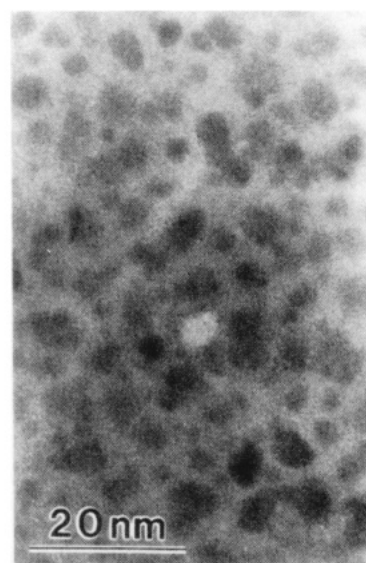


Figure 1. (a) Transmission electron micrograph from a field of GaAs particles. The bar is 20 nm. Analysis of a few hundred particles yields the average size of 45 Å by 35 Å. (b) Electron diffraction pattern from the particles. The domain size from the Debye-Scherrer formula is 24 Å.

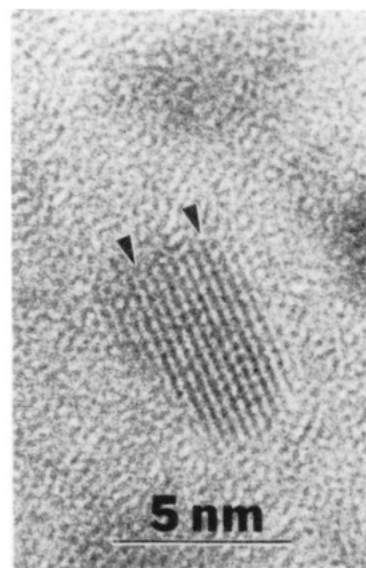


Figure 2. Transmission electron micrograph of one GaAs particle showing lattice planes.

TEM. The particles were deposited from solution onto an amorphous carbon overlayer on a Cu grid and were imaged on a JEOL 200cx microscope operating at an accelerating voltage of 200 kV. TEM reveals prolate GaAs particles with an average major axis of 45 Å and minor axes of 35 Å (Figure 1a). The size distribution of $\pm 10\%$ variation of each axis is broad compared to that of the best II-VI nanocrystal preparations. Figure 2 shows

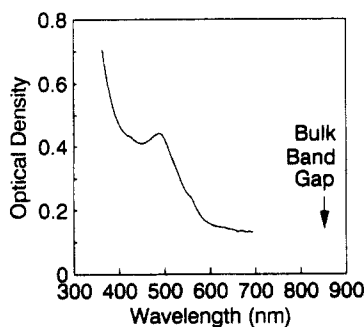


Figure 3. Optical absorption spectrum of a quinoline solution of the crystallites obtained after refluxing, but before flame annealing.

one GaAs particle taken from the field of Figure 1a, in which lattice planes can clearly be seen. Selected area electron diffraction on this region of the grid yields a diffraction pattern in which the (111), (220), and (311) zinc blende peaks of GaAs are evident, confirming the identity of the particles (Figure 1b). The widths of these peaks can be used to determine the domain size of the particles via the Debye-Scherrer formula:

$$\Delta(2\theta) = \frac{1.2\lambda}{D \cos \theta} \quad (1)$$

where λ is the electron wavelength and D is the crystallite diameter. The best fit is obtained for $D = 24 \text{ \AA}$. Since the domain size determined by electron diffraction is somewhat smaller than the mean particle diameter from the real space images, we conclude that the particles are not perfectly crystalline.

X-ray diffraction on the unflamed and flamed powders also shows the (111), (220), and (311) peaks of GaAs. The domain size from X-ray diffraction matches the value obtained from electron diffraction on the unflamed powder, although the signal-to-noise ratio is much worse. The domain size is 30 \AA in the flamed sample, but this improvement in crystallinity is obtained by compromising the solubility. Elemental analysis of the particles shows the presence of Ga and As in a 5:4 ratio, as well as carbon and nitrogen. These numbers are verified by XPS studies of the Ga and As core levels. The carbon and nitrogen may be from quinoline, which could bind to the Ga-rich surface via the nitrogen lone pair, and act as a capping moiety.¹⁶ Resonance Raman scattering on powders prepared in this manner shows a single peak at 292 cm^{-1} , the frequency of the LO mode of GaAs.

Since the particles are significantly smaller than the bulk exciton diameter, we expect the onset of optical absorption to be shifted to higher energy, according to the well-known formula

$$E = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_c} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\epsilon R} \quad (2)$$

where E_g is the bulk band gap (1.52 eV), R is the particle radius, m_c (0.07) and m_h (0.68) are the effective masses of the electron and hole, e is the fundamental charge, and ϵ is the high-frequency dielectric constant (10.9).⁷ For 40 \AA diameter particles, this predicts a shift in the spectrum of 1.33 eV. The absorption spectrum of the nanocrystals, dissolved in quinoline, does indeed show a pronounced quantum confinement effect (1 eV, Figure 3), but not quite as large as is predicted by eq 2.¹⁷

We are currently exploring the large range of parameters that can be changed in this reaction, including solvent, total reactant concentration, the use of capping moieties, etc., in order to adjust the average size of the particles. In addition, we are investigating the nature of the surface derivatization.

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Efficient and Enantiodivergent Synthesis of (+)- and (-)-Pinitol

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Pinitol **1** is the 3-*O*-methyl ether of chiro inositol, with both enantiomers occurring in various plant sources.² The structures and absolute stereochemistry of (+)- and (-)-pinitol were determined in 1952 by degradation studies³ and confirmed later by an independent synthesis of the (-) isomer as its diacetone.^{4a} Recently (+)-pinitol has been shown to possess significant hypoglycemic and antidiabetic activity in diabetic albino mice.^{5a} It also acts as a feeding stimulant for the larvae of the yellow butterfly *Eurema hecabe mandarina*^{5b} and inhibits larval growth of *Heliothis zaea*.^{5c,d} Ley has reported a synthesis of (\pm)-pinitol in which, by subsequent resolution of a racemic intermediate, he was able to achieve both antipodes.^{4b,c} An enantiodivergent and a general synthesis of a large number of cyclitols, especially the important inositol phosphates⁶ implicated as cell messengers,⁶ would be highly desirable, especially if such an approach took into account complete control in the stepwise functionalization of hydroxyl groups in cyclohexanehexols such as **1**.

One of the frequently cited disadvantages of enzyme-mediated synthesis is that usually only one enantiomer of a given target may be prepared. The chiral auxiliary approaches to enantiodivergent synthesis are frequently inefficient and long and rely on known sources of chirality. In this communication we report a short synthesis of both enantiomers of pinitol **1**, based on a novel concept of designing enantiodivergent synthesis as an indication that, with proper consideration of symmetry,⁷ both enantiomers may become available from a single isomer generated by biocatalytic means.

Our enantiodivergent approach to (+)- and (-)-**1** centered upon elaboration of a new cis-diol **2** obtained by the microbial oxidation of bromobenzene by the bacteria *Pseudomonas putida* 39-D.⁸

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(7) The enantiomers of **1** are related by a plane of chirality (Figure 1) and may be interconverted (and/or racemized) via a hypothetical [2, 3] methoxy transposition. Diol **2** possesses a similar chirality plane. Thus, enantiodivergence from **2** to **1** is realized by differentiating between olefin a and olefin b at the time of functionalization without destroying this plane of chirality. With meso diene diols, the olefins are enantiotopic and cannot be differentiated except by use of chiral reagents. This property (i.e., possessing a "latent" plane of symmetry, the creation of which is a function of only a single chemical operation) also exists in **2**, where the reduction of bromine at C2 or bromination of C4 would render this enantiomer meso. We would therefore like to refer to olefins in compounds such as **2** as "proenantiotopic", indicating that a carefully controlled sequence of operations can lead to enantiomeric distinction between the D and L series of the target molecule.