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Sterically Induced Shape and Crystalline Phase Control of GaP Nanocrystals

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Semiconductor nanorods and nanowires have drawn great interest not only because they exhibit novel optical properties arising from dimensional anisotropy, but also because they can be utilized as key materials in addressable two-terminal circuits for nanodevice applications.[1] For example, CdSe nanorods[2] exhibit linearly polarized emission, and InP nanowires[3] can be used for polarization-sensitive nanoscale photodetectors. Research on liquid-phase synthesis of anisotropic nanocrystals has largely focused on II-VI semiconductor systems,[2,4−6] but other systems have been poorly explored because their synthetic methodology is not well developed. In particular, studies on colloidal III-V semiconductor nanocrystals are very limited, despite the technological importance of these materials; III-V semiconductors that are luminescent from the near-infrared (e.g., InAs) to the blue (e.g., GaN) region are widely used for optical applications, and their large exciton Bohr radii allow them to show quantum confinement effects with relatively large sizes.[7] Colloidal quantum dots (e.g., InP, GaAs) and nanofibers (e.g., InAs, GaP) with large widths ($>\sim$100 nm) are examples of the important progresses.[8−10] Typical studies, however, tend to show colloidal III-V nanocrystals either polydispersed or much larger than quantum confinement region in size. Many regard the size and shape control of III-V nanocrystals to be difficult because they are hard to crystallize at low temperature ($<$400 °C); this is most likely due to a greater degree of covalent bonding and absence of suitable precursors.

In this paper, we demonstrate a surfactant driven shape-controlled synthesis of gallium phosphide semiconductor nanocrystals using thermal decomposition of a single molecular precursor, tris(di-*tert*-butylphosphino)gallane ($\mathrm{Ga(P^tBu_2)_3}$), in a hot mixture of amine stabilizers. In addition to their well-defined single crystallinities, the shape of the obtained GaP nanocrystals can be varied from nanospheres to rods with highly monodispersed size distributions by controlling the type and amount of stabilizing surfactants.

GaP nanocrystals were grown by thermal decomposition of 100 mg of $\mathrm{Ga(P^tBu_2)_3}$[11] in 2 mL of trioctylamine (TOA), which was injected into a mixture of TOA and hexadecylamine (HDA) at 330 °C. After 72 h, the resulting solution was quenched with cold toluene and treated with methanol to precipitate amber-colored flocculates that were separated by centrifugation. Nanocrystals were obtained as amber-colored powders and easily redispersed in toluene or dichloromethane. Without further selection processes, obtained nanocrystals are moderately monodisperse in size and shape.

When only trioctylamine (TOA) was used as a stabilizer, spherical particles were formed. Low magnification TEM images of GaP nanospheres show that nanocrystals obtained were highly monodisperse with the size of 8.1 nm ($\sigma \approx 5.4\%$) (Figure 1). High-resolution TEM (Figure 1b,c) analyses show measured interplanar distances are 3.094, 2.687 Å for the ⟨111⟩ and ⟨200⟩ directions, respectively, which is consistent with known values of zinc blende GaP.[12] In addition, selected area electron diffraction (SAED) and X-ray diffraction (XRD) patterns of the nanosphere reveal its crystalline phase as the zinc blende.[13]

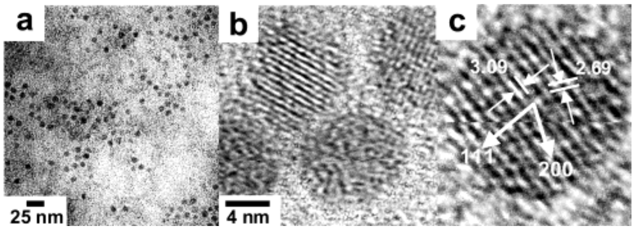

Figure 1. Large area TEM image (a) and HRTEM images (b, c) of GaP spheres.

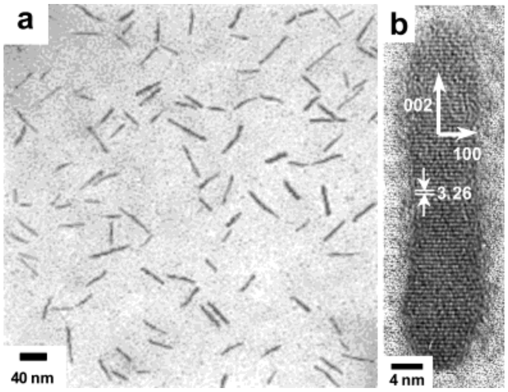

Figure 2. Large area TEM image (a) and a HRTEM image (b) of GaP nanorods.

Under the same conditions as above, addition of HDA into TOA leads to changes in the shape and crystalline phase of the GaP nanocrystals. When a mixture of 8.7 mL of TOA and 4.8 g of HDA (ratio = 1:1) was used instead of neat TOA solution, a mixture of nanospheres (70%) and nanorods (30%) of 42.3 nm ($\sigma \approx 16.2\%$) in length and 7.9 nm ($\sigma \approx 6.3\%$) in width was produced.[13] Finally, when the stabilizer ratio was increased to 1:2.5, the formation of nanorods (8 nm ($\sigma \approx 5.7\%$) in width and 45 nm ($\sigma \approx 22.6\%$) in length) dominated (Figure 2). The lattice fringes of HRTEM (Figure 2b) that orient in the ⟨002⟩ direction with an ABABAB... stacking sequence with an interplanar distance of 3.26 Å reveal that the rod has a highly ordered single crystalline wurtzite structure.[12] Consistently, SAED and XRD patterns for nanorods show additional peaks from wurtzite phase GaP and an intense ⟨002⟩ peak indicates that the nanorods anisotropically grow along the *c*-axis of the wurtzite phase.[13]

From these observations, a low HDA to TOA ratio seems to favor the formation of zinc blende nanospheres, but a high concentration of HDA leads to the formation of the wurtzite phase

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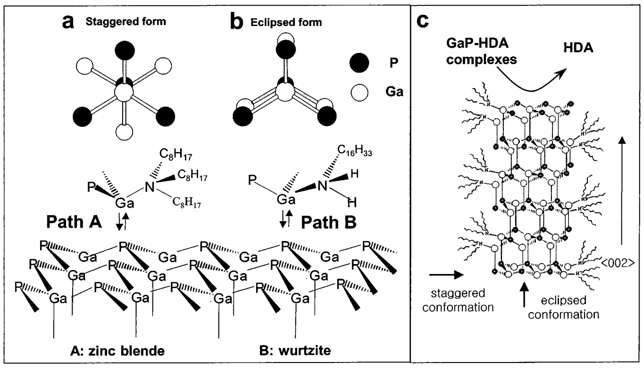
Scheme 1. Proposed Mechanism for Surfactant Driven Steric Effects on the Crystalline Phases (a, b) and Rod Growth (c) of GaP Nanocrystals



and also induces anisotropic growth of the nanocrystals. These results can be understood as arising from steric effects of the stabilizers during crystal growth. GaP crystals have two different crystalline phases[14] which are in rotational isomerism − the thermodynamically stable zinc blende structure is a staggered conformation with ⟨111⟩ directions, and the kinetically stable wurtzite structure is an eclipsed conformation with ⟨002⟩ directions (Scheme 1).[15] Kinetic stability of the wurtzite structure is induced by strong dipole interaction of incoming GaP monomers with surface GaP lattice atoms. Because stabilizers dynamically bind to the crystal surfaces during the GaP crystal growth, the conformation of crystal structures is highly affected by changing the stabilizer. When the highly bulky tertiary amines (e.g., TOA) are used as stabilizers, staggered conformation is favored, minimizing steric hindrance between these ligands and GaP lattices (Scheme 1, path A), and zinc blende GaP is preferred rather than wurtzite. In contrast, when an excess amount of less sterically hindered HDA is added to TOA, the rotational barrier between GaP-HDA complexes and GaP lattices is reduced. Therefore, the formation of the kinetically stable wurtzite GaP is now facilitated (Scheme 1, path B) under the kinetic growth regime induced by a high monomer concentration.[15,16]

Moreover, the steric difference between these two stabilizers seems to induce the anisotropic growth of the wurtzite GaP. It is likely that, when wurtzite seeds are formed, sterically bulky TOA selectively binds to the other faces (e.g., 100 and 110 faces) with staggered conformation rather than to 002 faces and blocks growth on these faces.[17] On the other hand, GaP-HDA complexes continuously supply monomers on the 002 faces with high surface energy and therefore promote the growth in the *c*-direction of a rod structure (Scheme 1c).

The nanocrystals obtained showed unique spectroscopic features originating from quantum mechanical effects.[18] The absorption spectra exhibited strong shoulders (3.48 and 3.46 eV for spheres and rods, respectively) and shallow tails that are attributed to direct and indirect transition, respectively.[19] The photoluminescence maximum was 2.94 eV for spheres corresponding to the direct transition of 8 nm GaP, while red shift (2.79 eV) was observed for rods (8 × 45 nm), which may arise from shape anisotropy (Figure 3).[6,20]

In summary, a novel route for shape and crystalline phase control of GaP nanocrystals has been successfully developed using a single-molecular precursor approach. Even without selection processes, the nanocrystals obtained are decently monodisperse in size and shape. Our results are the first liquid-phase syntheses of anisotropic III-V semiconductors within a quantum-confined region with a width of less than 10 nm.

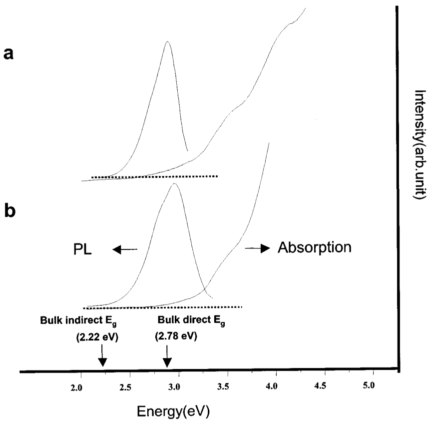


Figure 3. Absorption and photoluminescence spectra of GaP rods (a) and spheres (b).

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Supporting Information Available: XRD, SAED, and EDAX of GaP nanocrystals. A TEM image of mixed shapes of nanocrystals (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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