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Communications

New Pyrolysis Route to GaN Quantum Dots

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GaN is a technologically important semiconductor for development of short wavelength optoelectronic devices.[1] Colloidal nanocrystals, or quantum dots (QDs) made from this material, are expected to combine good thermal, chemical, and radiation stability with excellent optical properties. Although colloidal GaN QDs have been an important target material for some time, they have proven to be difficult to synthesize and to study.[2,3] Methods to produce colloidal GaN QDs include pyrolysis of polymeric gallium imide[3,4] and reaction of gallium cupferron with hexamethyldisilazane.[5] Complexes of $GaCl_3$ with urea have also been converted to nanostructured GaN upon thermal decomposition.[6] Despite these promising results, the development of new and improved routes to GaN QDs remains an important goal. Here, we report a new pyrolysis reaction that produces GaN QDs in high yield with improved luminescence characteristics over those obtained by previous methods.

Mićić et al. pyrolyzed poly(imidogallane) in a high-boiling, coordinating solvent mixture (trioctylamine, TOA, and hexadecylamine, HDA).[3] There are several drawbacks associated with the poly(imidogallane) precursor. First, the procedure requires difficult and hazardous manipulations of pure ammonia. Second, the polymer has poor solubility, which is detrimental to particle size control and thus to high yield production of QDs. Even the presence of coordinating solvent and high temperature failed to prevent precipitation of the product as bulk GaN. Only a small percentage of the product was recovered as nanosized, colloidal particles. These colloidal particles were subjected to further study, which revealed evidence for quantum confinement in the UV−visible absorption spectra. Unfortunately, no band edge photoluminescence (PL) emission was observed from those samples, perhaps as a result of poor surface capping of the GaN nanocrystals.

The observed precipitation of large particles from that reaction is not surprising; indeed it is probably unavoidable because the polymer precursor begins to precipitate even before it is converted to GaN. We have re-examined the reaction sequence used to produce GaN nanocrystals in ref 3. Recently, we have discovered that the same dimeric amidogallium precursor ($Ga_2[N(CH_3)_2]_6$) used to produce the poly(imidogallane) can be converted directly to GaN through pyrolysis without the need for the polymeric intermediate. The new reaction is a significant improvement over the previous process because it produces colloidal GaN nanoparticles in high yield, offers the possibility of controlling particle size, and eliminates the need for gaseous ammonia. Scheme 1 compares the previously reported polymer pyrolysis route (top) to the new process reported here (bottom).

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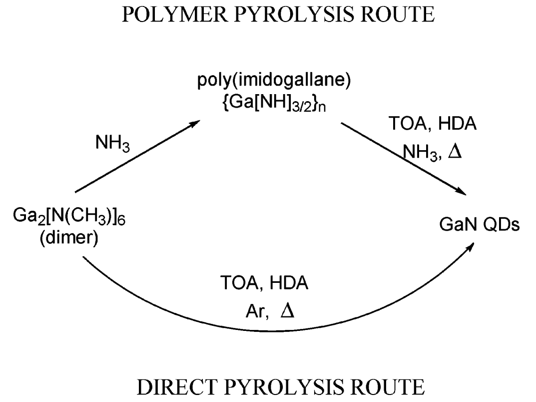
Scheme 1. Comparison of Old (Top) and New (Bottom) Methods for Pyrolysis Synthesis of GaN



To produce GaN QDs, the dimeric amidogallium precursor was prepared according to the literature method[4] and then directly pyrolyzed to the GaN product under Ar atmosphere in a mixture of coordinating solvents.[7]

The identity of the product was confirmed using several methods. Initial characterization was performed on the solid obtained following flocculation and precipitation of the solid powder from the reaction mixture.

Powder X-ray diffractometry measurements yielded broad peaks characteristic of nanosized crystalline GaN domains (Figure 1). In the case of the product obtained after 24 h of reaction time, only two broad peaks were observed at 35 and 62°. After 60 h, three peaks could be resolved, and these resembled closely the diffraction patterns published in earlier accounts describing the synthesis of nanocrystalline GaN powders from poly(imidogallane).[3,4,8,9] The obtained data matches the known *d* spacings and peak intensities of zinc blende GaN,[10] whose diffraction pattern is shown at the bottom of Figure 1.

A single, broad, intense peak was observed in the Fourier transform infrared (FTIR) spectrum near 600 cm^{-1}, matching spectra of GaN obtained by the polymer pyrolysis method as well as literature reports. [11] The single, broad peak at 600 cm^{-1} differentiates our reaction product from the most likely alternative, β-Ga_2O_3, which gives two distinct peaks near 450 and 700 cm^{-1}.[9]

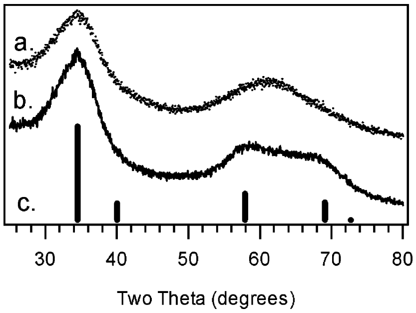


Figure 1. Powder X-ray diffraction study of the pyrolysis products produced after (a) 24 h and (b) 60 h. The diffraction pattern for zinc blende GaN is shown at the bottom.

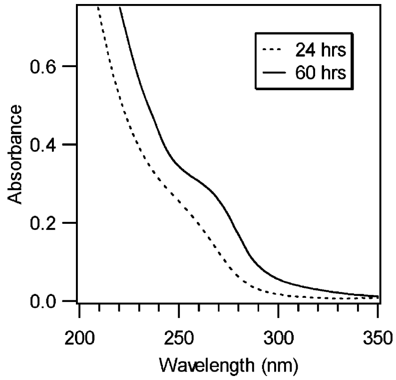


Figure 2. UV−visible absorption spectrum of the GaN product obtained after 24 h (dashed curve) and 60 h (solid curve) of pyrolysis under an argon atmosphere.

Figure 2 shows UV−visible absorption spectra for the product obtained after reaction times of 24 and 60 h. Each spectrum shows an absorption edge in the ultraviolet that is blue-shifted relative to the absorption edge of bulk GaN (365 nm). This blue shift is expected for nanoscale particles and is the result of spatial confinement of the exciton. While the broad X-ray diffraction peaks shown in Figure 1 do indicate small crystalline domains within the solid, they cannot provide direct evidence for small particle size. On the other hand, the absorption data in Figure 2, which show strong evidence for excitonic quantum confinement, do suggest the presence of separated, nanosized, GaN particles. Both spectra in Figure 2 are shoulders on a large, sloping absorption background that increases with decreasing wavelength. Such spectra are typically associated with broad QD size distributions and can be contrasted with the spectra obtained from monodisperse suspensions, which exhibit a series of narrow, well-resolved peaks.[12] Despite the broad size distributions, the differences between the two spectra provide initial evidence that this new method allows some control over the particle size distribution. This possibility distinguishes this new method from previously reported polymer pyrolysis routes.

PL emission from the as-prepared sample also shows evidence of quantum confinement (Figure 3). Room temperature PL emission is observed near the absorption edge with a peak at 305 nm (4.07 eV) suggesting radiative exciton recombination at the band edge. Broad, visible emission from

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(7) Briefly, 2 g of $GaCl_3$ and 1.8 g of $LiN(CH_3)_2$ were combined in 100 mL of hexanes in an Ar-filled glovebox and reacted for 2 days at room temperature. A 10 mL aliquot of the product mixture was used to synthesize GaN QDs. The $Ga_2[N(CH_3)_2]_6$ dimer was isolated from the 10 mL aliquot of this reaction mixture by removing the hexane solvent under vacuum. To this dimeric precursor, 4 mL of TOA and 1 g of HDA were added. The pyrolysis was carried out by refluxing this mixture under Ar for 1−3 days. The colloidal GaN product was recovered in high yield by centrifugation, and the recovered solid was washed with copious hexanes. The washed particles were then suspended in methanol to produce optically clear suspensions for spectroscopic studies and TEM grid preparation. Approximately 50% of the GaN product could be suspended in this clear methanol suspension. The colloidal suspension was stable for more than 2 months. The dried particles used for FTIR and X-ray diffraction measurements were a whitish-yellow color.

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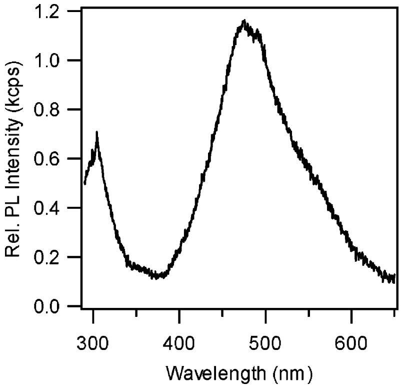

Figure 3. PL emission spectrum of colloidal GaN QDs. Peaks are observed at 305 nm near the absorption band edge and from deep traps emitting in the visible region. The sharp peak atop the band edge emission peak is Raman scattering from the solvent.

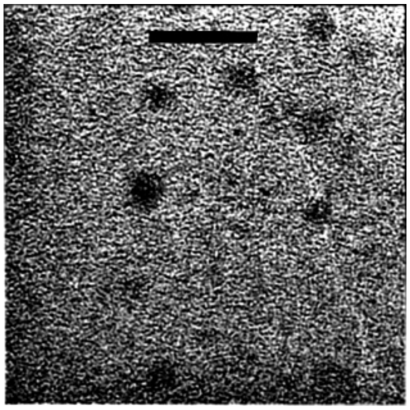

Figure 4. TEM image of GaN nanoparticles obtained from pyrolysis of $Ga_2[N(CH_3)_2]_6$. Scale bar is 10 nm.

trap states is also seen in this spectrum. The observation of confinement-shifted PL emission is significant, as reports of quantum-confined PL emission have been rare in colloidal GaN nanocrystals. GaN nanocrystals obtained from pyrolysis of poly(imidogallane) typically emit only in the visible range at room temperature.[9,13] Mićić et al. observed spectrally broad PL emission which peaked near the bulk GaN band gap energy, significantly to the red of the absorption edge in their sample.[3]

Confirmation of isolated, colloidal QDs was achieved via transmission electron microscopy (TEM) imaging. Figure 4 shows a high-resolution transmission electron microscopy (HRTEM) image of the nanoparticle product produced after 60 h. The figure shows several spherical particles with diameters of 2−4 nm. The extremely small size of these particles and low material density (6 g/cm^3) result in low contrast in the electron beam, making these particles difficult to image and measure. The broad size distribution suggested by the optical spectra is confirmed in this TEM image. Although the particle size distribution obtained here is not comparable with those obtained in the highly optimized II−VI systems, there is reason to believe that this reaction will permit improvements through optimization of reaction conditions. The average particle diameter measured from several such images ($N = 35$) is 24 Å with a standard deviation of 4 Å. The effective mass equation[14] applied to GaN[8] predicts a band gap energy of 4.8 eV (∼260 nm emission) for 24 Å particles. This equation is known to systematically exaggerate the band gap of for tiny particles, so the observed relationship between measured particle size and optical band gap seems reasonable.

Lattice fringes were never observed in TEM images of these samples, although the instrument used here is certainly capable of resolving lattice fringes. The failure to visualize the lattice is apparently due to the poor crystallinity of the as-prepared particles.

The pyrolysis reaction described here appears to involve transamination by HDA. When HDA is eliminated from the reaction mixture, no GaN is produced. Elemental analysis (Desert Analytics, Tucson, AZ) on the GaN product obtained in the presence of HDA revealed a Ga/N ratio of 4.88:1 (theoretical 4.98:1), indicative of nearly stoichiometric GaN. The product also had a high carbon content (C/N = 2.27:1). This high carbon content does not necessarily indicate that carbon is incorporated into the particles; rather, it is consistent with capping of nanosized particles by capping ligands such as HDA or TOA that contain long aliphatic chains. We note that the slight stoichiometric nitrogen excess may also be associated with the presence of these capping ligands. Thorough encapsulation of the GaN particles by capping ligands is a requirement both for the production of stable colloidal QDs such as those produced here and for the observation of significant PL emission at the band gap energy. Despite the efficacy of the capping ligands, the product was not completely dispersible in methanol. The most likely reason for this is the broad size distribution and the presence of large particles.

This new route to GaN QDs represents a significant improvement over the previously reported reaction involving poly(imidogallane). The new method is safer and far simpler because it does not require the use of ammonia. Compared with the bulk polymer pyrolysis, this method produces a much higher yield of colloidal QDs. Presumably, this is due to the good solubility of the dimeric precursor and the ability of the coordinating ligands to cap the particle surfaces as soon as GaN nuclei are formed. The nature of this precursor also offers an opportunity to tune the particle size by controlling reaction conditions such as precursor concentration, pyrolysis temperature, reaction time, and identity and concentration of the capping ligands. Finally, the QD product shows superior optical characteristics with quantum-confined, excitonic PL emission.

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