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Multicolor Light-Emitting Diodes Based on Semiconductor Nanocrystals Encapsulated in GaN Charge Injection Layers

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ABSTRACT

Numerous technologies including solid-state lighting, displays, and traffic signals can benefit from efficient, color-selectable light sources that are driven electrically. Semiconductor nanocrystals are attractive types of chromophores that combine size-controlled emission colors and high emission efficiencies with excellent photostability and chemical flexibility. Applications of nanocrystals in light-emitting technologies, however, have been significantly hindered by difficulties in achieving direct electrical injection of carriers. Here we report the first successful demonstration of electroluminescence from an all-inorganic, nanocrystal-based architecture in which semiconductor nanocrystals are incorporated into a p−n junction formed from GaN injection layers. The critical step in the fabrication of these nanocrystal/GaN hybrid structures is the use of a novel deposition technique, energetic neutral atom beam lithography/epitaxy, that allows for the encapsulation of nanocrystals within a GaN matrix without adversely affecting either the nanocrystal integrity or its luminescence properties. We demonstrate electroluminescence (injection efficiencies of at least 1%) in both single- and two-color regimes using structures comprising either a single monolayer or a bilayer of nanocrystals.

Estimations indicate that as much as 20% of the world’s electricity is used for lighting.1,2 While the general lighting market continues to be dominated by incandescent and fluorescent systems, advantages such as reduced operating expenses, lower energy consumption, and more reliable performance are the promises of solid-state lighting technologies.2 Current approaches to solid-state lighting have generally focused on combinations of phosphors and InGaN-based light-emitting diodes (LEDs).1 Since efficient InGaN LEDs typically produce light in the blue region of the optical spectrum, a phosphor is required to perform color conversion to other desired wavelengths or to multiple wavelengths to produce, e.g., white light. This strategy leads to significant energy losses associated with below-unity conversion efficiencies of electrical power into optical output from the LED, relatively low efficiencies of light capture by the phosphor, nonradiative carrier losses during the re-emission processes, and re-absorption of the “color-converted” photons by the phosphor material. Considerable energy savings can be achieved by approaches that directly incorporate color-selectable chromophores into the LED structure, thus allowing direct excitation of the chromophores by electrical current. In this configuration, the ultimate efficiency of a device will be determined by two factors: the injection efficiency of charges into chromophores and the probability of radiative recombination of the injected electron−hole (e−h) pairs. In this paper we experimentally demonstrate the feasibility of this approach using colloidal semiconductor nanocrystals (NCs) as color selectable chromophores that are directly excited electrically using semiconducting GaN injection layers.

The potential for NCs as the active media in light-emitting devices and as viable alternatives to conventional phosphor emitters is apparent. NCs are unique in their ability to offer size-tunable, narrow emission bands, high photoluminescence (PL) quantum yields (QYs) (>80%), and chemical flexibility3,4 without the drawbacks associated with other “soft-matter” emitters such as π-conjugated molecules that are characterized by broad emission spectra and poor stability with regards to photooxidation.5 However, an important concern related to light-emitting applications of NCs is the difficulty in achieving electrical pumping.

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The most common approach to electrical injection of charges into NCs involves the use of hybrid polymer/NC devices that demonstrate electroluminescence (EL) in both the visible6,7 and near-infrared8,9 spectral ranges (using, e.g., CdSe, InAs, and PbS NCs). In these cases, low carrier mobilities in the organic components and poor conduction through the NC emissive regions lead to low device efficiencies. Recently, Coe et al.10 used a monolayer of NCs sandwiched between hole- and electron-transport layers to avoid the problem of poor conduction through a thick NC active region, thereby achieving an improvement in external efficiencies.

Methods for combining NCs with semiconducting matrix materials have not been extensively pursued as a means of achieving operation in the electrical injection regime. The recent and most successful attempt at NC overgrowth by a semiconducting material was demonstrated by Hanna and co-workers,11 who used metal-organic chemical vapor deposition (MOCVD) to deposit GaInP2 films on colloidal InP/GaInP2 core/shell NCs such that the crystallinity, shape, and PL characteristics of the NCs were retained. However, neither the transport properties of the composite nor the EL of the structure were reported. We have recently described an optically pumped device consisting of an InGaN quantum well overcoated with a monolayer of CdSe/ZnS core/shell NCs, in which energy-transfer pumping of the NCs by the quantum well with an efficiency of 55% was observed.12

While experimental and theoretical evidence indicate that NCs can be combined with an electrically driven quantum well to achieve “noncontact” pumping of NCs via energy transfer, to realize such a device, engineering challenges, including the fabrication of thin, highly doped GaN top barriers, must first be met. Our new p–i–n NC/GaN structures reported here represent a novel, alternate strategy in which electrons and holes are delivered to NCs in the quantum well with an efficiency of 55% was observed.12

![Diagram](image)

Figure 1. Deposition of ENABLE GaN. (A) XRD scans of GaN films deposited by MOCVD at 1050 °C onto low-temperature buffer layers (dashed line) and by ENABLE at 500 °C onto untreated sapphire (solid line) (θ is the angle of the incident X-ray radiation with respect to the surface normal). Full-width at half-maximum values for the GaN (002) peak are 0.28° and 0.45° for the ENABLE- and MOCVD-grown films, respectively. The single-crystal sapphire substrate (006) peak half-width of 0.21° represents the instrumental peak broadening. A schematic of ENABLE-based thin film synthesis is shown in the inset. (B) Complete pole figure scans for the same samples showing that the mosaic spreads for both films are comparable at <3.0° (φ is the polar angle of rotation of the sample with respect to the plane of the incident X-ray beam). The high-resolution transmission electron micrograph shown in the inset is illustrative of the interface quality of the sample.

degradation that would be associated with high-temperature growth techniques. Deposition of GaN semiconducting thin films by ENABLE circumvents the need for elevated substrate temperatures and organometallic precursors. It utilizes a beam of neutral N atoms with kinetic energies tunable within a range of 0.5–5.0 eV (50–500 kJ/mol) to activate nonthermal surface chemical reactions13 with Ga metal co-deposited by e-beam evaporation, as depicted in the inset of Figure 1A. Although grown at much lower temperatures, ENABLE-deposited GaN films have characteristics equivalent to materials grown by conventional MOCVD techniques. Deposition of ENABLE GaN films onto bare sapphire substrates heated to 500 °C yields highly ordered films with crystallinity analogous to films grown at...
1050 °C by MOCVD on low temperature buffer layers. Comparison of X-ray diffraction (XRD) scans of GaN films grown by ENABLE and MOCVD, shown in Figure 1A and B, indicates that the perpendicular alignment and the mosaic spread of the ENABLE-deposited film is comparable to or slightly better than in the MOCVD sample. The high resolution transmission electron micrograph (TEM) (inset Figure 1B) confirms the atomically abrupt interface between the sapphire substrate and the ENABLE GaN film. Even at lower growth temperatures (i.e., 300 °C), device-quality intrinsically n-type doped films can be produced. GaN p-n junctions fabricated at this temperature show rectifying behavior and “clean” blue GaN emission at 413 nm with no “yellow” defect band detectable (see Figure S-1, Supporting Information).

Our NC encapsulation procedure employs temperatures of 300 °C to deposit ENABLE GaN onto Langmuir–Blodgett (LB) monolayers of CdSe/ZnS core/shell NCs capped with trioctylphosphate oxide (TOPO)/trioctylphosphine (TOP) ligands, prepared as previously described. Under these growth conditions, the NC absorption and emission spectra are preserved, as seen in Figure 2A, indicating that the NC integrity (i.e., its size and shape) is maintained following encapsulation. In fact, we do not observe any significant changes in the PL QY of the NCs upon encapsulation, indicating that the deposition does not adversely affect the surface properties of the NCs (i.e., does not create new surface trapping sites). Encapsulation with GaN stabilizes the NCs by preventing additional oxidation by the ambient atmosphere and by providing an environment that protects the sample from photodegradation. As an example, continuous exposure of an untreated LB film of NCs deposited on a sapphire substrate to a 400 nm pulsed laser beam (femtosecond frequency doubled Ti:sapphire laser) at 300 mJ/cm² (1 kHz repetition rate) resulted in a 32% decrease in the PL signal after 40 min of exposure. An identical NC film encapsulated in GaN showed no reduction in PL intensity over the same time interval.

Although GaN encapsulation of NCs is performed at 300 °C in clean, high vacuum conditions, we observe some evidence of the organic capping ligands following processing. Energy-dispersive X-ray fluorescence analysis indicates the presence of phosphorus in the NC layer (from the TOPO/TOP capping agent) after GaN deposition. This result is confirmed by the observation of the C–H stretching frequencies in the Fourier transform infrared spectrum of the material. These data suggest the TOPO/TOP ligands remain on the NCs throughout the low temperature ENABLE processing, although it is unclear whether the ligands remain completely intact or are partially decomposed.

The decreased GaN film crystallinity in this sample can be attributed to the reduced GaN growth temperature (300 °C) used for the encapsulation procedure and the nonepitaxial substrate (i.e., the NC LB film) onto which the GaN is grown. An XRD scan of a GaN film deposited on a sapphire substrate that is covered with an LB monolayer of TOPO/TOP-capped CdSe/ZnS NCs is shown in Figure 2B. The resulting material can be characterized as a semiconducting, polycrystalline, intrinsically n-type GaN film that retains ~80% c-axis orientation with some misoriented domains (as evidenced by the presence of the GaN (101) peak). XRD scans show no significant in-plane orientation, consistent with relatively low in-plane mobility (~0.2 cm² V⁻¹ s⁻¹). While not measured, the mobility perpendicular to the surface is expected to be significantly higher as a result of the considerable out-of-plane orientation of the films. This latter parameter is most important in defining the device performance because the top, ENABLE-grown GaN layer is likely to be covered by an electrode in NC-based LEDs designed for maximum light extraction efficiency, thereby minimizing any adverse effects that the low in-plane mobility would have on current spreading.

Our NC charge injection structure, depicted schematically in Figure 3A, consists of an LB monolayer of TOPO/TOP-passivated CdSe/ZnS NCs deposited on a 2 μm thick, high...
quality, p-type GaN layer grown by MOCVD on a sapphire wafer. The NC layer is then covered by a thin layer (100–400 nm) of intrinsic n-type GaN deposited at a rate of 5–10 nm/min by ENABLE, and the resulting architecture comprises an NC layer incorporated at a semiconducting GaN p–n junction, as confirmed by the TEM in Figure 3B. To complete the device, gold paste and indium metal electrodes are applied to contact the p- and n-type GaN layers of the structure, respectively. The energy level diagram of the active device, shown in Figure 3C, indicates that direct injection from GaN layers into the NCs is energetically favorable for both holes and electrons. In Figure 3D we compare the device PL and EL spectra. Optical excitation at 266 nm gives rise to emission from the GaN and NC layers in the device. In contrast, application of a forward bias across the structure results in the recombination of carriers exclusively in the NC layer (confirmed by the absence of a GaN EL signal).
carrier injection into NCs. At high bias (solid red line in Figure 4A and right photograph in Figure 4B), blue emission of the GaN junction resulting from carrier leakage through the NC layer is observed in the EL spectrum as a weak, broad luminescence band on the high energy side of the NC peak (when the device is returned to low biases, the GaN EL disappears).

The structure used to demonstrate charge injection allows us to achieve emission tunability by varying the diameter of the NCs in the monolayers and multicolor operations by utilizing multilayer samples comprising NCs of different sizes. The EL spectra for two different LEDs are shown in Figure 4C. One device demonstrates EL at 573 nm by employing NCs with a core diameter of 3.6 nm (orange line), while the use of NCs with a core diameter of 5.2 nm gives rise to EL at 619 nm (red line). In a different approach, an LB bilayer sample assembled from NCs emitting at 617 and 589 nm is shown in Figure 4D. While the double peak structure in the EL spectrum clearly indicates injection of charges into both NC layers, we observe a reduction in the shorter wavelength band intensity when compared to the PL spectrum measured for an identical NC bilayer on glass. This decrease is likely due to differences in the mobilities of the electrons and holes across the bilayer structure. In the two-color device, the lower energy NCs are deposited onto the p-type GaN, and the smaller, higher energy NCs are adjacent to the n-type GaN. The EL data associated with this configuration are consistent with a lower mobility of holes in the NC bilayer. The analysis of absorption cross sections (see Supporting Information) indicates that reabsorption of
light by a monolayer of larger NCs does not appreciably change the intensity of emission produced by smaller NCs.

To assess the output power of our device, PL and EL spectra were acquired from a brightly emitting, few square micron area selected using a spatial filter. Given the measured absorption cross-section of the NCs, a comparison of PL and EL intensities allows a carrier injection efficiency of at least 1% to be determined. By combining the carrier injection efficiency of 1%, a measured QY of 10%, the NC density and EL intensities allows a carrier injection efficiency of at least 9 ns, we conclude that our device delivers more than 50 mW/cm² of external optical power from a single LB monolayer of NCs.

Because of the nonoptimal procedures for applying electrical contacts and the low doping levels of the top n-layer (it is doped intrinsically), our devices show a spatially nonuniform distribution of emission intensity and relatively low external quantum efficiencies of 0.001–0.01%. We believe, however, that these values are not due to the inherent limitations of our novel injection approach but rather result from a nonoptimized design of the structures. High injection efficiencies and large power outputs (see above) along with the high emission quantum yields of NCs following encapsulation (>10%) indicate that these structures (after some engineering improvements) can potentially be much more efficient than our first prototype devices.

The NC/GaN devices are robust and stable under ambient atmospheric conditions. No degradation in emission was detected after 72 h of continuous operation, nor have there been any deleterious “shelf life” effects noticed for devices that are now many months old. Additional long-term stability studies of these devices are in progress. Improper operation, i.e., overdriving the device, has resulted in resistive heating to temperatures that cause the electrical contacts to delaminate. Upon reapplication of the contacts, no change in device performance was noted.

In conclusion, we have successfully encapsulated high-quality, colloidal, semiconductor NCs into GaN matrices using a novel, low-temperature deposition technique that utilizes an energetic beam of neutral nitrogen atoms and an evaporated flux of Ga. This method is “soft” enough to preserve both the integrity of the NCs and their surface properties. We apply this technique to fabricate electroluminescent structures in which monolayers or bilayers of NCs are incorporated into the p–n junction formed by doped GaN injection layers. These structures demonstrate multicolor EL in both one- and two-color regimes by direct carrier injection into the NCs.

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Supporting Information Available: Electrical and EL properties of plain GaN p–n junctions and hybrid p–NC–n structures and analysis of absorption cross sections. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(18) Incomplete NC monolayers containing large defect areas do show GaN p–n junction emission resulting from “short circuit” paths throughout the NC region.
(19) As the diameter of a CdSe NC decreases, its band gap increases because of the effects of quantum confinement. In CdSe NCs, this increase occurs primarily by a shift of the NC conduction band edge to higher energies, which moves it closer to the conduction-band offset of GaN. This trend limits the applicability of GaN as the electron injection layer to NCs with radii larger than 0.8 nm corresponding to emission wavelengths longer than ca. 440 nm (blue color). This estimation indicates that our approach can potentially be used with CdSe NCs emitting over the entire range of visible wavelengths from red to blue.
(21) The reduction in the radiative lifetime from the usual 20 ns is the result of NC encapsulation in a high index material (n = 2.2).

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