Communication

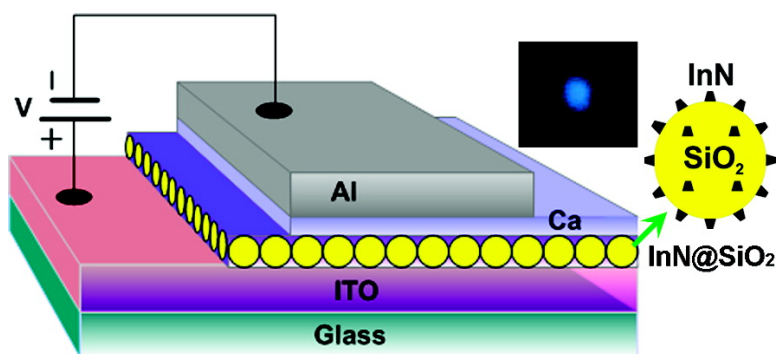# Blue Electroluminescence from InN@SiO Nanomaterials

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Blue Electroluminescence from InN@SiO₂ Nanomaterials

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Blue electroluminescence (EL) emitters play a very important role in the realization of full-color display. Efficient blue EL emitter remains a formidable challenge because of the lack of appropriate synthetic routes to prepare larger band-gap emission materials. Considerable efforts have been devoted to the development of traditional organic blue emitting materials.[1-3] However, their complicated multistep synthesis route and low long-term stability argue for the exploration of new strategies to make other materials. Over the past few years, core/shell colloidal quantum dots (QDs) are of particular interest in the development of blue-light-emitting materials.[4-6] Multicolor EL from nanocrystal-based light-emitting diodes (LEDs) has been reported by encapsulation QDs within a gallium nitride matrix.[7] Despite the advances of core/shell nanocrystals, QD-based LEDs that emit pure blue light are still difficult to fabricate because of the lack of appropriate methods to synthesize sufficiently small QDs (roughly in the order of 1.5 nm in diameter).[4] Since nitride semiconductors have proved quite successful in the realization of optoelectronic devices,[8] an alternative approach would be to investigate nitride-based semiconductor *nanomaterials* for blue electroluminescence.

Indium nitride (InN) is an important semiconductor of the group-III nitrides with high electron mobility, low band gap, and low toxicity.[9] Generally, InN thin films are made through a high-temperature process, such as reactive magnetron sputtering, metal-lorganic vapor-phase epitaxy (MOVPE), and molecular-beam epitaxy (MBE).[9] However, it remains relatively less studied compared to other group-III nitrides owing to its low thermal stability, low dissociation temperature, and high equilibrium vapor pressure.[10] Recently, InN nanomaterials have attracted increasing attention because of their potential applications in building opto-electronic nanodevices.[10-13] The development of InN-based nanomaterials enables the possibility of separation between the high-temperature synthesis and the formation of the emission layer. Solution-processed thin-film semiconductors can potentially provide a less-expensive, flexible, and more processable emission layer via mass-manufacturing roll-to-roll processes.

So far, there have been several efforts on preparing nanosized InN semiconductors,[10-13] however, investigations on blue EL from InN-based nanoparticles have not been reported although blue-green *photoluminescence* (PL) from InN-based nanomaterials has been reported in recent works.[14,15] Quite recently, we have developed a method to grow InN semiconductor nanocrystals on silica nanoparticles, by a nitridation step of In₂O₃@SiO₂ nanoparticles with NH₃ at elevated temperature.[16] The resulting InN@SiO₂ hybrid nanomaterials exhibit an intense blue PL at 445 nm. The exact origin of the blue emission is still under investigation but seems to be due to nitrogen-induced defects near the InN−SiO₂ interface.[16] The strategy to grow InN on silica is crucial in introducing the "right" defect at the interface. Many defects will be produced at the interface between semiconductor and SiO₂ owing to a large difference in structure. In addition, the presence of InN over the
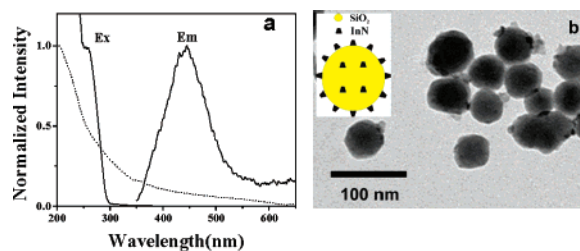

Figure 1. (a) Absorption (dotted) and photoluminescence (solid) spectra of InN@SiO₂ nanomaterials. Photoluminescence spectra were measured with a 450 W Xe arc lamp excitation in KBr pellet. (b) TEM image and cartoon structure (insert) of InN@SiO₂ nanomaterials.

insulating silica can be advantageous in making semiconductor/insulator-based EL devices because the carriers would be confined at the semiconductor-insulator interface, which could be helpful to increase the carrier density in the recombination region and thus obtain more intensive electroluminescence.[17] In this Communication, we report on the observation of blue EL from InN@SiO₂ nanomaterials at room temperature.

Figure 1a shows the absorption and *photoluminescence* spectra of InN@SiO₂ nanoparticles measured at room temperature. These nanoparticles exhibit a blue emission centered at 445 nm when excited in the UV region, but no luminescence was observed corresponding to the most quoted band gap value, 1.89 eV (656 nm),[18] or the recently reported band gap of ca. 0.70 eV (1771 nm).[19] The blue luminescence is most likely not due to the quantum confinements in the InN nanostructure because of their irregular shapes observed on the surface of SiO₂ nanoparticles (Figure 1b). A control sample such as InN−SiO₂ hybrid material prepared by directly mixing the same amount of In₂O₃ and pure SiO₂ nanoparticles and treated under identical nitridation conditions did not show the blue emission in the visible region (Figure S1). A detailed characterization of the InN@SiO₂ nanomaterials is reported elsewhere.[16]

EL device with a configuration of ITO//InN@SiO₂//Ca//Al was fabricated by simply spin-coating the nanoparticles onto indium tin oxide (ITO) covered glass substrate. After drying, the metallic cathode (Ca protected by Al) was thermally deposited onto the emission layer with a shadow mask (see Supporting Information for the details). The current−voltage (I−V) characteristic of the InN@SiO₂ EL device is displayed in Figure 2. The data show a clear diode-like behavior, with blue emission observed only in the forward bias, that is, when a positive voltage was applied to the ITO electrode (Figure 3). The log I/log V plot in insert of Figure 2 shows an ohmic behavior at low voltages (<4 V), following the $I \propto V^{1.4}$ relation, which indicates that current is limited by the InN@SiO₂ layer. At higher voltages (>4 V), the I−V data fit well to the trapped-charge-limited (TCL) current model, that is, the $I \propto V^m$ relation with $m \approx 4$.[20] This suggests that the filling of the limited traps results in a rapid increase (power−law increase) in current at
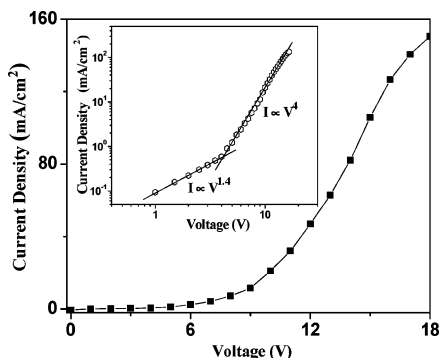
Figure 2. Current−voltage characteristic and log *I*−log *V* characteristic (insert) of the InN@SiO₂ EL device.
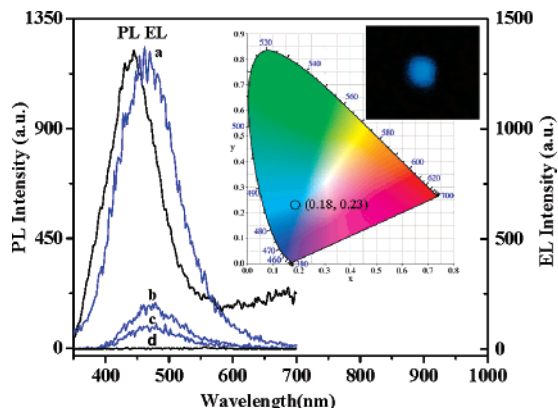

Figure 3. PL and EL spectra of InN@SiO₂ nanoparticles. The applied voltages for EL are (a) 14 V, (b) 10 V, and (c) 9 V, respectively. (d) EL of In₂O₃/SiO₂ control nanoparticles at a driven voltage of 18 V. The inset shows the CIE color coordinates of the resulting blue EL emission and a photo taken from the working device.

higher forward bias.[21] QD-based LEDs and organic light-emitting devices have been reported to exhibit an $I \propto V^m$ relation with variations in *m* values.[20,22,23] Here, *m* is the signature of the charge condition mechanism and is related to the type of the emitting materials, the temperature, and the trap energy.[20,23]

The EL device started to emit blue light, which was visible to naked eye, at 9 V, when a dc voltage was applied to the device. As shown in Figure 3, the intensity of EL emission increased with increased applied voltage with no change in emission wavelength. The EL occurs at ∼460 nm, that is, exhibiting ∼15 nm red-shift versus the PL peak at 445 nm. The red-shift of the EL, relative to the PL, is well-known in nanocrystal-based EL.[20,24] In our case, the reason for the red-shift of the EL could be explained by local Joule heating from the large current injection and relatively poor thermal conductivity of the emitting layer.[24,25] Because there is no additional hole or electron-transfer layers into which the recombination zone can extend, all the EL emission originates from InN@SiO₂ layer. This results in excellent color purity. Control devices fabricated using In₂O₃@SiO₂ or pure SiO₂ as emission layers did not show any blue EL (Figure 3d and Figure S2), substantiating that the blue EL occurs from the InN@SiO₂ nanomaterials. The calculated CIE (Commission International de l'Eclairage) coordinates for the EL spectrum in Figure 3 are 0.18 and 0.23, falling well within the blue region of the 1931 CIE diagram.[26] The calculated brightness of the blue emission is ∼0.3 cd/m² at 18 V

with a luminous efficiency of 0.2 mcd/A at a current density of 150mA/cm². The reason for the low brightness could be attributed to the poor charge injection efficiency on the inorganic nanomaterials surface. Though the observed brightness seems to be low, we emphasize that it is observed from an unoptimized device. Optimization of the devices could be achieved by the following ways: (i) formation of a close packed monolayer for nanomaterials, (ii) combination with electron/hole transporting layers, and (iii) optimization of the device structures.[27]

In conclusion, blue *electroluminescence* from InN@SiO₂ nanomaterials has been observed when the EL device was driven at a forward bias voltage. Our control experiments and the comparison analysis of PL and EL show that electron−hole recombination does occur in the InN@SiO₂ nanomaterials layer.

Supporting Information Available: InN@SiO₂ nanomaterials synthesis, devices fabrication, PL and EL spectra of control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Laskar, I. R.; Hsu, S. F.; Chen, T. M. *Polyhedron* **2006**, *25*, 1167.
(2) Pei, Q. B.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
(3) Breen, C. A.; Tischler, J. R.; Bulovic, V.; Swager, T. M. *Adv. Mater.* **2005**, *17*, 1981.
(4) Rizzo, A.; Li, Y. Q.; Kudera, S.; Della Sala, F.; Zanella, M.; Parak, W. J.; Cingolani, R.; Manna, L.; Gigli, G. *Appl. Phys. Lett.* **2007**, *90*, 051106.
(5) Jun, S.; Jang, E. *Chem. Commun.* **2005**, 4616.
(6) Steckel, J. S.; Zimmer, J. P.; Coe-Sullivan, S.; Stott, N. E.; Bulovic, V.; Bawendi, M. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2154.
(7) Mueller, A. H.; Petruska, M. A.; Achermann, M.; Werder, D. J.; Akhadov, E. A.; Koleske, D. D.; Hoffbauer, M. A.; Klimov, V. I. *Nano Lett.* **2005**, *5*, 1039.
(8) Nakamura, S. *Science* **1998**, *281*, 956.
(9) Bhuiyan, A. G.; Hashimoto, A.; Yamamoto, A. *J. Appl. Phys.* **2003**, *94*, 2779.
(10) Schwenzer, B.; Loeffler, L.; Seshadri, R.; Keller, S.; Lange, F. F.; DenBaars, S. P.; Mishra, U. K. *J. Mater. Chem.* **2004**, *14*, 637.
(11) Zhang, J.; Jiang, F. H.; Yang, Y. D.; Xu, B. L.; Li, J. P.; Wang, X. C.; Wang, S. M. *Mater. Lett.* **2006**, *60*, 2153.
(12) Sardar, K.; Dan, M.; Schwenzer, B.; Rao, C. N. R. *J. Mater. Chem.* **2005**, *15*, 2175.
(13) Sardar, K.; Deepak, F. L.; Govindaraj, A.; Seikh, M. M.; Rao, C. N. R. *Small* **2005**, *1*, 91.
(14) Yang, W. D.; Wang, P. N.; Li, F. M.; Cheah, K. W. *Nanotechnology* **2002**, *13*, 65.
(15) Zhang, J.; Xu, B. L.; Jiang, F. H.; Yang, Y. D.; Li, J. P. *Phys. Lett. A* **2005**, *337*, 121.
(16) Munusamy, P.; Venkataramanan, M.; van Veggel, F. C. J. M. Submitted for publication.
(17) Chen, P. L.; Ma, X. Y.; Yang, D. R. *Appl. Phys. Lett.* **2006**, *89,* 111112.
(18) Tansley, T. L.; Foley, C. P. *J. Appl. Phys.* **1986**, *59*, 3241.
(19) Wu, J.; Walukiewicz, W.; Yu, K. M.; Ager, J. W.; Haller, E. E.; Lu, H.; Schaff, W. J.; Saito, Y.; Nanishi, Y. *Appl. Phys. Lett.* **2002**, *80*, 3967.
(20) Yang, H. S.; Holloway, P. H. *J. Phys. Chem. B* **2003**, *107*, 9705.
(21) Burrows, P. E.; Shen, Z.; Bulovic, V.; McCarty, D. M.; Forrest, S. R.; Cronin, J. A.; Thompson, M. E. *J. Appl. Phys.* **1996**, *79*, 7991.
(22) Jeong, H. Y.; Lee, Y. K.; Talaie, A.; Kim, K. M.; Kwon, Y. D.; Jang, Y. R.; Yoo, K. H.; Choo, D. J.; Jang, J. *Thin Solid Films* **2002**, *417*, 171.
(23) Caruge, J. M.; Halpert, J. E.; Bulovic, V.; Bawendi, M. G. *Nano. Lett.* **2006**, *6*, 2991.
(24) Huang, J. M.; Yang, Y.; Xue, S. H.; Yang, B.; Liu, S. Y.; Shen, J. C. *Appl. Phys. Lett.* **1997**, *70*, 2335.
(25) Dabbousi, B. O.; Bawendi, M. G.; Onitsuka, O.; Rubner, M. F. *Appl. Phys. Lett.* **1995**, *66*, 1316.
(26) http://hyperphysics.phy-astr.gsu.edu/hbase/vision/cie.html#c1.
(27) Aharon, E.; Kalina, M.; Frey, G. L. *J. Am. Chem. Soc.* **2006**, *128*, 15968.

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