

Luminescence from processible quantum dot-polymer light emitters 1100–1600 nm: Tailoring spectral width and shape

L. Bakueva,^{a)} G. Konstantatos, L. Levina, S. Musikhin, and E. H. Sargent

Department of Electrical & Computer Engineering, University of Toronto, Toronto M5S 3G4, Canada

(Received 22 December 2003; accepted 5 March 2004; published online 20 April 2004)

Electroluminescent devices combining two families of PbS colloidal quantum dots to achieve spectrally tailored two-color emission are reported. Depending on device structure selected—the use of two separated layers versus a mixture of nanocrystals—the structures demonstrated light emission either in two infrared frequency peaks corresponding to the spectral region 1.1–1.6 μm or in a wide band spanning this same spectral region. Separated-layer devices exhibit wide tunability in the relative intensity of the two peaks by varying excitation conditions. Replacing oleate with octadecylamine ligands increases the internal electroluminescence efficiency to 3.1%. © 2004 American Institute of Physics. [DOI: 10.1063/1.1737072]

Solution-processible devices based on colloidal quantum dots embedded in a semiconducting polymer matrix represent a promising basis for monolithic integration of optoelectronic functions on a variety of substrates including silicon, glass, III–V semiconductors, and flexible plastics. Reports of electroluminescence in the visible and infrared,¹ as well as photovoltaic² and optical modulation³ phenomena in the visible, point to the possibility of combining a variety of useful optical and optoelectronic functions on a single platform.

Much work, including that on size-selective precipitation of nanocrystals to achieve the greatest possible monodispersity, has focused on narrowing emission, absorption, and modulation linewidths. Once such control over spectral properties has been achieved, it then becomes attractive to combine a number of different families of quantum dots in order to engineer a broader spectral shape: applications of such broadband or spectrally engineered devices include multi-color light emitters for color displays; white light emitters for illumination; and, in the infrared, multi-wavelength emitters for coarse wavelength-division multiplexing and code-division multiple access.⁴

We report the fabrication and investigation of electroluminescent devices which combine two families of colloidal quantum dots to achieve spectrally tailored two-color emission. Our work employs PbS quantum dot nanocrystals in the 1.1–1.6 μm spectral range.

Colloidal PbS nanocrystals were synthesized using an organometallic route requiring a single, short nucleation followed by slower growth of existing nuclei. We used the hot injection technique with rapid addition of reagents into the reaction vessel that contains the hot coordinating solvent.⁵ We modeled our synthesis after the method of Ref. 6 to provide monodisperse colloidal PbS nanocrystals over a wide range of possible sizes. For our subsequent experiments, two groups of nanocrystal with different sizes were chosen. Group I labels the larger nanocrystals with smaller effective band gap; and group II the smaller nanocrystals.

As in Ref. 7, a postsynthetic ligand exchange was per-

formed to replace the initial oleate ligands used for passivating the nanocrystal surface with octadecylamine (C18). In contrast, Ref. 7 reported the use of octylamine (C8). From a donor–acceptor analysis, the alkylamines act as a Lewis base. The electron-donating groups (the alkyl chains) increase the basicity of the capping ligands, providing an increase in electron density on the nitrogen atom in the amines. Strongly polarized capping molecules create a surface dipole layer, easing the coordination of ligands to the nanocrystal surface and decreasing the density of surface traps, resulting in an increase of the luminescence quantum yield. The ligand exchange also results in etching of nanocrystals, increasing their effective band gap. This effect is seen in Fig. 1, in which the absorption spectra of two groups of nanocrystals before and after ligand exchange are shown. Following exchange, the effective band gap of passivated nanocrystals used for further technological operations is 0.947 eV ($\lambda = 1309$ nm) for group I and 1.106 eV ($\lambda = 1121$ nm) for group II.

Light-emitting structures were fabricated on glass substrates with a transparent indium tin oxide anode electrode covered with layer of poly(*p*-phenylenevinylene) (PPV). Devices were fabricated which employed two distinct nanocomposite layer structures. The first (Fig. 2) consisted of a layer

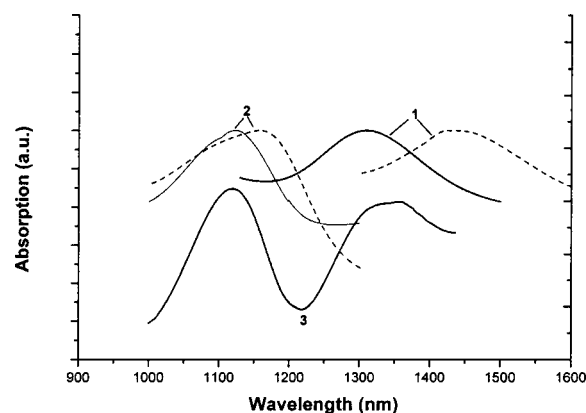


FIG. 1. Absorption spectra of two groups of nanocrystals (1,2) in solution before (dashed lines) and after (solid lines) ligand exchange. Curve 3 provides the absorption spectrum of the light-emitting structure.

^{a)}Author to whom correspondence should be addressed; electronic mail: luda.bakoueva@utoronto.ca

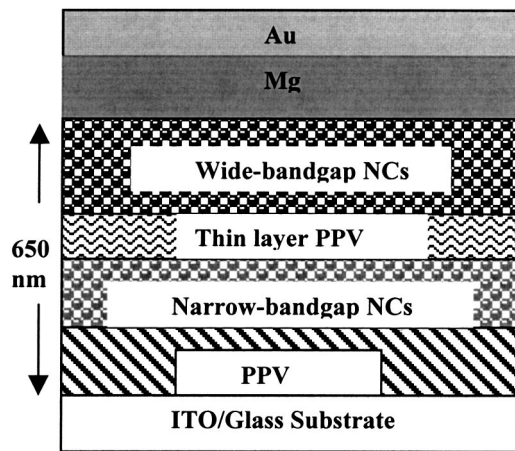


FIG. 2. Schematic view of the device structure.

of narrow-gap group I nanocrystals; an intervening hydrophilic polymer layer to prevent mixing between the families; and a layer of widergap group II nanocrystals twice as thick as the first layer. The total thickness of the whole polymer-nanocrystal composite was measured using the Dektak profilometer to be 650 nm. The second structure employed a uniform mixture of the two families of nanocrystals inside a PPV matrix, resulting in total thickness of 1 μm .

Both structures exhibited absorption spectra with two maxima corresponding to the two types of nanocrystals (Fig. 1). The structures were investigated using optical methods and then completed via the deposition of a metallic cathode similar to that used in Ref. 7 comprising a Mg film obtained by vacuum evaporation and protected from the ambient atmosphere by a thin capping Ag film. In both device structures, the active region is separated from the anode by a polymer layer, but is in direct contact with the cathode, as required⁸ by the less efficient transport of electrons in PPV.

Photoluminescence spectra of the structures were obtained using continuous wave excitation by a semiconductor laser at 831 nm. At this wavelength the polymer matrix is transparent and the exciting light absorbed only in the nanocrystals. The resulting spectra for a typical sample with two separate layers of different nanocrystals are shown in Fig. 3.

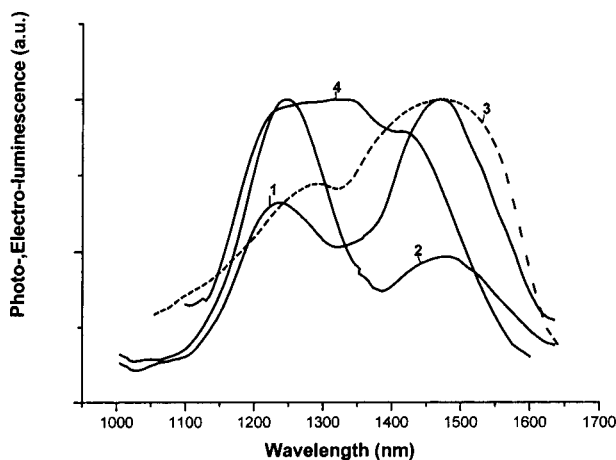


FIG. 3. Photoluminescence spectra of the double-layer structure for excitation through the substrate (1) and from the upper side (2), its electroluminescence spectrum (3), and photoluminescence spectrum of the mixture layer (4).

These have two distinct peaks at $\lambda=1240$ nm and $\lambda=1475$ nm. Comparison with the absorption spectra shows a noticeable Stokes shift $\cong 106$ meV, the same for both peaks. Relative intensities of the peaks depend on the geometry of excitation: illumination through the substrate increases absorption and hence luminescence in the narrow-gap nanocrystal layer adjacent to the substrate, while illumination from the opposite side excites preferentially the wide-gap layer adjacent to the illuminated surface. If we define the absorbance of the narrow- (group I) and wide-gap (group II) layers to be, respectively, α and β , then for illumination from the substrate the fractions of absorbed light for these two layers are α and $\beta(1-\alpha)$ so that the ratio of luminescence peak intensity should be $\alpha/\beta(1-\alpha)$. For illumination from the opposite side this ratio is $\alpha(1-\beta)/\beta$. Comparing these formulas with relative peak intensities for curves 1 and 2 in Fig. 3, we find that $\alpha \approx 30\%$ and $\beta \approx 60\%$, in good agreement with the thickness ratio of these two layers mentioned above.

In contrast to the two-layer structures, those containing a mixture of different nanocrystals demonstrated one wide luminescence band covering the entire spectral region of interest, 1.1–1.6 μm . Since the absorption spectrum in the same samples does have a distinctive double-peak structure (Fig. 1), the widening of the spectrum is attributed to reabsorption, reemission, as well as interdot energy transfer among nanocrystals within and between the two groups. In the structures with well-separated layers, the latter process is expected to be negligible.

Prior to electroluminescence experiments, the samples were subjected to electrophysical measurements with the complex impedance measured in large intervals of applied bias and signal frequencies. The current–voltage characteristic in all samples was almost symmetric and slightly super-linear. Noticeable electroluminescence began at $V=3$ V. All data for spectral dependence and internal efficiency of electroluminescence provided herein were obtained at biases of $V=3.5$ V and current densities of 10 mA/cm².

Curve 3 in Fig. 3 shows the spectrum of electroluminescence in a two-layer structure. The position of the long-wavelength peak is almost the same as in the photoluminescence spectrum while the short-wavelength peak has a noticeable redshift compared to the photoluminescence spectrum. In contrast to photoluminescence, electroluminescence can be measured only through the transparent substrate. The shift of short-wavelength peak might be attributed to partial reabsorption by the layer of group I nanocrystals.

Absolute values of internal electroluminescence efficiency were found to vary from sample to sample; the largest measured value was 3.1%.⁷ When the polarity of the applied bias was reversed, electroluminescence was still observed, consistent with the essentially symmetric character of the current–voltage characteristic.

In the present work, the approach to ligand exchange was found to play a crucial role in the realization of increased-efficiency electroluminescent devices. The nanocrystals capped by oleate ligands as a result of the synthetic procedure exhibited a good photoluminescence efficiency as high as 23% in solution. When used to make devices, these nanocrystals exhibited no measureable electroluminescence.

It was necessary to use nanocrystals on which ligand ex-

change had been carried out, thus which were capped with octadecylamine, to achieve 3.1% measured electroluminescence internal efficiency. We reported previously⁷ the necessity of carrying out ligand exchange to achieve an observable electroluminescence signal. We noted that the ligand exchange alters both the end function group passivating the nanocrystal surface and also the length of the ligand which presents a potential obstacle to energy transfer from electrodes and polymer matrix into nanocrystals. The present work suggests that the longer octadecylamine ligand used in the present work, compared to the octylamine ligand used in Ref. 7, provides more effective passivation while not seriously impeding energy transfer.

In sum, we have fabricated and investigated nanocomposite structures containing PbS nanocrystals of two different sizes which allow tailoring of the emission spectrum of luminescent devices. Depending on device structure selected—in particular the use of two separated layers versus a mixture of nanocrystals—the structures demonstrated light emission either in two infrared frequency peaks corresponding to the spectral region 1.1–1.6 μm or in a wide band spanning this same spectral region. For two-color structures, it was shown that it is possible to vary the relative intensity

of the peaks over a wide range through the choice of excitation conditions. The replacement of oleate with octadecylamine ligands allowed us to increase the internal efficiency of electroluminescence to 3.1%.

The authors are indebted to A. Shik for valuable discussions. They acknowledge Nortel Networks, the Natural Sciences and Engineering Research Council of Canada, and Materials and Manufacturing Ontario for support of this research.

¹*Handbook of Organic-Inorganic Hybrid Materials and Nanocomposites*, edited by H. S. Nalva (American Scientific, Stevenson Ranch, 2003).

²W. U. Huynh, X. Peng, and A. P. Alivisatos, *Adv. Mater.* (Weinheim, Ger.) **11**, 923 (1999).

³S. Coe, W.-K. Woo, M. Bawendi, and V. Bulovic, *Nature* (London) **420**, 19 (2002).

⁴A. Stok and E. H. Sargent, *IEEE Network* **14**, 42 (2000).

⁵M. A. Hines and G. D. Scholes, *Adv. Mater.* **15**, 1844 (2003).

⁶C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).

⁷L. Bakueva, S. Musikhin, M. A. Hines, T.-W. F. Chang, M. Tzolov, G. D. Scholes, and E. H. Sargent, *Appl. Phys. Lett.* **82**, 2895 (2003).

⁸A. Shik, S. Yu, E. Johnson, H. Ruda, and E. H. Sargent, *Solid-State Electron.* **46**, 61 (2002).