Extended Abstracts of the 2017 International Conference on Solid State Devices and Materials, Sendai, 2017, pp95-96

B-4-01 (Invited)

The Excitonics in Photonic Colloidal Nanostructures and Devices

Heejae Lee[1], Yujin Kim[1], and Seonghoon Lee [1]

[1] Seoul National Univ.
1 Gwanak-ro, Gwanak-gu, NS 60
Seoul 08826, Korea
Phone: +82-2-880-1456 E-mail: shnlee@snu.ac.kr

Abstract

Ever since colloidal semiconductor quantum dots were known as nanocrystalline nonbleachable giant artificial atoms with facile color tunability, high color purity, and high photoluminescence quantum yield, the practically useful highly bright and efficient, thin flexible less-than 6 V driven red-, green-, blue-, natural-look white light-emitting devices (R/G/B/white-LEDs), and UV light-emitting devices have been realized. In addition, real time traceable bioconjugated quantum dot probes for bioimaging were developed. .

1. Introduction

Colloidal quantum dots(CQDs) have given great attention for the last decades owing to their unique electrical and optical properties that depend on their size and shape, which is termed the "quantum confinement effect (QCE)" [1-2].

Quantum dots are semiconductor nanocrystals (~1–100 nm) or so-called giant artificial atoms with quantum confinement effect, quantized electron and hole states, and δ function-like densities of states. Compared with self-assembled quantum dots under certain conditions during molecular beam epitaxy or metal organic vapor phase epitaxy, colloidal quantum dots by the wet chemical synthetic methods are promising for commercial applications, due to the facile scale-up and the convenient synthetic set-up. The spectra of colloidal quantum dots are inhomogeneously broadened due to fluctuations in quantum dot size, shape, and composition. Their typical inhomogeneous line widths are >20 meV, but can be reduced by the uniform size and shape, composition control. Due to their easy color tunability ranging from near ultraviolet to visible to near infrared, broad excitation profile and narrow spectral emission bandwidth, high photoluminescence quantum yield, and optical multiplexing- multiple colors and intensities are combined to encode genes, proteins and small-molecule libraries-, CQDs have currently been applied in bioimaging and electronic devices [3-4].

Here, we report very bright, low-voltage driven, red-, green, blue-, white- quantum dot light-emitting devices (QLEDs), and ultraviolet QLEDs enabled by the direct exciton formation within QD active layers in an organic–inorganic hybrid device structure and bioconjugate QDs for real time bioimaging. The practically useful highly bright and efficient, thin flexible less-than 6 V driven R/G/B/white-QLEDs, and UV QLEDs, and bioconjugated quantum dot probes for bio-imaging were achieved.

2. Method of Approach

CQDs were synthesized by wet chemical methods, or so-called molecular beaker epitaxy. By tuning their sizes and shapes, we can control excitonic energies, and thus we can realize the desired absorption and emission. More specifically described, we produce artificial atoms, using the La Mer fast nucleation and slow growth, aggregating growth & oriented attachment (or epitaxial attachment) via specific reactive facets, and Ostwald ripening processes.

The QD surface are closely associated with the performance, photostability, and solubility of CQDs. In order to achieve the high photoluminescence quantum yield and photostability, the surface states associated with surface atoms on CQDs were carefully passivated. Utilizing the reactivity differences in precursors, we produce the artificial atoms the structure of which have the core with energy-gradient shell that is helpful to suppress Auger recombination processes, in a large scale by single-step synthetic method [5-6]. Fig. 1 shows the synthesis scheme for the CQDs having the core with energy-gradient shell structure.

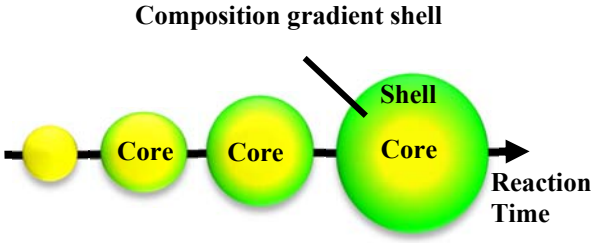

Fig. 1 Composition gradient shell growth using the reactivity difference between precursors

With a layer-by-layer assembly method combined with the patterning method, we have fabricated various useful optoelectronic devices. The layer-by-layer (L-b-L) assembly employs specific interaction forces such as electrostatic interactions, hydrogen bonding, or covalent bonding between each deposited layer. The multilayer films were fabricated by L-b-L assembly method using electrostatic interactions between each layer through the sequential deposition of oppositely charged QDs onto the substrates. The L-b-L assembly method ensured the formation of a homogeneous and uniform layer over a large area [7].

The hybridization of QDs with conducting polymers or biomolecules through the chemical bonding between them were done to enhance good optical and electrical transport properties or to get good bioimaging probes. The uniformity and homogeneity of hybrid films were examined on both the nanometer and micrometer scales in terms of fluorescent optical microscopy and cross sectional TEM analysis [8].

The semiconductor quantum dots are very stable inorganic nanocrystals, so they have a valence band edge located deeply (~ -6 to -7 eV) due to strong chemical bonding. We introduce easily processable, high-performance, red, green, and blue (RGB), or UV QLEDs with the inverted device structure. The inverted device structure consists of the patterned ITO (cathode), ZnO nanoparticle film as an electron injection layer (EIL) and an electron transporting layer (ETL), organic conjugated molecules as a hole transporting layer (HTL), MoO_3 as a hole injection layer, and Al (anode).

3. Results and Discussions, Conclusion

We synthesized various types of colloidal QDs, CdSe@CdS@ZnS, CdSe@ZnS, and $Cd_{1-x}Zn_xS$@ZnS as the red, green, and blue & UV emitters, respectively, possessing high photoluminescence (PL) quantum yields (70−80%) at room temperature, by the wet chemical method described earlier. In addition, for the purpose of bioimaging, highly luminescent and cost-effective quantum dot (QD)-neutravidin (NTV) bioconjugates were synthesized to probe the tyrosine kinase B (TrkB) receptors distributed in the cultured hippocampus neurons. QD-protein bioconjugates were also synthesized to study the structural and functional plasticity of Aplysia mechanosensory presynaptic neurons in relation with the mechanism underlying learning and memory [9-10].

Such toxic elements as Cd, Pb, and Hg are restrained by the restriction of hazardous substances (RoHS) directive. Since then, our research group have sought environmentally benign and highly photoluminescent CQDs such as $In_{1-x}Ga_xP$@GaPZnS alloy-core with chemical composition gradient shell.

Single or multicolored QLEDs in a large-area array were fabricated by the L-b-L assembly method ensuring the formation of a homogeneous and uniform layer over a large area combined with patterning techniques such as inkjet printing or micro contact printing (μCP). One of the most advantageous features of QLEDs fabricated from QD multilayer films is the facile scale-up capability to larger areas without any additional elaborate optimization processes.

The creation, recombination, annihilation, and separation, transport of excitons were investigated in colloidal quantum dot-embedded carbon-based matrix. The optimum thickness of the exciton-recombination zone was found to be 1.2 to 1.5 monolayers for the best QLED performance. And thus, 2 monolayers of QD active emission region are more than good enough in QLED devices. The light emission in various QLEDs was enabled by the direct exciton formation within gigantic artificial atom-embedded active layers in a conducting polymer matrix. If the hole mobility through a conducting polymer is improved or new crystalline conducting polymers are applied, then we still have a room to enhance further the performance of QLEDs.

The thin flexible highly bright, efficient, low-voltage driven red, green, blue, and natural white light-emitting devices (R/G/B/white-LEDs), have been accomplished. The luminances of red-, green-, and blue-emitting devices are 23040, 218800, and 2250 cd/m^2 at the maximum, respectively. In addition, the external quantum efficiencies (EQEs) of the RGB devices were 7.3, 5.8, and 1.7%, respectively. White-QLEDs with a luminance of 5,000 cd/m^2 at an applied bias less than 6 V and external quantum efficiency of 1% or more have been successfully realized. Genuine UV-emitting QLEDs with a 2.5-nm-sized CdZnS ternary core and a ZnS shell were achieved. The irradiance is as high as 2.0−13.9 mW/cm^2 at the peak wavelengths of 377~390 nm, several orders of magnitude higher than that of any other thin-film UV LEDs developed so far. Practically useful, thin flexible RGB-, White-, and UV- quantum dot light-emitting devices are shown below in the Fig. 3.

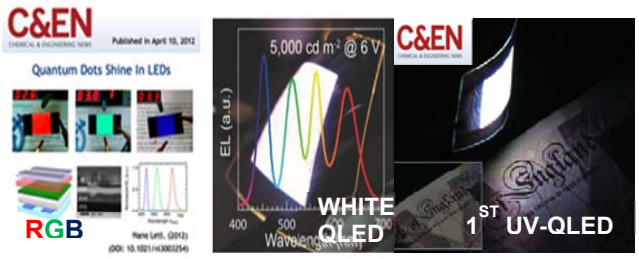

Fig. 3 Thin Flexible RGB-, White-, and UV- Quantum Dot Light-Emitting Devices: RGB QLEDs (left); White- or Natural Look QLEDs (middle); UV-QLEDs (right)

Acknowledgements

This work was financially supported by the National Research Foundation of Korea (NRF) through the grants (NRF-2014R1A2A1A11054246)

References

[1] L. Brus, J. Phys. Chem. **90** (1986), 2555–2560.
[2] A. P. Alivisatos, Science **271** (1996) 933–937.
[3] V. I. Klimov , Nanocrystal Quantum Dots, CRC Press, New York, U.S.A. (2010) 2nd. edn.
[4] B. A. Kairdolf, A. M. Smith, T. H. Stokes, M. D. Wang, A. N. Young, and S. Nie, Annu. Rev. Anal. Chem. **6** (2013) 143-162
[5] W. K. Bae, H. Hur, K. Char, and S. Lee, Chem. Mater. **20** (2008) 531-539.
[6] W. K. Bae, M. K. Nam, K. Char, and S. Lee, Chem. Mater. **20** (2008) 5307-5313.
[7] W. K. Bae, J. Kwak, J. Lim, D. Lee, M. K. Nam, K. Char, C. Lee, and S. Lee, Nano Lett., **10(7)** (2010), 2368-2373. Highlighted in MRS Bulletin, Aug. (2010) 35.
[8] J. Kwak, W. K. Bae, M. Zorn, H. Woo, H. Yoon, J. Lim, S. W. Kang, S. Weber, H.-J. Butt, R. Zental, S. Lee, K. Char, C. Lee, Adv. Mater., **21** (2009) 5022-5026.
[9] J. W. Park, A.-Y. Park, S. Lee, N.-K. Yu, S.-H. Lee, B.-K. Kaang, Bioconj. Chem. **21** (2010) 597-603.
[10] A.-Y. Park , Y.-S. Chae, S.-H. Lee, B.-K. Kaang, S. Lee, J. Phys. Chem. B, **117(17)** (2013) 4779-4788.
[11] J. Kwak, W. K. Bae, D. Lee, I. Park, J. Lim, M. Park, H. Cho, H. Woo, D. Y. Yoon, K. Char, S. Lee, C. Lee, Nano Lett., **12**(5), (2012) 2362-2366, also reported in C&EN News in April 10, 2012, and in PHYSORG.com in April 20, 2012.
[12] J. Kwak, J. Lim, M. Park, S. Lee, K. Char, C. Lee, Nano Lett., **15** (6) (2015) 3793–3799, also reported in C&E News in May 27, 2015