Hybrid Colloidal Quantum Dot Photonic Devices

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ABSTRACT

In recent years, colloidal quantum dots (CQDs) have been the focus of attention due to their highly efficient illumination, narrow linewidth emission, and widely tunable emission wavelength. Various types of devices have been implemented for the photonic devices to incorporate these novel materials. Both photon generation and absorption can be accomplished by CQDs and the corresponding light emitting diodes and solar cells can be designed to utilize their special characteristics. In this talk, we will provide our latest progress on such devices and the past experience we had in our lab. The highly reliable CQD package will play a crucial rule for the next generation photonic devices.

1 INTRODUCTION

Since the introduction of doped gallium nitride (GaN) material in the 1990's, the semiconductor based light emitting diodes have become the essential part of the display and lighting technologies[1]. The red, green and blue colors that can be provided by different combination of semiconductor compositions complete the requirement of full-color display and further increase the possibility of new applications. However, it is quite difficult to epitaxial grow the semiconductor active material of three colors on the same substrate (like sapphire or silicon or GaAs) because of the huge lattice mismatch in the crystal structure. To solve this problem, various solutions have been proposed in the past, for example, wafer/chip bonding, nanowire growth, etc.. Using light conversion materials is one of the candidates among all these solutions and thanks to the strong research and development, very good materials with high efficiencies are available for engineers to work on device integration and package. The choices of light conversion materials are abundant, from regular phosphors, nano-phosphors[2], polymers[3], to colloidal quantum dots[4]. Different formats such as liquid, gel, or solid state can also be found according to their chemical characteristics [5, 6].

Colloidal quantum dots (CQDs) are the particles in nano-meter scale (usually between 2 to 20nm), and they are usually made of semiconductor materials due to their high photonic efficiencies in illumination and absorption. When the particles are shrunk into this tiny scale, the quantum confinement effect is very strong. As shown in Fig. 1, although bearing the same energy bandgap (Eg), the larger quantum dot (on the left hand side) will have less energy separation between conduction and valance bands. The smaller dots, on the other hand, will have larger energy separation, and thus have shorter emission or absorption wavelength. In this figure, we can conclude that d1>d2, and E1<E2. The principle that dictates this phenomenon resides solely in the physical size of the dots, which can be controlled by their chemical synthesis processes. This tunability in emission wavelength makes CQD materials an excellent candidate for full-color, wide-gamut display applications. With the same material, the coverage of entire visible color is possible in quantum dot regime.





2 DEVICE FABRICATION

To incorporate the colloidal quantum dots into photonic devices, there are two different methods: 1. the electrical pumping method; 2. the photonic excitation method. In the first method, the proper chemical substances need to be used to have electrons and holes to be conducted into the quantum dot layers. The band alignment is the key for this method, and improper band structure can often lead to high resistance in the devices and cause extra heat generated in the devices. In most of the cases, the high driving voltage can be seen in such devices and the thermal issue can cause low efficiencies and bad reliability. In the meantime, this type of the devices has much thinner physical structure and thus can be applied in flexible substrate and other volume-critical cases.



Fig. 2. The schematic of the hybrid integration of colloidal quantum dots with traditional photonic devices: (a) a light emitting diode, and (b) a solar cell device.

The second method is guite different from the first one. The colloidal quantum dots in this method do not need to be electrical pumped and thus the band-alignment issue does not exist. The photonic excitement is used to have the CQD performing its duty in the device. The high energy photons can be absorbed and re-emitted by colloidal quantum dots. This re-emission process, although bears the Stoke's shift and loss, can ease the design of the device greatly. Either in light emitting condition or light absorbing condition, the colloidal quantum dot layer can be placed properly in the traditional photonic devices. As shown in Fig. 2, the light emitting device can have a layer of CQD on the surface of the pumping LED chip. The mixture of CQD and silicone material is not that different from the traditional phosphors package of the white-light LED, and so it will be ready to be adapted into the manufacturing processes once we solve the reliability and toxicity issues of the quantum dots. On the solar cell side, the luminescent down-shifting (LDS) effect can be applied to convert the ultra-violet (UV) photons impinging on the surface of the semiconductor solar cell into the visible ones. As shown in Fig. 2(b), the implementation can be seen as the colloidal quantum dot layer coated on the surface of a regular solar cell device. Because of the high density of surface traps in the semiconductor and air interface, the photo-generated electron-hole pairs that are produced by UV photons near the surface can be easily consumed by these traps and not get collected by the external electrodes. The LDS conversion can help some of UV photons to become visible ones which can be effective absorbed and collected deeper into the semiconductor. Thus the overall power conversion efficiency (PCE) can be enhanced by this thin colloidal quantum dot layer.

Finally, after the device fabrication and package procedures, the CQD-contained device can be seen in Fig.

3 (a) and (b), with and without electrical current injection.



Fig. 3. The CQD coated light emitting diode (a) no injection current (b) with injection current.

3 RESULTS AND DISCUSSIONS

In this section, we will discuss how we interpret the outcome of the hybrid colloidal quantum dot devices. Two different aspects can be displayed: the light emitting one and the light absorbing one. In both cases, we can observe the enhancement through the photonic spectrum and external quantum efficiency of the devices. The comparison between the results with and without quantum dot layer is very crucial in terms of evaluation of the effectiveness of our methods.

For the emission device, the optical spectrum before and after CQD coating can be seen and analyzed in Fig. 4(a). Before the CQD coating, the only peak in the spectrum is the pumping source, usually a UV or blue LED. After the coating, a combination of the pumping source and the CQD emission can be seen at the same time. The color conversion efficiency (PCE) can be calculated by counting the difference of the spectra before and after [5, 7]:

$$PLQY = \frac{\# of excited QD photons}{\# of pumping photons} = \frac{\int \frac{\lambda}{hc} (I_{em}^{QD}(\lambda) - I_{em}^{ref}(\lambda)) d\lambda}{\int \frac{\lambda}{hc} (I_{ex}^{ref}(\lambda) - I_{ex}^{QD}(\lambda)) d\lambda}$$
(1)

, where the $l_{em}{}^{QD}$ and $l_{em}{}^{ref}$ are the spectra intensity at the wavelength of QD emission, and $l_{ex}{}^{ref}$ and $l_{ex}{}^{QD}$ are the spectrum of the pumping source. All the calculation are converted into the number of photons in the spectra and thus with the coefficient of (λ /hc) in the formula. From our experiments in the past, as high as 70% of conversion efficiency can be found in the ionic-sealed CQD samples[5]. The high PCE is crucial for the energy saving and also for the less generation of heat in the system.

For the solar cell part, the spectra of external quantum efficiency (EQE) can reveal the extent of improvement due to CQD coating[8, 9]. As shown in Fig. 4(b), the comparison between the before and after EQE spectra can demonstrate the enhancement at shorter wavelength part. Since the wavelength dependent

absorption is expected in the ordinary solar cell, certain wavelength dependence on the CQD emission towards EQE enhancement can also be expected. From the past experience, the green color CQD performed best when compared to other colors in the single junction solar cell[10]. In the dual or multiple junction solar cell, the current-matching condition needs to be fulfilled and thus impose certain restrains on the effectiveness of addition of the CQD layer[11].



Fig. 4. (a) the emission spectra between pumping source and the hybrid CQD LED. (b) the EQE spectra comparison before and after CQD coating.

4 CONCLUSIONS

To sum up, the introduction of CQD coating in the traditional photonic devices such as light emitting diodes and solar cells can be achieved via various package methods and the improvement in efficiency can be observed clearly. With good design of package methods and incorporation of filling materials, the CQD particles can have good reliability as well as good efficiency. With its wide coverage in the photonic spectrum, we believe that the colloidal quantum dot can play an important role in the

next generation of high-performance photonic devices.

REFERENCES

- A. P. Alivisatos, "Semiconductor Clusters, Nanocrystals, and Quantum Dots," *Science*, vol. 271, no. 5251, pp. 933-937, February 16, 1996 1996.
- [2] H. Chander, "Development of nanophosphors—A review," *Materials Science and Engineering: R: Reports*, vol. 49, no. 5, pp. 113-155, 2005/06/16/ 2005.
- [3] H.-Y. Lin *et al.*, "Fabrication of Flexible White Light-Emitting Diodes from Photoluminescent Polymer Materials with Excellent Color Quality," *ACS Applied Materials & Interfaces*, vol. 9, no. 40, pp. 35279-35286, 2017/10/11 2017.
- [4] S. C. Hsu *et al.*, "Fabrication of a Highly Stable White Light-Emitting Diode With Multiple-Layer Colloidal Quantum Dots," *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 23, no. 5, pp. 1-9, 2017.
- [5] S. C. Hsu *et al.*, "Highly Stable and Efficient Hybrid Quantum Dot Light-Emitting Diodes," *IEEE Photonics Journal*, vol. 7, no. 5, pp. 1-10, 2015.
- [6] C.-W. Sher *et al.*, "A high quality liquid-type quantum dot white light-emitting diode," *Nanoscale*, 10.1039/C5NR05676D vol. 8, no. 2, pp. 1117-1122, 2016.
- [7] K. Suzuki *et al.*, "Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector," *Physical Chemistry Chemical Physics*, 10.1039/B912178A vol. 11, no. 42, pp. 9850-9860, 2009.
- [8] H.-C. Chen *et al.*, "Enhanced efficiency for c-Si solar cell with nanopillar array via quantum dots layers," *Optics Express*, vol. 19, no. S5, pp. A1141-A1147, 2011/09/12 2011.
- [9] C.-C. Lin *et al.*, "Highly efficient CdS-quantum-dotsensitized GaAs solar cells," *Optics Express*, vol. 20, no. S2, pp. A319-A326, 2012/03/12 2012.
- [10] H.-V. Han *et al.*, "A Highly Efficient Hybrid GaAs Solar Cell Based on Colloidal-Quantum-Dot-Sensitization," *Scientific Reports*, Article vol. 4, 07/18/online 2014.
- [11] S. Hsu, Y. Huang, Y. Kao, H. Kuo, R. Horng, and C. Lin, "The Analysis of Dual-Junction Tandem Solar Cells Enhanced by Surface Dispensed Quantum Dots," *IEEE Photonics Journal*, vol. 10, no. 5, pp. 1-11, 2018.