

Chapter 16

Synthesis of InP Quantum Dots and Their Application

Hung-Chia Wang and Ru-Shi Liu

Abstract For more than two decades, research interest has been focused on groups II–VI of quantum dots (QDs) because of their potential applications in lasers, light-emitting diodes, and biological imaging. Given the highly intrinsic toxicity of cadmium, the biological applications of Cd-QDs have been limited. The European Union prohibits the use of Cd-QDs in electronic devices by 2017 (Anc et al. in *ECS J Solid State Sci and Technol* 2:R3071, 2013 [1]). This problem is addressed by developing Cd-free QDs. Groups III–V QDs exhibit narrow full width at half maximum compared with other Cd-free QDs, such as CuInS₂, and are suitable for backlight units. With increasing number of related publications, the main attraction to these semiconductors focuses on the robustness of the covalent bond in groups III–V semiconductor materials rather than the ionic bond in groups II–VI semiconductors. Moreover, the covalent bond can enhance the stability of Cd-free QDs. Indium phosphide (InP) core easily facilitates non-radiative decay because of the surface environment. Thus, other semiconductors with larger bandgap should be preferred over InP to prevent solvent quenching. The recombination of hole and electrons decreases with increasing shell thickness, and the photoluminescence intensity consequently increases. Many synthesis strategies are available for InP QDs, including one-pot, hydrothermal, and continuous heating-up methods. In this chapter, we introduce these three techniques, and an example is given for each method to achieve further understanding.

H.C. Wang · R.S. Liu (✉)

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
e-mail: rslu@ntu.edu.tw

R.S. Liu

Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology,
National Taipei University of Technology, Taipei 106, Taiwan

© Springer Science+Business Media Singapore 2016

R.S. Liu (ed.), *Phosphors, Up Conversion Nano Particles, Quantum Dots and Their Applications*, DOI 10.1007/978-981-10-1590-8_16

473

16.1 Comparison of Three General Synthesis Method of InP/ZnS

16.1.1 One-Pot Method for InP

We introduce high-quality InP/ZnS QDs by using a simple one-pot synthesis method [2]. The precursors of indium and phosphorous are initially mixed in a glove box and then transferred to a three-neck bottle. In this method, the precursors are mixed under low-temperature condition, which can easily tune the color of the QDs compared with the common hot-injection method, in which the precursor is injected into the reaction solution under high temperature. The novel method accelerates nucleation and then rapidly cools to avoid overreaction. Moreover, the hot-injection method is difficult to control. Another advantage of the new method is the small size distribution. By contrast, traditional hydrothermal methods require long-term reaction under high pressure and temperature. The size distribution is very wide, and the yield of particular wavelength is low. The following schematic illustrates an example of one-pot synthesis. In 2012, Yang et al. [2] used indium myristate ($\text{In}(\text{MA})_3$) and tris(trimethylsilyl)phosphine $\text{P}(\text{TMS})_3$ as precursors to synthesize InP QDs. Figure 16.1 shows the synthesis of this method. The precursors are mixed in a glove box. The first step presents a nuclear reaction, and then, zinc stearate is added as a stabilizer. In the nuclear reaction, the proportion of Zn and In can control the specific wavelength. A higher proportion of zinc precursor indicates a stronger blueshift. In the present case, we use a single precursor for another zinc sulfide shell, which is expected to improve its stability and quantum efficiency. This method can tune the wavelength from 450 to 750 nm with high yield.

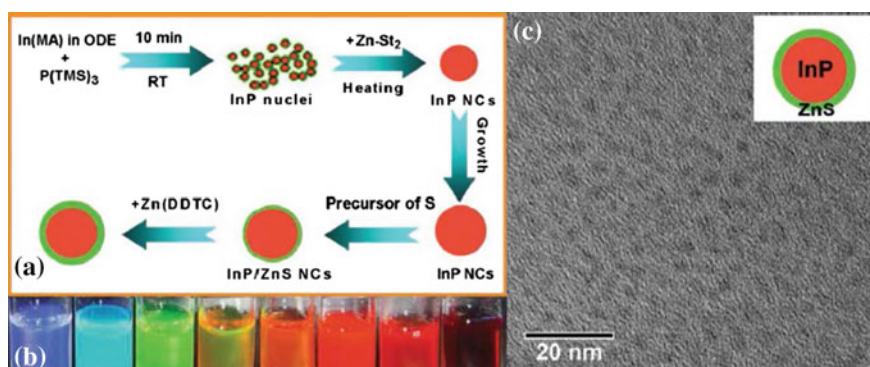


Fig. 16.1 **a** Synthesis of InP/ZnS quantum dots. **b** Image of different wavelengths of InP/ZnS quantum dots excited by UV light. **c** TEM image of resulting InP/ZnS quantum dots. *Inset* in **c** illustrates core-shell structure of InP/ZnS quantum dots. Reproduced from Ref. [2] by permission of John Wiley & Sons Ltd

16.1.2 Hydrothermal Method for InP

In hydrothermal method, the precursor is placed in an autoclave and heated in a high-temperature oven for a long period. This method requires size-selective precipitation to acquire the different wavelengths of QDs. In 2012, Byun et al. [3] proposed a low-toxicity phosphorus compound tris(dimethylamino)phosphine $P(N(CH_3)_2)_3$ to replace the highly toxic $P(TMS)_3$; however, the yield is low, and the synthesis is long; thus, mass production of this application is not easy. The photoluminescence spectra and different wavelengths of QDs under UV-light irradiation are presented in Fig. 16.2.

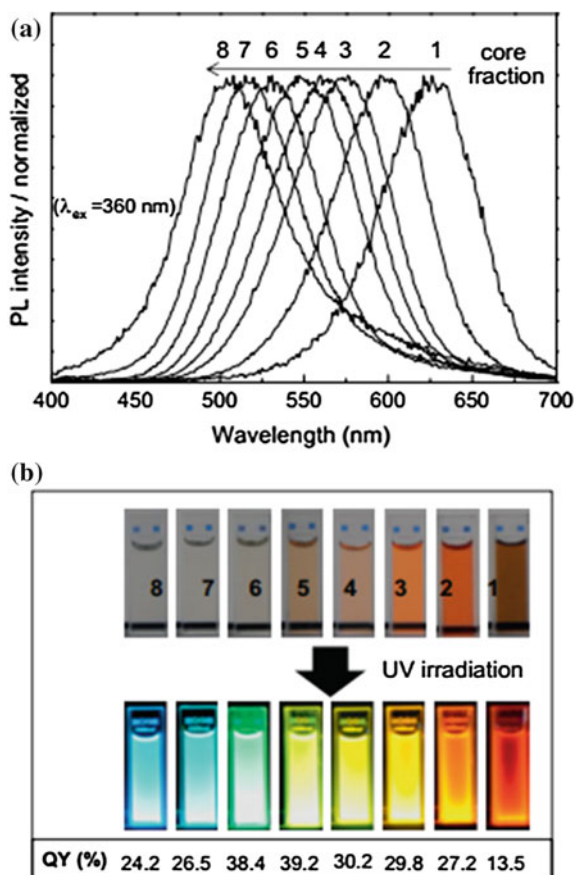


Fig. 16.2 **a** Photoluminescence spectra of InP/ZnS quantum dots. **b** Image of different wavelengths of InP/ZnS quantum dots excited by UV light. Reprinted from Ref. [3]. Copyright 2010, with permission from Elsevier

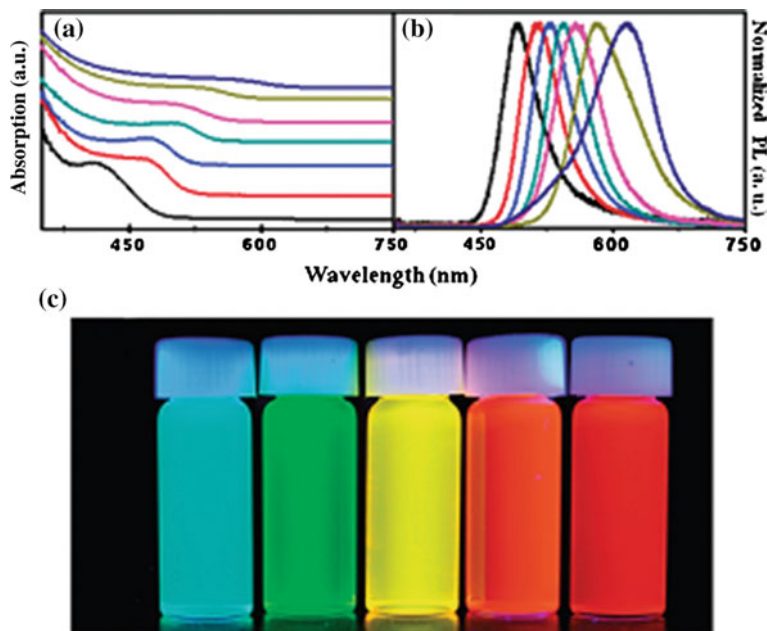


Fig. 16.3 **a** Photoluminescence spectra of InP/ZnS quantum dots. **b** UV spectra of InP/ZnS NCs. **c** Image of different wavelengths of InP/ZnS quantum dots excited by UV light. Reprinted with the permission from Ref. [4]. Copyright 2012 American Chemical Society

16.1.3 Continuous Heating-up Method for InP

Numerous researchers focus on fitting the commercial model to produce QDs, but it is difficult for mass production. In this section, we introduce continuous heating-up method, in which the precursor is slowly injected under stable condition. In 2011, Kim et al. [4] proposed a QD mass production method. In this production method, the precursors are mixed together in a three-neck flask, and then, phosphorous precursor tris(trimethylsilyl) phosphine $P(TMS)_3$ is slowly injected inside the solution with a high-pressure pump. This method can make the QD nucleation uniform and reduce unreacted precursors, thereby significantly increasing the yield. This method can also improve future optimization for mass production of Cd-free QDs (Fig. 16.3; Table 16.1).

16.2 InP Application in Electroluminescence and Photoluminescence

Colloidal semiconductor QDs have shown great potential as light emitters in solar cells and biological imaging. Therefore, we will focus on this type of QDs for its application in light-emitting diodes (LEDs).

Table 16.1 Comparison of the three methods

Synthetic method	Advantages	Drawback
One pot method	<ul style="list-style-type: none"> ✓ High production ✓ Good size distribution ✓ Good quantum efficiency ✓ Short reaction time (core: 60 min) shell: 20 min) 	<ul style="list-style-type: none"> • Vacuum system • Multiple step
Hydrothermal Method	<ul style="list-style-type: none"> • Easy • Non-toxic precursor 	<ul style="list-style-type: none"> • Long time (24 h) • Low production • Wide size distribution
Continuous heating-up method	<ul style="list-style-type: none"> • Mass production 	<ul style="list-style-type: none"> • Long time (10 h) • Multiple step

16.2.1 Introduction of QD-LEDs

QDs have shown great promise as visible emitters for both fabrication of electroluminescent QD-based LEDs and photoluminescence. In this section, we introduce the general model of QD-LEDs and the development of Cd-free QDs in QD-LEDs. The basic principle of QD-LEDs indicates that the emitting layer materials are placed between two electrodes in the form of thin layers. When holes (or electrons) are injected into the emission layer through the hole-transport layer (HTL) from an anode with high-work function or through the electron-transport layer (ETL) from a cathode with low-work function, the electron-hole pairs are injected into the emitting layer and radiated photons by recombination process. For the injection of electrons to conduction band/LUMO levels, low-work function cathodes, such as magnesium, calcium, and lithium fluoride/aluminum, are often used, whereas O₂ plasma-treated indium tin oxide is often employed for high-work function transparent anodes. The schematic is shown in Fig. 16.4. Several advantages of using QDs as emitting layers in these electrically pumped LEDs include tunable emission, saturated color, stability, and processable solution.

In the QD-LED system, we are confronted with four great challenges, which we will introduce and discuss with their corresponding solutions.

1. The mismatch of the QDs between HTL and ETL shows that the well match of QDs is the inorganic ETL and organic HTL (Fig. 16.5) [5].
2. Fluorescence resonance energy transfer (FRET) [6]. FRET phenomenon occurs when the distance between the two QDs is approximately <10 nm. However,

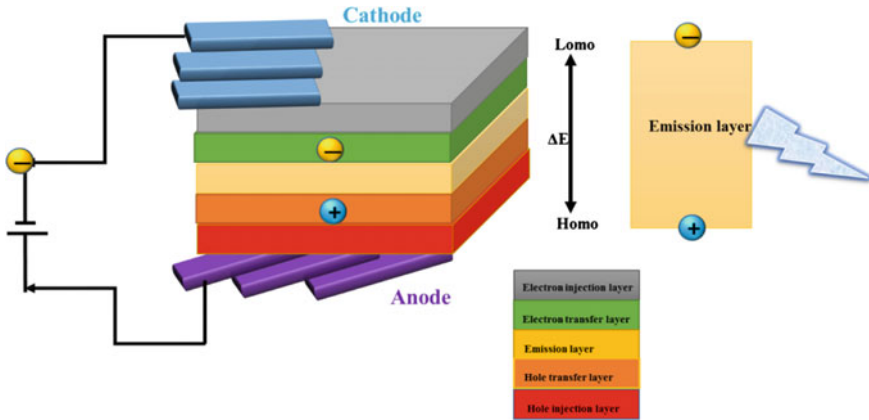


Fig. 16.4 QD-LED structure, QD emitting layer was sandwiched between an organic hole-transport layer (HTL) and an organic electron-transport layer (ETL)

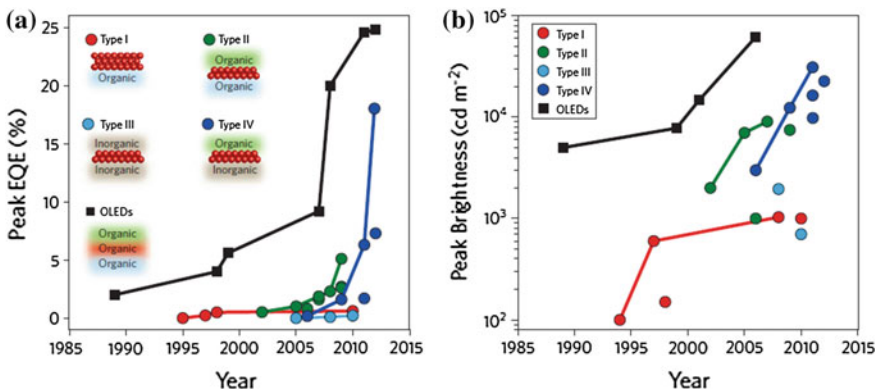


Fig. 16.5 QD-LED structure, with emitting layer sandwiched between an organic hole-transport layer (HTL) and an organic electron-transport layer (ETL). Reprinted by permission from Macmillan Publishers Ltd: Ref. [5]. Copyright 2012

given that the QY of QDs is not 100 %, this process will cause QY decline. When the pieces are coated with QDs into a film structure, these QDs are mostly close-packed and tightly stacked because their quantum yield may decrease from 100 to 10 % compared with solution.

3. Endurance to water, oxygen, and temperature [7]. Little surface oxidation or structural changes result in decreased QY because the shell is very thin. Moreover, when the carrier injection in the electron–hole complex exhibits a similar p–n junction, the QLED device temperature increases, resulting in more excitons. Large thermal kinetic energy can be provided over the limitations of the shell to reach the surface defects, and the electron–hole recombination rate decreases.

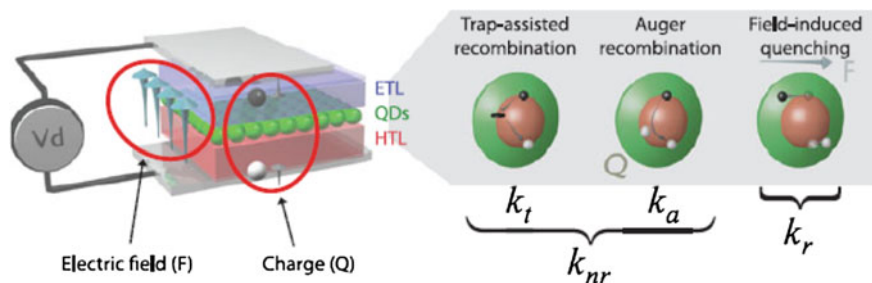


Fig. 16.6 Schematic of QD-LED structure. The QD-emitter layer is located between ETL and HTL. Non-radiative emission involves trap-assisted recombination (k_t) and Auger recombination (k_a). Radiative emission results from the electric field, which is caused by the LED operation process. Reprinted with permission from Ref. [8]. Copyright © Materials Research Society 2013

4. Non-radiative emissions between different layers. In a QD-LED device, the major contributions to non-radiative emissions are the electronic trap states and free-charge carriers. If the QD layer exhibits a surface defect, trap-assisted recombination occurs, in which the hole and electron recombine on the surface defect. Free-charge carriers may cause an imbalance between electron and hole injections. This phenomenon is known as Auger non-radiative recombination, which is clearly illustrated in Fig. 16.6 [8].

Overcoating of QDs is a good solution for high-efficiency QD-LEDs. To date, the optimum EQE device uses red [9], green [10], and blue [11] colors for the overcoating method. Subsequently, the QDs are enlarged by more than 10 nm. Hence, these QDs are called “giant quantum dots.”

16.2.2 InP QD Application in QD-LEDs

QD-LEDs present two types of devices: normal and inverted. The example in this paper [12] is an inverted-type device. Figure 16.7 shows that the ETL is composed of zinc oxide, which is made by the sol-gel method. The HTL is composed of an organic material Tris(4-carbazoyl-9-ylphenyl) amine. This Cd-free device is bright, efficient, and environmentally friendly. The InP/ZnSeS heterostructure of QDs is passivated by ZnSeS shell. This shell can increase the efficient recombination of electron and hole in the emission layer. Thus, the quantum yield is higher than those in previous reports. The resulting QLEDs record 3.46 % of external quantum efficiency and 3900 cd m⁻² of maximum brightness. We speculate that such comprehensive scheme in designing device architecture and structural formulation of QDs provides a reasonable guideline for practical realization of environmentally benign, high-performance QLEDs in the future.

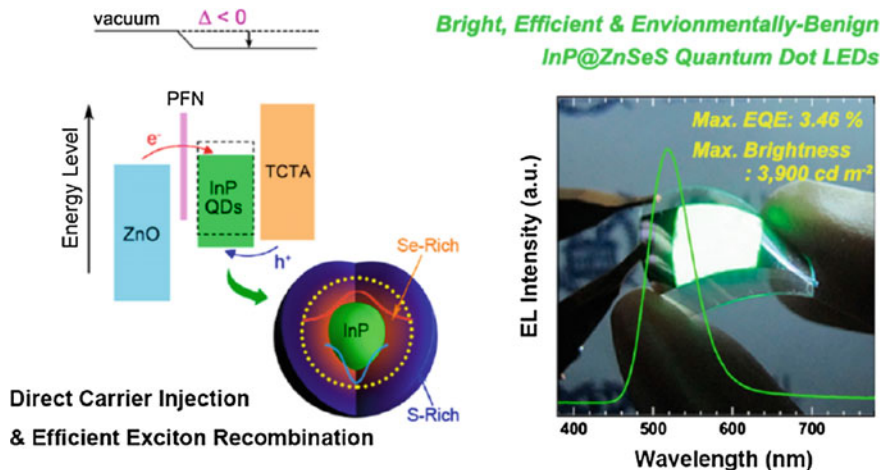






Fig. 16.7 Schematic of Cd-free QD-LED structure, with QDs sandwiched between an organic hole-transport layer (HTL) and an organic electron-transport layer (ETL). Reprinted with the permission from Ref. [12]. Copyright 2013 American Chemical Society

16.2.3 InP QD Application in White-Light LED

In this section, we focus on the application of QDs as LED wavelength converters to decrease the consumption of electrical energy. Studies showed that most lighting devices, such as incandescent and fluorescent lamps, consume high energy. Therefore, many people focus on low-power consumption devices. QD-LEDs present a good alternative. Such LEDs do not only decrease the consumption of energy but also exhibit high color quality. LED purchase provides a potential alternative to other types of lighting devices with higher efficacy, lower power

Table 16.2 Comparison of different types of light source in color temperature, CRI, luminescence, and lifetime

Light source	Color temperature	CRI	Lum. efficacy (lm W ⁻¹)	Lifetime (h)
 Sunlight	5600	100	93	Billions
 Tungsten light bulb	2790	100	<18	1000
 Fluorescent lamp	3000–5000	50–80	50–100	10000
 Commercial white-light LED	3200–6500	70(90)	30–70	50000

White LED

Reproduced from Ref. [13] by permission of John Wiley & Sons Ltd

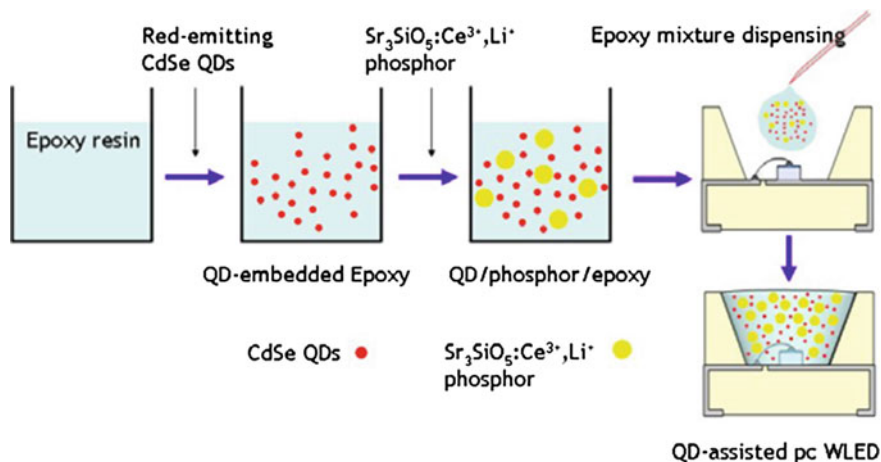


Fig. 16.8 Schematic of fabrication process of QD-assisted phosphor-based white-light LEDs. Reproduced from Ref. [13] by permission of John Wiley & Sons Ltd

consumption, longer lifetime, and a rapid response time. White-light LEDs are recently introduced with blue LED chip and yellow light-emitting $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) phosphors [13]. Although this type of white-light LEDs has shown simple fabrication, high efficacy, and good stability, such LEDs also exhibit a poor color rendering index (CRI), which is a quantitative measure of the ability of a light source to reproduce the colors of various objects faithfully in comparison with an ideal or natural light source (Table 16.2).

To fabricate LEDs with QDs and phosphors, we can follow the method in Fig. 16.8. We initially need to mix the epoxy resin with our QDs and then dry at

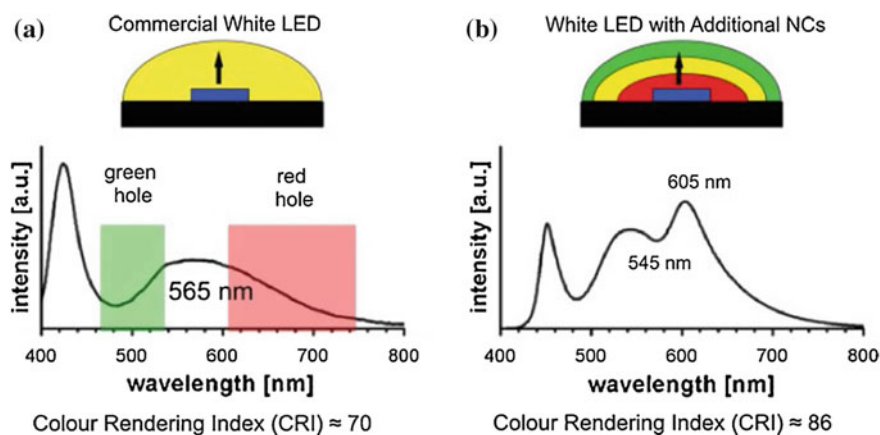


Fig. 16.9 **a** Photoluminescence of commercial white-light LED. **b** Photoluminescence of QD-based white-light LED. Reproduced from Ref. [14] by permission of John Wiley & Sons Ltd

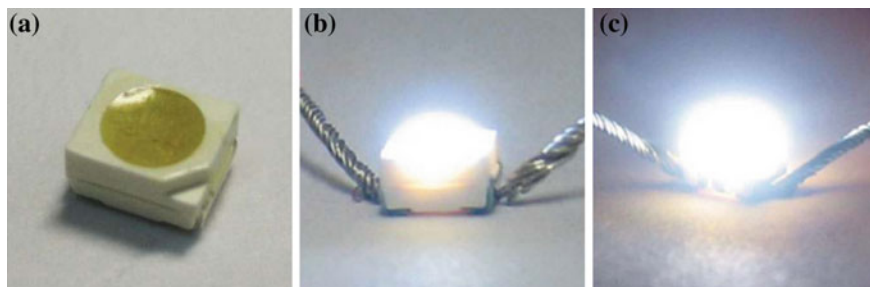


Fig. 16.10 **a** Image of CdSe QDs and $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+}$, Li^{3+} phosphor-based white light LED, **b** LED device operated at 5 mA, **c** LED device operated at 20 mA. Reproduced from Ref. [13] by permission of John Wiley & Sons Ltd

60 °C. After the cooling step, we add the yellow YAG phosphor to the mixture and dry at 150 °C for 2 h. Epoxy mixture dispenses on the blue chip, and the device emits white light. In contrast to phosphors, QDs can obviously enhance the CRI value and color saturation of the device. Ziegler et al. [14] used red InP/ZnS QDs to increase the CRI value and make the light more colorful (Fig. 16.9). We can see the result of the QDs-based white-light LED operated at different current (Fig. 16.10).

16.3 Conclusions

Colloidal QDs exhibit unique optical properties depend on the particle size, which can be changed by tuning their particle sizes. Given their unique size-dependent photoluminescence spectra, these QDs have attracted great interest for their application in LEDs. QDs demonstrate good luminescence efficiency and photostability. These unique properties make QD-LEDs promising candidates for the application in backlight display. Cd-free InP QDs are non-toxic and environmentally friendly; thus, many people prefer this devices. The Cd-free-based display is the optimal choice for the next generation display.

References

1. Anc MJ, Pickett NL, Gresty NC, Harris JA, Mishra KC (2013) Progress in non-Cd quantum dot development for lighting applications. *ECS J Solid State Sci and Technol* 2:R3071
2. Yang X, Zhou D, Leck KS, Tan ST, Tang YX, Zhao J, Demir HV, Sun XW (2012) Full visible range covering InP/ZnS nanocrystals with high photometric performance and their application to white quantum dot light-emitting diodes. *Adv Mater* 24:4180
3. Byun HJ, Lee JC, Yang H (2010) Solvothermal Synthesis of InP Quantum Dots and Their Enhanced Luminescent Efficiency by Post-synthetic Treatments. *J. Colloid Interf.* 355:35

4. Kim T, Kim S, Woo KM., Kim S-W (2012) Large-scale synthesis of InP/ZnS alloy quantum dots with dodecanethiol as a composition controller. *J Phys Chem Lett* 3:214
5. Shirasaki Y, Supran GJ, Bawendi MG, Bulovic V (2012) Emergence of colloidal quantum-dot light-emitting technologies. *Nat photonics* 7: 13
6. Chen CJ, Lin CC, Lien JY, Wang SL, Chiang RK, (2015) Preparation of quantum dot/polymer light conversion films with alleviated Förster resonance energy transfer redshift. *J Mater Chem C* 3:196
7. Boldt K, Kirkwood N, Beane GA, Mulvaney P (2013) Synthesis of highly luminescent and photo-stable, graded shell CdSe/CdxZn_{1-x}S nanoparticles by in situ alloying *Chem. Mater* 25:4731
8. Bozyigit D, Wood V (2013) Challenges and solutions for high-efficiency quantum dot-based LEDs. *MRS Bulletin* 38:731.
9. Dai X, Zhang Z, Jin Y, Niu Y, Cao H, Liang X, Chen L, Wang J, Peng X (2014) Solution-processed, high-performance light-emitting diodes based on quantum dots *Nature* 515:96
10. Lee KH, Lee JH, Kang HD, Park B, Kwon Y, Ko H, Lee C, Lee J, Yang H (2014) Over 40 cd/A Efficient Green Quantum Dot Electroluminescent Device Comprising Uniquely Large-Sized Quantum Dots *ACS Nano* 8:4893
11. Lee KH, Lee JH, Song WS, Ko H, Lee C, Lee JH, Yang H (2013) Highly efficient, color-pure, color-stable blue quantum dot light-emitting devices *ACS Nano* 7:7295
12. Lim J, Park M, Bae WK, Lee D, Lee SH, Lee CH, Char K (2013) Highly efficient cadmium-free quantum dot light-emitting diodes enabled by the direct formation of excitons within InP@ZnSeS quantum dots *ACS Nano* 10:9019
13. Jang, HS, Yang H, Kim SW, Han JY, Lee S, Jeon DY (2008) White light-emitting diodes with excellent color rendering based on organically capped CdSe quantum dots and Sr₃SiO₅:Ce³⁺, Li⁺ phosphors *Adv Mater* 20:2696.
14. Ziegler J, Xu S, Kucur E, Meister F, Batentschuk M, Gindele F, Nann T(2008) Silica-coated InP/ZnS nanocrystals as converter material in white-light LED *Adv Mater* 20:4068.