Fabrication of a light-emitting device based on the CdS/ZnS spherical quantum dots

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Abstract
In this work, we focus on the colloidal quantum dot based light-emitting diodes (QD-LEDs) performance. First, we synthesize the spherical QDs with a CdS core that covered with a wider band gap II–VI semiconductor acting as a shell (ZnS). In order to synthesize this nano crystal QDs with structure of CdS/ZnS/CdS/ZnS, we use a reverse micelle process. These four-layer quantum well quantum dots (QWQDs) can generate the white light emission. The positional design of different layers i.e., core/shell QD emitters is a critical factor for white emissive devices. The blue emission generated by CdS core mixes with green/orange components originating from ZnS inner shell and creates an efficiency white light emission. Then, we fabricate a white-QDLED with a device structure of FTO/ ZnO / QD / CBP/ MoO 3 / Al films. A thin film of CdS/ZnS/CdS/ZnS QDs is deposited by electrostatically assembled colloidal QD solutions. The experimental results show that the emission spectra of QDs and current density through the LED are controlled by varying the particle sizes. The peaks of absorbance and Photoluminescence (PL) spectrums for core/shell structures get the red shifted as the dot size increases. Furthermore, this QD-LED with a smaller nano particle layer has a higher current density.

Keywords: Colloidal quantum dot, Light-emitting diodes, Photoluminescence, Absorbance, Reverse micelle method, Current density

Introduction
Recently, QD-LEDs have been extensively investigated due to their unique and fantastic optical properties of colloidal synthesized quantum dots (QDs) [1–4]. QD films exhibit easy color tenability over the entire visible spectrum, broad absorption spectrum and high photoluminescence quantum yield. These attractive properties and advantages make them to be promising for the light emitting applications [5–9]. Solid state white light emitting diodes (WLEDs) as the new generation of light sources can offer the chance to lower thermal resistance and longer lifetime [10, 11].

Group II–VI metal chalcogenide semiconductors specially CdS, CdSe and ZnS have been of interest because they show high photoluminescence (PL) in the visible region. Emission from the QD-LEDs depends strongly on the size of the QDs and their composition [8].

Cadmium compounds QDs arising from the color-saturated photoluminescence (red, green, blue) have attracted more attention as a good potential utility of the design and fabrication of the QD-based WLEDs. CdS has the best PL and is also widely used in solid state applications [12–15].

ZnS is another important semiconductor to investigate. It is extensively studied as a luminescent material for optoelectronic application [5, 12].

Many different deposition techniques have been utilized to affect device performance and improve the optical properties of LEDs [16–18]. Some authors reported that the core-shell type nanoparticles such as CdSe/ZnS [5] are good candidates for white emission QD- LEDs. In this type of nanostructures that are composed of two different semiconductors, first semiconductor is the core and the second one, with a wider band gap than the core, is the shell.
Enhancing the light-extraction efficiency is one of the key issues for realizing highly efficient LEDs. The experimentally researchers introduced several features to improve this efficiency in AlGaN-based diodes [19]. It has been demonstrated that the bright and efficient QD-LEDs fabricated from thin and uniform CdSe/ZnS colloidal QD films show high optical quality [20] and have maximum luminance and current efficiency [5].

This study aimed to investigate experimentally the performance of the QWQD diodes. In the present work, CdS/ZnS/CdS/ZnS QDs are prepared by a reverse micelle process. In this nano structure, blue emission from CdS core combines by the green and red emissions from ZnS inner shell and this recombination products efficiently white light emitting. In the following, we fabricate a deposition of luminescent QDs film by electrostatically assembled colloidal QD solutions. The experimental results have shown that the QDs size can manage the absorbance and PL spectrums. Finally, we investigate the influences of the dot size on the current density and present how this parameter can control the current density through this six layer WLED.

Experimental

White light emitting diode based on the CdS/ZnS/CdS/ZnS QDs is prepared by following two synthetic protocols. First, we have to synthesize the colloidal QDs, then we fabricate the a QD-WLED with ITO/ ZnO / QD / CBP/ MoO 3 / Al structure.

CdS/ZnS QDs synthesis
At first, we need solutions of Cd (CH 3 COO) 2.2H 2 O, Na 2 S and Zn (CH 3 COO) 2 precursors in water with concentrations 0.1 M and 0.26 M, respectively. Now, we solve the dioctyl sulfo succinate sodium salt (AOT) in heptane to prepare 0.1 M surfactant solution and then add it to solution of each precursor. It should be mentioned that the volume ratio $W = \frac{[\text{AOT}]}{[\text{DOS}]}$ must be the same for Cd 2+, Zn 2+ and S 2− solutions. CdS core is formed after 15-min reaction of 70 cc S 2− with 12 cc Cd 2+ micellar stock solutions. In order to generate CdS/ZnS core/shell QDs, we slowly add 20 cc Zn 2+, 12 cc Cd 2+ and finally 50 cc Zn 2+ solutions to CdS core [12]. Finally, the resulting QWQDs are washed with heptane and methanol and dispersed in methanol for characterization.

QDLED fabrication
The FTO-coated glass substrates were cleaned in ultrasonic baths of detergent, de-ionized water, and acetone, then were immediately put it in the oven. After the above cleaning, fabrication of the QD-LEDs starts with a zinc oxide (ZnO) electron-transport layer formation by

![Fig. 1](image.png)

**Fig. 1** (a) Cross-section schematic of a white-QLED with a device structure of ITO/ ZnO / QD active layers/CBP/ MoO 3/ Al films. ZnO layer was prepared by spin coating, QDs film was formed by EPD technique and CBP, MoO 3, and Al were deposited by sequential thermal evaporation on top of the ZnO/QD layers. (b) Energy level schematic diagram, and (c) band profile of CdS/ZnS/CdS/ZnS colloidal spherical QD.
spin-coating method of zinc acetate solution onto the FTO and heating it at 300 °C for 5 min. Then, a thin QDs film as the emissive layer is electrophoretically deposited in an electrophoretic deposition (EPD) process [21–24]. In EPD procedure, we applied 45 V cm\(^{-1}\) electric field for 5 min on two ZnO-on-FTO substrates fixed in 4 mm apart from each other. After that, we transferred the samples into a vacuum chamber to deposit the dicarbazolebiphenyl (CBP) as a hole transporting layer, molybdenum oxide (MoO\(_3\)) as a hole-injection layer, and an aluminum (Al) by sequential thermal evaporation. The same method is described in detail in Ref. [20]. A schematic of the device structure and cross-sectional view of the multilayer white-emitting QDLED is shown in Fig. 1.

Our QD-LED structure was designed to reach efficient electron and hole injection from these electrodes to the QDs. We also required to effectively block electrons and holes passing through the QD layer. It is well known that the ZnO particles is highly advantageous for QLEDs with conventional structures owing to high electron mobility \((2 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1})\) and low temperature behavior.

**Results and discussion**

The proposed spherically grown QDs composes of two different emitter layers in which each layer can emit specific wavelengths in the visible range (RGB spectrum). In introduced nano structure QD, CdS as a core is coated by shell ZnS. The core CdS with band gap \(E_g = 2.58\ eV\) can emit the blue spectrum and shell ZnS can emit both of the green and red spectrums. Hence, this novel type of QWQD achieves efficiently white light emission. The absorption and photoluminescence spectra were investigated to explore the optical properties of theses QDs. Experimental results have shown that the dot size has central role in control of the output light properties.

The absorbance spectrums of WLED at different time after the synthesis are shown in Fig. 2. The water-to-surfactant molar ratio is \(W = 5\). The absorbance spectrums show two peaks centered at \(\lambda \approx 486\ nm\) for core CdS and \(\lambda \approx 525\ nm\) for core/shell CdS/ZnS that exhibit

![Fig. 2 Time evolution of QWQDs absorbance spectrum for a) core CdS, b) core/shell CdS/ZnS, C) CdS/ZnS/CdS, and d) white light emitting CdS/ZnS/CdS/ZnS. Here we assume that W = 5](image-url)
slightly red shift with time passing. CdS/ZnS QDs samples have higher stability than CdS core and retain their PL properties for longer time.

After time focusing, we investigate the QDs size dependence of the absorption and PL spectra. QWQDs emission can be tuned by varying the dot size, which is easily controlled by $W$ [25, 26]. Particle size of dots in reverse micelle method decreases with the reducing of $W$ values as $(1 + \frac{15}{W})^3 - 1 = \frac{27.5}{W}$ [12], thus it leads to a blue-shift of emission wavelength.

PL photos of QWQDs synthesized at different $W$ values for a) CdS, b) CdS/ZnS, c) CdS/ZnS/CdS and d) CdS/ZnS/CdS/ZnS are shown in Fig. 3. At higher magnitudes of $W$ parameter, PL spectra of QDs shifts to right hand due to the increase of particle size.

The absorbance spectrums as a function of the $W$ for three different values of $W$ are shown in Fig. 4 that presents how the absorption intensity is dependent on the concentration of a solution. This figure reveals the absorption spectra from two important observations: (a) absorbance decreases with the increase in $W$ value and core thickness; (b) the absorbance peak gets blue shifted as $W$ increases in which the peak at $\lambda = 480$ nm for $W = 10$ shifts to $\lambda = 483$ nm for $W = 6$ and $\lambda = 486$ nm for $W = 3$.

Similar performance was achievable for CdS/ZnS core/shell absorbance spectrum (Fig. 5). As shown, increasing of $W$ values corresponds to a red-shift of emission wavelength. A red shift of about 25 nm in the absorption peak was observed. The absorption spectra of CdS/ZnS shifted from 515 nm to 540 nm due to the $W$ increasing. Moreover, the absorbance of core/shell nanocrystals strongly depends on the thickness of the passivating shell. CdS QDs with the passivation of ZnS shell shows higher stability of the PL efficiency than a CdS core. Figures 6 and 7 show the absorbance as a function of the emission.

It should be mentioned that the defect emission of ZnS inner-shell can create both of the green emission
peaked at $\lambda \approx 525$ nm and orange emission at $\lambda \approx 580$ nm 
[12, 26]. So, in presented structure, blue emission from core CdS can combine with green and red emission from the shell ZnS and generates the white light. We manage dot size to study the absorbance, PL intensities and chromaticity coordinates diagram of the output light [12, 27].

Absorbance, PL intensity and CIE coordinates for QDs with $W = 6$ and core/ double shell layer structure are shown in Fig. 8. As shown in this figure, water-to-surfactant molar ratio plays an important role in optical properties of QDs emission. In following, we demonstrate how $W$ parameter can manage the current density of QD-LED fabricating with thin and uniform CdS/ZnS/ CdS/ZnS colloidal QDs film.

Different correlated color temperature (CCT) and color rendering index (CRI) values with corresponding CIE (Commission Internationale de l'Eclairage) coordinates are presented in Table 1. The values of CRI and CCT were calculated according to equations defined by the CIE. The maximum CRI value is 94.88 at a CCT of 1625 K. In addition, one of the CIE coordinates is (0.3335, 0.3464) which is close to the standard neutral white light (0.33, 0.33) [28, 29]. Thus, these results indicate that CdS/ZnS spherical colloidal quantum dots are promising potential in solid-state lighting for light emitting devices [30].

Figure 9 shows the Current density vs. applied voltage characteristics under an applied voltage of 4 V for two different QD sizes of LED, one including dots with $W = 6$ and another with $W = 3$. First, the Current gradually increases until $2 \text{ mA/cm}^2$ and the I–V characteristics remain approximately the same for both $W$ values. Then dot size controls the I–V curves. A comparison of the electrical properties of this QWQD based LED with $W = 3$ and that of with varied ratio $W = 6$ exhibits that
the QDLED with larger nano particle layer ($W = 3$) has a higher current density. Thus, the increases in the QD size result in increased current density. From the enlarged current density, we can conclude that QD layer with $W = 3$ is superior to that for $W = 6$ in our device structure.

Finally, Fig. 10 presents the electroluminescence (EL) spectra obtained from the fabricated CdS/ZnS/CdS/ZnS QD-LED for $=3$. This spectrum has two distinct peaks; the blue emission peak at $\lambda \approx 456$ nm due to CdS and a red emission peak at $\lambda \approx 590$ nm due to ZnS, as we expected.

**Conclusion**

In summary, we report the white light emission QWQDs enable us to fabricate the WLED based on the thin and uniform CdS/ZnS/CdS/ZnS colloidal QD film. Two-layer CdS/ZnS as a core/shell QD structure result the
Fig. 7 Absorbance spectra of CdS/ZnS core/shell QDs with different thickness of ZnS shell. (a) CdS/ZnS, (b) CdS/double ZnS. Here we assume $W = 6$. 
Fig. 8 (a) Absorbance, (b) PL spectra and (c) CIE coordinates of QDs (W = 6). The white light emission is obtained from the mixture of blue and green/orange emission originated from core CdS and the inner shell ZnS, respectively. The excitation wavelength is $\lambda = 400$ nm. The CIE coordinates of this white light emission is $(0.33, 0.34)$.

### Table 1

The values of CIE coordinates, CCT and CRI

| $x$    | $y$    | CCT(K) | CRI  |
|--------|--------|--------|------|
| 0.3335 | 0.3464 | 5457   | 91.12|
| 0.4001 | 0.4    | 3695   | 93.29|
| 0.5    | 0.4503 | 2491   | 94.1 |
| 0.6001 | 0.3999 | 1625   | 94.88|
| 0.6502 | 0.3001 | 4154   | 92.93|
white light emission in which the blue and green/orange emission originate from CdS core and ZnS shell, respectively. Experimental results are shown that the emission properties and the current density critically depend on the water-to-surfactant molar ratio or dots size. We find a blue shift of absorbance and PL spectrums and smaller current density for mentioned core/shell structure at larger dot size.

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Authors’ contributions
K. hasanirokh carried out the experiment and fabricated the QDLED sample with support from S. Mohammadi. K. hasanirokh wrote the manuscript. A. Asgari conceived the original idea supervised the project. All authors read and approved the final manuscript.

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Declarations
Competing interests
The authors declare no competing interest.

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