Synthesis of ZnS Quantum Dots for QDs-LED hybrid device with different cathode materials

Ahmed F. Mohammed$^{1,*}$ and Wasan R. Salah$^2$

$^1$Ministry of Education, General Directorate of Education of Najaf, Iraq
$^2$Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Email: ahmedasker85@gmail.com (Corresponding author: Ahmed F. Mohammed)

Abstract. In this study, a chemical method was used to synthesise ZnS quantum dots (QDs) with low cost and simple process. A fixed molar ratio 1:1 of zinc chloride and sodium sulfide has been used for preparing two samples A and B. The X-ray diffraction (XRD) analyses prove the cubic phase of ZnS with an average particles size of (3-29) nm. According to UV-Vis. spectra analyses, a large blue shift over 32 and 48 nm was observed, while the band gaps energy ($E_g$) were 3.55 and 3.8 eV for A and B samples respectively. The emission spectrum of quantum dots carries more evidence on the presence of shallow at 373 and 367 nm originated from the interstitial Zn and traps at 428 and 439 nm, whose origin ascribed to defects zinc vacancy (VZn), while 541 nm was due to sulfide vacancy (VS). QDs-LED hybrid devices were fabricated using ITO/ PEDOT: PSS/ Poly-TPD/ ZnS-QDs/ layers with two types of cathode materials LiF and Al. Using LiF as cathode in addition to the Al gives good enhancement to light generation in compares with that of Al cathode only. The spectra 350-700 nm appeared a wide emission band according to the EL measurement.

1. Introduction

Semiconductor QDs are very important nanomaterials with unique physical, chemical, optical and electronic properties owing to the quantum confinement effect. These properties are the result of the confinement of electronic wave functions which can be manipulated by controlling the size of the QDs. To observe the confinement effects, the nano crystals size has to be in the range of nanometers a variety of low dimensional nanostructures such as zero-dimensional (0D) nanoparticles, one dimensional (1D) nanowire, nanotube and nanorods, two dimensional (2D) nanobelt and nanosheet are investigated extensively due to their novel and fascinating properties compared to their bulk counterparts. Nanoscale light sources have found numerous applications in biology, bioanalytics, and optoelectronics [1, 2]. (QDs) semiconductor particles have drawn considerable interest recently for their properties; large surface-to-volume ratio, quantum tunneling effect, increased activity, special electronic and optical properties in comparism with bulk materials [3, 4]. These luminescents nanomaterials possess suitable characteristics for various applications in biological labeling and optoelectronic devices. Along with the direct use of QDs as efficient phosphors showing narrow emission, they can also be applied as host materials for accommodating dopant ions of interest [5]. Zinc sulfide (ZnS), as one of the most important members of the family of group II-VI wide-gap semiconductors with direct band gap for the bulk cubic as 3.66 eV. ZnS has been extensively investigated because of its potential applications in flat-panel display, light-emitting diodes (LEDs),
infrared windows, electroluminescence, sensors, lasers and photocatalysis due to its diverse range of possible structures and morphologies, and superior chemical and thermal stabilities. The optical properties can be tunable by modulating the QDS size, chemical composition and defects concentration. It has been reported that QDs contain few hundred atoms and emit only one wavelength of light when they are excited. The color emitted is determined by the size of the quantum dots [6, 2].

Light emitting diodes (LEDs) based on colloidal QDs emitting layer are highly promising for the next generation of lighting and displays and come into being an undeniable competitor to organic LEDs due to their advantageous properties, such as the tunable color emission spectra, the narrow emission line width, and the cost-effective fabrication techniques [7]. The quantum dot light-emitting diodes (QD-LEDs), because of their unique potential properties, have attracted much attention and considered most practical candidates for flat panel displays and solid-state lighting sources, offering significant advantages over organic LEDs (OLEDs) [8].

Organic electronic devices required Ohmic contacts for most efficient performance. Metals-organic semiconductors contacts can be improved by placing charge injection layers between the semiconductor and the metal [9]. In this work, the structural and optical properties of synthesized ZnS QDs were studied. QDs-LED hybrid devices were fabricated using ITO/ PEDOT: PSS/ Poly-TPD/ ZnS-QDs layers with two types of cathode materials lithium florid (LiF) and aluminum (Al).

2. Experimental Procedure Chemical Materials

The chemical materials which is used in this research like zinc chloride (ZnCl₂, Merck, 99%), sodium sulfide (Na₂S, Merck, 99%) and ammonium hydroxide (NH₄OH, Merck, 99%) were used without further purification. The materials used for the QDs-LED fabrication are; Poly (3, 4 ethylenedioxythiophene): styrene sulfonic acid (PEDOT: PSS) were supplied from Ossila Limited. Poly [N, N’-bis(4-butylphenyl)-N, N’-bis(phenyl)-benzidine] (Poly-TPD) was purchased from American Dye Source co., while Lithium fluoride (LiF) of 99% from Riedel-de Haen.

3. Synthesis of ZnS Quantum Dots Colloidal

A fixed molar ratio 1:1 of zinc chloride and sodium sulfide has been used for preparing the aqueous solution at room temperature to produce two samples A and B. An equimolar concentration of both ZnCl₂ and Na₂S were used to prepare QDs of ZnS. (ZnCl₂) solution has been prepared by dissolving 0.68 g of zinc chloride powder (ZnCl₂) in 50 ml of distilled water (d.w.). The solution is acidic with pH value of 6.1. In order to have a base solution with pH of 7.2, adding alkaline solution of ammonium hydroxide (NH₄OH) drop by drop to the previous (ZnCl₂) solution. Using alkaline solutions instead of the acidic solution because the rapid decay of the quantum dots doesn't occupy in the acidic range, as well as to reduce the aggregation [10]. (Na₂S) solution has been prepared by dissolving 0.39 g of sodium sulfide powder (Na₂S) in 50 ml of d.w. and gather in a three-neck flask. The flask put on a magnetic stirrer under a high stirring rate (700 r.p.m.) and flowing of argon gas continuously at room temperature. After which, the second solution was added drop by drop to the first solution, quit reaction for one hour until the mixture appears completely milky color, this indication of forming ZnS QDs. Stopped the flowing of argon gas and the solution was poured in a redundant amount of methanol. Two steps lead to diminishing the chemical reaction: first take amount of the deposited material to represent A sample. Secondly centrifuge the remaining residue and then wash with distilled water to have sample B. The reaction can represent as:

\[ \text{ZnCl}_2 + \text{Na}_2\text{S} \rightarrow \text{ZnS} + 2\text{NaCl} \]

4. Assembling layers of Hybrid Devices

For fabrication process of the QD-LED device, the ITO conductive glass of resistivity of 12 Ω/ square as the substrate was used with dimensions of 25x25 mm² after cleaning by distilled water and then by isopropanol alcohol in the acoustic-wave ultrasonic and for a period of 10 minutes. All solutions were deposited layer by layer on the ITO glass by a spin-coating method. PEDOT: PSS as an anode buffer layer of 30 nm thickness was deposited on ITO glass at 6k r.p.m. for 30 s then annealed at 150°C for
15 minutes. After that, poly-TPD which represent a hole transport layer was prepared by dissolving 70 mg/ml in chlorobenzene solution then deposited a layer with thickness 135 nm at 2.5k r.p.m. for 30 s then annealed at 80°C for 30 minutes. Thereafter, ZnS QDs as an electron transport layer was prepared (250 mg/ml) in ethanol solution then deposited of 165 nm layer thickness at 2.5K r.p.m. for 30 s and then annealed at 60°C for 50 minutes. Finally, cathode layer was deposited once using Al material along with the first device, while for the second device using Al then LiF material. Al layer of 200 nm was deposited by a thermal evaporation method in high vacuum ~10⁻⁶ Torr with deposition rate ~11 Å/s, while LiF layer of 2 nm thickness was deposited by ion coater method at 3 mA/40s. The films thicknesses have been measured by the BLK-CXR-SR-25 spectrometer.

**Figure 1.** Schematic of QDs-LED with cathode layer materials of: (a) LiF with Al and (b) only Al.

### 5. Results and Discussion

#### 5.1 Structural Measurements

The QDs of ZnS prepared by the chemical method which considers a low cost and simple process. The structural investigation of ZnS QDs was carried out and recorded using XRD - 6000 Labx, supplied by Shimadzu. Figure (2) shows the X-ray diffraction pattern of samples A and B respectively. Figure (2a) shows that sample A has scattering peak at (2θ) = 28.6°, 47.9° and 56.8° corresponding to (111), (220) and (311) crystal planes of the zinc-blende (cubic) phase of ZnS. These results are according to card [JCPDS NO: 5-0566] while the peak at (2θ) = 31.7° referred to the appearance of sodium chloride in the prepared ZnS QDs. This is meaning that sample A was not pure ZnS QDs because of containing ions of reaction compounds that have not reacted due to a decrease in the base concentration of the solution these ions produced by adding hexamethylenetetramine [(CH₃)₆N₄] [11].

**Figure 2.** The XRD patterns for samples A and B: inset: XRD pattern for sodium chloride according to card number [JCPDS NO: 5-628].
Figure (2b) shows that sample B has characteristic diffraction peaks at \( (2\theta) = 28.4^\circ, 47.9^\circ \text{ and } 57.6^\circ \) that appointed to (111), (220) and (311) reflection planes respectively of the face-centered cubic of ZnS. These results conformance according to card number [ICDD PDF 65-1691]. The absence of (NaCl) or any other peaks in sample B refer to the purity ZnS QDs as a final product. The average size (D) of ZnS QDs can be calculated according to Scherrer’s equation [2].

\[
D = \frac{0.9 \lambda}{B \cos \theta}
\]

where \( \lambda \) is the X-ray wavelength and equals to 0.15406 nm, \( B \) is the full width at half maximum.

The average size (D) of ZnS QDs can be calculated according to Scherrer’s equation [2].

It is clear that the crystal size for sample A is smaller than that for B. The reason may be attributed to the little period of staying sample A in alcohol, which led to has smaller crystal size.

| Samples | \( 2\theta \) (degree) | B (degree) | Crystal Size (nm) | (hkl) |
|---------|-----------------------|------------|-------------------|-------|
| A       | 28.6\(^\circ\)       | 2.54       | 3.37              | (111) |
|         | 47.9\(^\circ\)       | 1.05       | 8.65              | (220) |
|         | 56.8\(^\circ\)       | 0.48       | 19.43             | (311) |
| B       | 28.4\(^\circ\)       | 2.23       | 3.82              | (111) |
|         | 47.9\(^\circ\)       | 0.54       | 16.77             | (220) |
|         | 57.6\(^\circ\)       | 0.31       | 29.91             | (311) |

It is clear that the crystal size for sample A is smaller than that for B. The reason may be attributed to the little period of staying sample A in alcohol, which led to has smaller crystal size.

5.2 Optical Measurements
The UV-Vis. spectra of ZnS QDs were measured using OPTIMA SP- 3000 UV –Vis. spectrophotometer and figure (3) shows these spectra. It is evident from the figure that the absorption edge \( \lambda_0 \) of the prepared ZnS QDs is observed at 318 and 302 nm for samples A and B respectively, which are very much shorter than 350 nm of the bulk ZnS [2] which indicating a clear blue shift. These blue shifts of the absorption edge can be attributed to the quantum confinement effect of the ZnS QDs. The band gap energy (\( E_g \)) can be estimated from the figure (4) using Tauc equation [2] by extrapolating the linear portions of \((\alpha h\nu)^2\) vs \( h\nu \) graph on the \( h\nu \) axis to \( \alpha = 0 \).

\[
(\alpha h\nu)^2 = A (h\nu - E_g)
\]

where \( \alpha \) is the absorption coefficient, \( h\nu \) is the incident photon energy and \( A \) is a constant depends on the electron–hole mobility. The energy gaps for direct transitions were found to be 3.55 and 3.8 eV for A and B samples respectively. Photoluminescence spectra were taken by SL 174 spectrofluorometer with an excitation wavelength of 300 nm and 280 nm respectively for samples A and B, figure (5) shows these spectra. Since QDs have a very high surface to the volume ratio, so they susceptible to various surface defects. The sources from PL are due to self-activated centers and then to crystal lattice vacancies such as sulfide vacancies according to [12]. The first emission peaks were detected at 373 and 367 nm for A and B samples respectively which originated from the interstitial Zn, while the decay time was 5.6 ns for both which consider quite fast such as in [13]. The second emission peaks which appeared at 428 and 439 nm for A and B samples, the origin were ascribed to defects zinc vacancy (\( V_{\text{Zn}} \)). The third peak at 541 nm for A sample was due to sulfide vacancy (\( V_{\text{S}} \)). The decay time was slow as 140 ns for the second peaks and 7.7 \( \mu \)s for third peak as in [14, 15].
5.3 Morphological Measurements

The topography of the film surface was recorded using CSPM AA3000 Atomic Force Microscope (AFM) supplied by Angstrom Company. Figure (6) shows the 3 dimensions AFM images and granularity distribution charts of ZnS QDs samples A and B. The average particles size according to the AFM images is about 2.88 and 36.44 nm for samples A and B respectively.
Figure 6. 3 dimensions AFM images and granularity distribution charts of ZnS QDs samples A and B.

Table (2) displays a summary of surface topography parameters of ZnS QDs. According to figure (6) sample B has low aggregation from sample A which is important for producing a homogeneous light from the QD-LED.

Table 2. AFM parameters of ZnS QDs.

| Samples | Roughness Average \( Sa \) (nm) | Root Mean Square \( Sq \) (nm) | Ten Point High \( Sz \) (nm) | Average Diameter \( D \) (nm) |
|---------|---------------------------------|------------------------------|-----------------------------|-------------------------------|
| A       | 0.74                            | 0.86                         | 2.99                        | 76.08                         |
| B       | 7.25                            | 8.55                         | 21.4                        | 93.57                         |

5.4 Hall Effect Measurements
Hall Effect was used to electrically characterize the prepared films. The measurements carried out using Ecopia HMS-3000 Hall measurement system. Table (3) summarizes Hall Effect results which revealed that both films n-type conductivity. Sample A has conductivity and mobility values larger than that of sample B, and this is may be attributed to existence of salts.
Table 3. Electrical parameters of ZnS QDs films.

| Samples | Conductivity $(\Omega \cdot cm)^{-1}$ | Mobility $(cm^2/Vs)$ | Hall coefficient $(m^2/C)$ | Resistivity $(\Omega \cdot cm)$ |
|---------|--------------------------------------|----------------------|--------------------------|-------------------------------|
| A       | 1.16x10^{-5}                        | 2.56                 | -2.20x10^{5}             | 4.30x10^{5}                  |
| B       | 0.11x10^{-5}                        | 1.22                 | -1.21x10^{5}             | 0.98x10^{5}                  |

5.5 Current-Voltage Characteristics

Figure 7 shows the current-voltage measurements under forward bias voltage. By observing the curve, one can find that the two samples behave as diode behavior. This is called the exponential increase due to the increased saturation current between the hybrid junction, after the holes moved from PEDOT: PSS to the p-(Poly-TPD) towards depletion zone. At the same time, when the electrons moved from LiF to the n-(ZnS-QDs) towards the junction, reducing the potential barrier. Thin film LiF layers play a role in reducing the barrier for electron injection from Al layer into the organic semiconductors according to a change in the effective work function of the LiF/Al contact [16].

![Figure 7](image)

Figure 7. I-V forward characteristics of hybrid devices with and without using LiF as a cathode layer: inset behavior the devices from 5.5-9v.

According to the results of the current-voltage, thin film layer of LiF has provided the flow current largest in the device. However, the intensity of the light without using LiF is less than with that of LiF and this is what obvious in the electroluminescence measurements and photographic plat in both cases. Turn-on voltage of the devices are between (5.5 - 9 V), but at voltage greater than 9 V causes the device to collapse. Therefore, 8 V was chosen for electroluminescence measurements and device operating. The I-V characteristics of ITO/ PEDOT: PSS/ Poly-TPD/ ZnS-QDs/ LiF/ Al and ITO/ PEDOT: PSS/ Poly-TPD/ ZnS-QDs/ Al hybrid devices shown in figure (7).

5.6 Electroluminescence Measurements

The EL measurements for the QD hybrid devices shown in figure (8) were carried out using a photomultiplier detector at room temperature under forwarding bias voltage of 8 V.
Figure 8. EL spectra of hybrid devices with and without using LiF as a cathode layer with forward bias voltage of 8 V.

The carrier transport mechanism in QDs-LED devices can be summarized as follows; the Poly-TPD which consider a hole transporting material. Holes are injected from PEDOT: PSS, the buffer ITO anode, into the HOMO of the Poly-TPD matrix and transported to the valence band (V.B) or to the acceptor levels ($V_{Zn}$ and $V_{S}$) of the ZnS QDs. Meanwhile, electrons are injected from the LiF (which consider as buffer to the Al) cathode into the conduction band (C.B). This is called the excitons from band edge recombination. The process of recombination of holes and electrons through defects in order to emitting different wavelength light called Shockley-Read Hall (SRH) recombination. [11].

According to figure (8), the device with LiF cathode has more intensity than the device without LiF. Actually the existence of LiF and PEDOT: PSS layers play a role in producing a large difference in work function between the cathode and anode to be about 2.5 eV, which is very important in the manufacturing of diodes, which rapid the exciton production process and increase the resulted intensity also. Figure 9 shows a photographic plate of the light generation of ITO/PEDOT: PSS/Poly-TPD/ZnS/LiF/Al and ITO/PEDOT: PSS/Poly-TPD/ZnS/Al hybrid according to the emission lines of the EL spectrum at the 8 V. It is clear that the intensity of the device with LiF is higher and the color is closer to the white than the device without LiF which is closer to yellow light.

Figure 9. A photographic plate of the light generation of (a) ITO/PEDOT: PSS/Poly-TPD/ZnS/LiF/Al (b) ITO/PEDOT: PSS/Poly-TPD/ZnS/Al hybrid devices.
6. Conclusion

ZnS QDs were synthesized by a simple chemical method with low cost. XRD, UV-Vis., and PL measurements confirmed the presence of zinc and sulfide. The prepared ZnS QDs have a small average grains size of 3.37 and 3.82 nm. Optical measurements proved that the absorption edge was shifted largely towards blue region of the spectrum because of the confinement effect on the carriers. The PL spectrum of ZnS shows the defect related emission. The deep traps are attributed to the process of recombination at Zn$^{2+}$ and S$^{2-}$ vacancy levels. AFM images proved that the purified sample (B) has low aggregation which is important for producing a homogeneous light from the QD-LED. (I–V) characteristics indicate that for few voltages of (8V), the output current is good which consider acceptable for light generation process. Fabrication of QDs-LED devices from two layers’ hole injection organic Poly-TPD and electron injection QDs using LiF as cathode in addition to the Al gives good enhancement to light generation in compares with that of Al cathode only.

7. References

[1] Dorokhin D V 2010 Surface engineered quantum dots in photoelectron chemistry and supramolecular assembly Ph.D. Thesis University of Twente MESA+ Institute for Nanotechnology Enschede, The Netherlands.
[2] Bodo B and Singha R 2016 Structural and optical properties of ZnS quantum dots synthesized by CBD method International Journal of Scientific and Research Publications 6(8) 461-65.
[3] Nirmala Jothi N S, Joshi A G, Jerald Vijay R., Muthuvinayagam A and Sagayaraj P 2013 Investigation on one-pot hydrothermal synthesis, structural and optical properties of ZnS quantum dots Materials Chemistry and Physics 138 186-91.
[4] Wu M, Wei Z, Zhao W, Wang X and Jiang J 2017 Optical and Magnetic Properties of Ni Doped ZnS Diluted Magnetic Semiconductors Synthesized by Hydrothermal Method Journal of Nanomaterials 2017 (1603450)1-9.
[5] Thuy U T D, Maurice A, Liem N Q, Reiss P 2013 Europium doped Int(Zn)P/ZnS colloidal quantum dots. An international journal of inorganic chemistry 42(35) 12606-10.
[6] Zeng Z, Garoufalis C S, Baskoutas S and Bester G 2015 Excitonic optical properties of wurtzite ZnS quantum dots under pressure Journal of Chemical Physics 142(114305) 1-5.
[7] Zhang X, Dai H, Zhao J, Wang S and Sun X 2016 All-solution processed composite hole transport layer for quantum dot light emitting diode Thin Solid Films 603 187-92.
[8] Ji W, Tian Y, Zeng Q, Qu S, Zhang L, Jing P, Wang J and Zhao J 2014 Efficient quantum dot light-emitting diodes by controlling the carrier accumulation and exciton formation ACS Applied Materials and Interfaces 6(16) 14001-7.
[9] Bory B F, Rocha P R F, Janssen R A J, Gomes H L, Leeuw D M D and Meskers S C J 2014 Lithium fluoride injection layers can form quasi-Ohmic contacts for both holes and electrons. Applied Physics Letters 105(123302) 1-4.
[10] Saleh W R and Kadim A M 2017 Synthesis of ZnS QDs with Different Values of pH and White Light Generation from Fabrication of TPD: PMMA/ZnS Hybrid Devices. Nano Hybrids and Composites 14 49–57.
[11] Ibrahim O A 2015 Electroluminescence of White Light from ZnO Nanostructures/ TPD Hybrid, Ph.D. Thesis, Physics Department, College of Science, University of Baghdad.
[12] Ni Y, Liu H, Wang F, Yin G, Hong J, Ma X and Xu Z 2004 Self-assembly of CuS nanoparticles to solid, hollow, spherical and tubular structures in a simple aqueous-phase reaction. Applied Physics A: Materials Science and Processing 79(8) 2007–11.
[13] Yanagida T, Fujimoto Y and Yanagida S 2014 Optical and scintillation properties of pure ZnS crystal, Proceedings of the 12th Asia Pacific Physics Conference JPS Conf. Proc.1(014031) 1-4.
[14] Koda T and Shionoya S 1964 Nature of the self-activated blue luminescence center in cubic ZnS: Cl Single Crystals Physical Review 136(2A) 541-55.

[15] Georgobiani N, Kotlyarevskii M S, Mikhalenko V N and Shvetsov Y V 1981 Nature of luminescence in zinc sulfide with intrinsic-defect hole conductivity Journal of Applied Spectroscopy 35(4) 1097–100.

[16] Willander M, Nur, Sadaf J R, Qadir M I, Zaman S, Zainelabdin A, Bano N and Hussain I 2010 Luminescence from zinc oxide nanostructures and polymers and their hybrid devices. Materials 3(4) 2643–67.