Synthesis of emission tunable AgInS₂/ZnS quantum dots and application for light emitting diodes

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Abstract

Indium-rich environmentally-friendly quantum dots (QDs) have received widespread attention due to the absence of cadmium. In this paper, AgInS₂ (AIS) QDs are synthesized by hot injection method. By adjusting the ratio of indium/silver (In/Ag = 1, 2, 3, 4, 5), the AIS QDs exhibit a blue shift from 868 nm to 603 nm with the indium composition increases. Therein, the AIS QDs with the ratio of In/Ag = 4 show a highest photoluminescent (PL) quantum yields (QYs) up to 57%. AIS QDs are coated with ZnS shell to passivate the surface defects, and the PL QYs of obtained core/shell AIS/ZnS QDs is increased to 72%. By using these AIS/ZnS QDs as light emitters, light emitting diodes are assembled with a stacked multi-layer structure ITO/PEDOT:PSS/Poly-TPD/QDs/ZnO:Mg/Al. The resulted electroluminescent (EL) device exhibits a maximum external quantum efficiency (EQE) of 1.25% and an open circuit voltage of 4.6 V corresponding to a maximum brightness of 1120 cd m⁻². Although the performances of the as fabricated AIS/ZnS-based device lag much behind than those of the Cd-based ones, they are expected to be enhanced with much more studies on the synthesis of the QDs and the optimization of device structure.

1. Introduction

Quantum dots have been recognized as a new-generation of photoelectric materials owing to their advantages such as size- and shape- controlled optoelectronic properties, low-cost solution processibility and so on [1–5]. During the past several decades, scientific synthesis methodologies for various types of QDs have been developed rapidly, and they have found extensive applications in light-emitting diodes (LEDs), solar cells, bio-imaging etc [6–9]. However, most part of the predominant work focused on the Cd-based II-VI QDs, Pb-based IV-VI and perovskite ones [10–12], in which the heavy metals such as cadmium and lead are harmful for human health as well as the environment and detrimental to the commercial development of corresponding QD materials. Therefore, it is of great significance to carry out research work on non-toxic QDs and relevant applications. In recent years, I-III-VI QDs, such as CuInS₂ (CIS) and AgInS₂ (AIS), being free of heavy metals, have attracted substantial attention. Generally, I-III-VI QDs exhibit large Stokes’ shift and wide full-width at half-maximum (FWHM), which enable them to be excellent color-converters for fabricating photoluminescent white LEDs with high color render index (CRI) [13, 14]. They also have been reported to be used to assemble electroluminescent LEDs. An orange electroluminescent QD-based LED (QLED) based on CIS/ZnS QDs with a current efficiency of 18.2 cd A⁻¹ and a high external quantum efficiency (EQE) of 7.3% has been reported [15]. However, only a relatively few references reported about the electroluminescent QLEDs based on AgInS₂ (AIS) QDs, and the device performance lagged behind those based on CIS QDs and much behind those based on II-VI ones.

Ternary or quaternary I-III-VI QDs have been recognized as a choice to avoid the heavy metals, such as Zn–defused CIS and AIS QDs [2, 16]. Xiang et. al synthesized high–quality luminescent ternary AgInS₂ QDs by varying the reaction conditions with a simple one-step hot injection method. The peak wavelength and the
absorption spectra of the AgInS$_2$ QDs synthesized under a same reaction temperature exhibited a blue-shift as In:Ag ratio increased, and that of the QDs with In/Ag = 4 showed a red shift as the reaction temperature increased. With the introduction of Zn ions, quaternary Ag-Zn-In-S QDs whose emission wavelength moved to higher energies were obtained. For the first time, AgInS$_2$ QDs were used as emitters to fabricate sandwich-like structured QD-LED. Despite the performance of the EL was not that excellent, AgInS$_2$ QDs were confirmed their applications in the optoelectronic devices [17]. In our paper, the synthesis method in the aforementioned paper was used to prepare AIS QDs, but with different indium and zinc salts, different reaction time and under different reaction temperature. The PL emissions of our AIS QDs, which can be tuned from 603 nm to 868 nm by adjusting the ratio of In and Ag precursors, show similar blue shift with increasing In/Ag ratio, as well as the results in the aforementioned paper and other published articles [18, 19]. Core–shell structure have been applied in QDs to passivate the surface defect and restrain the dot-dot Forster resonant energy transfer (FRET), so that QDs with high photoluminescence (PL) quantum yields (QYs) can be obtained [14, 15]. Here in this work, different from the synthesis method of quaternary Ag-Zn-In-S QDs in the [17], ZnS shell were introduced upon the AIS (In/Ag = 4) cores with the highest PL QY to obtain core/shell AIS/ZnS QDs, whose PL QY was increased from that of the AgInS$_2$ ones 57% to 72%, owing to the passivation of surface defects. However, as reported in reference, PL quantum yields of Ag-Zn-In-S QDs decreased compared to that of AgInS$_2$ ones, and this decrease can be attributed to the large amount of defects on the surface [17]. The obtained AIS/ZnS QDs were employed as emitters to fabricate electroluminescent QLEDs. The optimized device exhibited a luminance 1120 cd m$^{-2}$ and a maximum EQE of 1.25%. As far as we known, these results are by far the best of the reported devices based on AIS/ZnS QDs. With more studies on the synthesis strategies of AIS/ZnS QDs, and the structure optimization of device, performance of device free of toxic heavy metals are expected to increase substantially in the future.

2. Experiment

2.1. Materials
Silver nitrate (AgNO$_3$, 99.8%, powder), sulfur (S, 99.99%, powder), magnesium acetate tetrahydrate (Mg(CH$_3$CO$_2$)$_2$·4H$_2$O, 99.0%), tetramethylammonium hydroxide (TMHA, AR), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), hexane (AR), ethanol (AR), isopropanol (AR), acetone (AR) and chlorobenzene (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Indium acetate (In(CH$_3$CO$_2$)$_3$, 99.99%, powder), zinc acetate (Zn(CH$_3$CO$_2$)$_2$, analytically pure (AR)), zinc acetate dihydrate (Zn(CH$_3$CO$_2$)$_2$·2H$_2$O, AR, 99.0%), dimethyl sulfoxide (99.7%), 1-dodecanethiol (DDT, 98%), n-octane (99%) and triocylphosphine (TOP, 90%) were purchased from Macklin. Poly[bis(4-phenyl)-4-(butylphenyl)amine] (Poly-TPD) was purchased from American Dye Source. Oleic acid (OA, 90%), oleylamine (OAm, 90%), 1-octadecene (1-ODE, 90%), toluene (99%) were purchased from Aladdin. Indium–tin oxide (ITO) glass substrates were purchased from Xiamen Weihua. All reagents were used as received without further experimental purification.

2.2. Synthesis of AgInS$_2$ cores
For the synthesis AgInS$_2$ cores, firstly, 0.1 mmol AgNO$_3$ and 0.4 mmol In(CH$_3$CO$_2$)$_3$ were loaded in a 50 ml three-neck flask. Then, 1 ml OA, 2 ml DDT and 5 ml ODE were added sequentially into the flask. Subsequently, the mixture was heated to 80 °C and then vacuumed for 30 min, during which nitrogen was pumped into the two or three times. When the bubbles disappeared totally, the mixture was heated to 130 °C under which S precursor (0.65 mmol S dissolved in 2 ml OAm under 60 °C) was injected. The reaction lasted for 20 min and AgInS$_2$ core solution can be obtained. By repeating precipitation/dispersion several times with hexane and ethanol, purified AgInS$_2$ cores can be obtained. AgInS$_2$ cores were dispersed in toluene for further use.

2.3. Synthesis of AgInS$_2$/ZnS QDs
For the synthesis of AgInS$_2$/ZnS QDs, AgInS$_2$ core solution of toluene was loaded in a three-neck flask. Then, 1 ml OA, 1 ml OAm, 1 ml DDT and 3 ml ODE were added into the flask sequentially. Next, the process of heating and vacuuming was repeated as described above, and then the mixture of Zn and S precursor (0.4 mmol Zn(CH$_3$CO$_2$)$_2$ and 0.4 mmol S dissolved in 2 ml TOP) was injected into the flask within 2 min. The reaction lasted for 20 min so that ZnS shell had enough time to grow.

2.4. Device fabrication
Three mmol Zn(CH$_3$CO$_2$)$_2$·2H$_2$O and 0.17 mmol Mg(CH$_3$CO$_2$)$_2$·4H$_2$O were dissolved in 30 ml dimethyl sulfoxide and the solution was denoted as A. Ten mmol tetramethyl ammonium hydroxide was dissolved in 10 ml ethanol and the solution was denoted as B. Solution B was dropped into solution A. Half an hour later, the
reaction solution was mixed with toluene to proceed the process of purification, and the purified ZnO:Mg was dispersed in ethanol for further use.

ITO glass substrates were cleaned ultrasonically by using deionized water, acetone and isopropanol sequentially (each for 15 min), and then etched with ozone under the radiation of UV for 20 min. Next, the cleaned substrates were transferred into the glove box filled with argon for spinning. PEDOT:PSS solution was spun onto the ITO glass with a speed of 4000 rpm for 40 s and then annealed for 15 min under 150 °C. Then Poly-TPD solution of chlorobenzene was spun onto the surface of PEDOT:PSS with a speed of 3000 rpm for 40 s and then annealed for 30 min under 150 °C. Subsequently, AgInS2/ZnS solution was spun onto the surface of Poly-TPD with a speed of 2000 rpm for 40 s and then annealed under room temperature for 20 min ZnO:Mg particles was dissolved in ethanol and then spun on AgInS2/ZnS QDs with a speed of 2000 rpm for 40 s followed by annealing at 60 °C for 30 min. Finally, 100 nm aluminum film was deposited on the surface of ZnO:Mg by using of vacuum thermal evaporation under a vacuum pressure of 4 × 10⁻⁴ Pa.

2.5. Characterization

The structure properties of the as prepared AIS/ZnS QDs were characterized using a high-resolution transmission electron microscope (TEM; JEM-2010, JEOL) and an x-ray diffractometer (XRD, MiniFlex II X-ray diffractometer, Rigaku). The steady-state PL spectra of the QDs were characterized by using a spectrophotometer (Cary Eclipse, Varian) and the UV–vis absorption spectra were characterized by using another spectrophotometer (Cary 300, Varian). Time-resolved PL were recorded with a spectrometer (Bruker Optics 250IS/SM) integrated with an intensified charge coupled device detector (Andor, IStar740). The PL QYs of the QDs were tested with an absolute QY test system (Quantaurus-QY C11347-11, Hamamatsu Photonics). The luminescent performances of the fabricated QLEDs were performed on a spectrometer (Maya 2000 Pro, Ocean Optics) coupling with an integrating sphere (3P-GPS-033-SL, Labsphere).

3. Results and discussion

3.1. Optical properties

Hot-injection method was employed to synthesis the AgInS2 cores and core/shell AIS/ZnS QDs. For AIS core QDs, their emission wavelength can be adjusted by control the precursor ratio of In and Ag. As shown in figure 1(a), the peak wavelength of AIS QDs shifts to the higher energy with the increase of In:Ag. With In : Ag = 1, 2, 3, 4 and 5, the corresponding emission wavelength are 868 nm, 808 nm, 721 nm, 666 nm and 603 nm respectively. Obviously, this composition-dependent blue shift in AIS QDs is resulted from a band gap widening, which is generally attributed to the lowering of valence band maximum due to the weakened repulsion between Ag d and S p orbitals in Ag-deficient material [17]. Surface defects and dot-dot FRET are the common non-radiation channels of excitons. Core/shell QDs usually exhibit higher PL QYs than that of pure core dots. Moreover, shell thickness have large influence on the optical properties of core/shell QDs and the performance of corresponding devices, and appropriate shell thickness is generally required [15, 20, 21]. QDs of
appropriate shell thickness is helpful not only for the passivation of the surface defects of the cores but also the restraint of the dot-dot FRET, so that benefit the improvement of PL QY of QDs and device performance. Reference reported that there exists a pronounced trade-off between the shell thickness and the quantum yield in CdSe/CdS system [20]. The PL QY of CdSe/2CdS core/shell QDs increased from ~30%–40% for pure CdSe cores to near unity, and the PL decay dynamics became single-exponential indicating complete elimination of detrimental traps. These excellent optical features were retained for the nanocrystals with up to ten monolayers of CdS shells. The PL QY began to decrease gradually when the CdS shell thickness exceeded ten monolayers, indicating possible traps resulted from the later epitaxy of the CdS shells [21]. QLEDs based on Cu-In-S/ZnS QDs with different shell thickness period of time and different shell thickness exhibit different device performance [15]. After optimizing the experiment condition, the AIS QDs with In : Ag = 4 peaked at ~660 nm exhibit a highest QY of 57%. Therefore, AIS QDs with In : Ag = 4 were used to synthesis AIS/ZnS QDs, and the PL QY of the obtained AIS/ZnS QDs with three layers of ZnS shell was tested to be 72%, which is enhanced by 26.3% than the pure cores. The luminescence of the AIS/ZnS QDs with shell more than three layers began to dim. Therefore, herein our work, AIS/ZnS QDs with three layers of ZnS shell were employed as emitters to fabricate QLEDs. ZnS or ZnSe layers usually were introduced upon the ternary CdZnS or CuInS2 cores to enhance their PL QYs [22]. Here, the PL QYs of AIS QDs were tested by using an absolute QY and the results are shown in figure 1(b). After optimizing the experiment condition, the AIS QDs with In : Ag = 4 peaked at ~650 nm exhibit a highest QY of 57%. Therefore, AIS QDs with In : Ag = 4 were used to synthesis AIS/ZnS QDs, and the PL QY of the obtained AIS/ZnS QDs was tested to be 72%, which is enhanced by 26.3% than the pure cores. This advancement of PL QY probably originate from a better passivation of the AIS cores by ZnS shell combined with the reduction of FRET [14, 23]. The UV–vis absorption and PL spectra of the AIS and AIS/ZnS QDs were also characterized and shown in figure 1(c). It can be seen from figure 1(c) that the UV–vis absorption spectra of AIS/ZnS exhibit a more obvious exciton peak than that of AIS cores, indicating the thinner size distribution and the reduced non-radiation recombination, which is also verified by the thinner FWHM of AIS/ZnS QDs (122 nm) than that of AIS ones (134 nm). In addition, the peak emission of the PL spectrum show a 60-nm blue shift to that of the AIS cores, which can be attributed to the diffusion of Zn2+ in the interface around the AIS core, and such marked blue-shift in emission has been observed in CuInS2/ZnS QD system [23, 24].

To get more insight into the optical properties of AIS/ZnS QDs, the time-resolved PL spectra of AIS cores and AIS/ZnS QDs were also recorded and shown in figure 1(d). Generally, the PL decay curves of I-III-VI QDs can be fitted well by a double-exponential function written as $I(t) = a_0 + a_1 e^{(-t/\tau_1)} + a_2 e^{(-t/\tau_2)}$, and amplitude $a$ and decay time constant $\tau$ for radiative recombination and non-radiative recombination can be obtained [17, 23]. However, the PL decay mechanisms of I-III-VI are still under debates. Xiang et al. attributed the short PL decay time of AIS QDs to the DAR combination of electrons and holes trapped in the intrinsic defects, and the long decay one to the surface defects [17]. However, For CuInS2/ZnS QDs, the fast decay time is ascribed to the radiative recombination process of the surface defects and the slower decay one to the high-lying defect donor states [3]. Despite this, it has been known that I-III-VI QDs usually exhibit long average PL lifetimes with the magnitude of hundreds of nanoseconds[3, 25, 26]. The PL decay curves of the as prepared AIS and AIS/ZnS QDs were also fitted by using the double-exponential function described above and the average lifetimes were calculated by using $\tau = \frac{a_1 \tau_1 + a_2 \tau_2}{a_1 + a_2}$. All the lifetimes are summarized and listed in table 1. It can be seen from table 1 that for AIS QDs, fast decay path with a time constant 0.674 ns had a contribution of 6% to the whole emission process, and the slow decay one with the time constant 16.988 ns devoted a contribution of 94% to the emission, and the final average lifetime is 16.01 ns. For AIS/ZnS QDs, both the short and the long decay time are much longer than those of the AIS QDs. However, similar to the AIS QDs, slow decay path occupied a major part in the whole emission profile (99.4%), and the average lifetime is 65.104 ns. Although the average lifetime of AIS/ZnS QDs exhibit remarkable enhancement compared to AIS QDs, it is still much shorter than those reported values [3, 25, 26]. It is expected that the PL decay mechanisms of the as prepared AIS QDs and AIS/ZnS can be uncovered with more deep studies.

| QDs      | $a_1$ | $a_2$ | $\tau_1$ (ns) | $\tau_2$ (ns) | $f_1$ | $f_2$ | $\tau$ (ns) |
|----------|-------|-------|---------------|---------------|-------|-------|-------------|
| AIS      | 0.272 | 0.178 | 0.674         | 16.988        | 0.06  | 0.94  | 16.01       |
| AIS/ZnS  | 0.072 | 0.599 | 3.488         | 65.476        | 0.006 | 0.994 | 65.104      |

Table 1. The fitting results of AIS and AIS/ZnS QDs.
3.2. Structure characterization

XRD patterns of AIS and AIS/ZnS QDs were recorded and shown in figures 2(a) and AIS/ZnS QDs, (c) TEM image of AIS QDs (with In : Ag = 4), (d) HR-TEM images of AIS/ZnS QDs, (e) Size distribution of AIS QDs (with In : Ag = 4), and (f) Size distribution of AIS/ZnS QDs.

Figure 2. (a) XRD patterns of AIS QDs with different In : Ag ratio, (b) XRD patterns of AIS (with In : Ag = 4) and AIS/ZnS QDs, (c) TEM image of AIS QDs (with In : Ag = 4), (d) HR-TEM images of AIS/ZnS QDs, (e) Size distribution of AIS QDs (with In : Ag = 4), and (f) Size distribution of AIS/ZnS QDs.

Figure 2. (a) XRD patterns of AIS QDs with different In : Ag ratio, (b) XRD patterns of AIS (with In : Ag = 4) and AIS/ZnS QDs, (c) TEM image of AIS QDs (with In : Ag = 4), (d) HR-TEM images of AIS/ZnS QDs, (e) Size distribution of AIS QDs (with In : Ag = 4), and (f) Size distribution of AIS/ZnS QDs.

XRD patterns of AIS and AIS/ZnS QDs were recorded and shown in figures 2(a) and (b). For AIG QDs with In : Ag ratio less than 2 : 1, the diffraction patterns agree well with those of orthogonal AgInS2 (JCPDS NO. 25-1328), whose lattice planes (002), (320) and (322) locate at 26.586°, 44.530° and 52.616°, respectively. With the increasing of In : Ag ratio, the diffraction peaks shift to higher angles and approach to those of cubic AgIn5S8 (JCPDS NO. 25-1329), with lattice planes (311), (511) and (620) locating at 27.334°, 43.406° and 53.478°, respectively. AgInS2 QDs usually exhibit chalcopyrite orthorhombic or tetragonal phases. The low temperature orthorhombic phase is more stable than the high-temperature one. Reference reported that AgInS2 QDs exhibited tetragonal phase with reaction temperature over 140°C. A cubic spinel structure with the general formula of AgIn5S8 is another phase of In-rich ternary AgInS2 QDs. AgIn5S8 has a wide operating window. As previously reported, cubic AgIn5S8 can be obtained irrespective of the temperature when In : Ag ≥ 3 [18]. As the reaction temperature for the synthesis of our QDs is 130°C, here we infer cautiously that with the increasing of In:Ag ratio, phase transformation from orthorhombic AgInS2 to tetragonal AgIn5S8 occurred, similar to the reported results [18]. For core/shell QDs, thin shell provides a tiny potential barrier and electrons are liable to access surface states. Shell with appropriate thickness not only provides a sufficient potential barrier hindering those processes, which leads to the effective confinement of excitons generated in the core domain and the reduction of non-radiative emission of surface states, but also suppress the inter-QD FRET by rendering the surrounding dipoles of QD cores distant [15, 27]. Here, three layers of ZnS shell were introduced upon the AIS cores with In : Ag = 4 to synthesize AIS/ZnS QDs. XRD measurements were also performed for these obtained AIS/ZnS QDs and the recorded patterns are shown in figure 2(b). For comparison, the XRD patterns for AIS QDs with In : Ag ratio of 4 : 1 are also shown in figure 2(b). As seen from figure 2(b), the three main diffraction peaks of AIS/ZnS QDs are similar to those of the wurtzite ZnS (JCPDS NO. 89-7334), whose lattice planes of (002), (110) and (200) locate at 27.852°, 47.532° and 55.465°, respectively. TEM images of AIS (with In : Ag = 4) and AIS/ZnS QDs, and their corresponding size distribution analysis are shown in figures 2(c)–(f), respectively.
In-Zn-S QDs, brie
d solid-solution such as AgInS2-ZnS can be synthesized during which the alloying process allow for gradual strain
ZnS layers tend to shell the AIS cores.

As can be seen from
2.5 nm. With the introduce of ZnS layers, HR-TEM image of AIS
shell ambient the AIS core is dif
gradient located at the core/shell interface [15, 28]. However, above discussions are not enough to verify that
ZnS layers tend to shell the AIS cores.

As previously reported, owing to lattice mismatch between AIS and ZnS, alloyed quaternary Ag-In-Zn-S and
solid-solution such as AgInS2-ZnS can be synthesized during which the alloying process allow for gradual strain
release, fewer surface defects, and improved PL properties [17, 19, 29]. For synthesizing typical quaternary Ag-
In-Zn-S QDs, briefly, metal precursors including silver, indium and zinc were mixed with ODE were heated to
170 °C and then sulfur solution of oleylamine was injected quickly [17]. By injecting sulfur solution into the
mixture of silver and indium precursors to prepare AIS cores, and then injecting zinc precursor into the AIS
solution, Ag-In-Zn-S QDs also were synthesized [29], and For synthesizing ZnS-AgInS2 solid solution, Zn
precursor was injected into the solution where AIS reaction solution was going on [19]. Different from
aforementioned methods, here for the synthesis of AIS/ZnS QDs, the mixture of Zn and S precursor was
injected into the prepared AIS solution within 2 min under 130 °C, and the reaction lasted for 20 min. To obtain
the highest PL QY, the injection process was repeated for three times. It can be seen that all the synthesis methods
of quaternary Ag-In-Zn-S QDs, AgInS2-ZnS solid-solution and AIS/ZnS QDs were based on or during the
reaction of AIS cores. However, following steps were different from each other. Only sulfur or zinc precursor
was injection into the reaction solution for the synthesis of quaternary Ag-In-Zn-S QDs, but both sulfur and zinc
precursors were needed for the formation of AIS/ZnS ones. The shelling processes for AIS/ZnS QDs is similar
to that for another I-III-VI system CuInS2 /ZnS ones [14, 30]. Combined with the results of XRD patterns for
AIS/ZnS QDs, it could be concluded that ZnS tends to shell the alloyed AIS cores.

3.3. Device performance
AIS QDs deposited as thin films were used to fabricated LEDs for the first time with a sandwich-like structure of
ITO/MnO2 /Poly-TPD/AgInS2 QDs/TPBi/LiF/Al, and it was reported that the device exhibited a maximum luminance of 6.2 cd m−2 and a highest current density about 220 mA/cm2, upon an applied voltage of 11.6 V [17]. With the structure of ITO/PEDOT-PSS/AgInS2 QDs/TPBi/LiF/Al, Lv et. al also fabricated AIS-based QLEDs which exhibited a maximum luminance intensity of 122 cd m−2 with a current density of 95 mA cm−2 at 4.9 V [31]. Here in this work, AIS/ZnS QDs with PL QY of 72% and emission peak of 590 nm were employed as emitters to assemble QLEDs according to a conventional multi-layer structure ITO/PEDOT:PSS/Poly-TPD/ QDs/ZnO:Mg/ Al (as illuminated in figure 3(a)). Besides the PEDOT:PSS/Poly-TPD interface, TEM image of
device given in figure 3(b) indicates that other function layers can be distinguished clearly. The
electroluminescence (EL) spectra of the devices under different applied voltages were recorded and stacked in
figure 4(a). With the applied voltage increasing from 4 V to 8 V, the luminance intensity ascends gradually with
constant FWHM about 85 nm. Owing to the Stark effect resulted from the field-induced spectra split, the
emission peak exhibits slight blue-shift as the voltage increasing [32, 33]. The J-V curve (current density versus
voltage), as well as the L-V curve (luminance versus voltage) is shown in figure 4(c). It can be seen from
figure 4(c) that the turn-on voltage is about 3.0 V, which is higher than that of the Cd-based devices (1.8 V), and
lower than that of the Cd-free ones. With the applied voltage varied from 0 to 8 V, the current density achieved a
maximum value of 1050 mA cm−2 at 5.8 V, and the luminance exhibited a maximum value of 1120 cd/m2 at
4.6 V. Multi-shell AIS QDs have been reported to demonstrate high PL QYs, 87% for three-layer shell and 80%
for double-shell, which is much higher than that of our AIS/ZnS QDs (72%). These improvements compared to
the reported AIS-based devices [17, 31] may be attributed to the different active materials and different device

Figure 3. (a) Structure diagram and (b) TEM image of the QLED based on AIS/ZnS QDs.
structure. The EQE-V curve (EQE versus voltage), as well as the CE-V curve (current efficiency versus voltage) is shown in figure 4(d). Under the applied voltage of 3.6 V, the device exhibited a highest EQE of 1.25% and a maximum CE of 0.331 cd/A. The device performance is certainly necessary to be improved further to satisfy the needs of some practical applications.

High PL QY of QD solution does not guarantee the good performance of devices. Therefore, the EL performance of the device was no better than the PL of AgInS2/ZnS QDs. This can be attributed to the reduced dot-dot distance leading to the increased inter dot energy transfer that may quench the emission [22]. For comparison, EL spectra of the device exhibited the highest luminance (under the applied voltage of 4.6 V) combined with the PL curve of the QDs is shown in figure 4(b). As the inset shown in figure 4(b), the device emitted bright yellow light under the driving voltage of 4.6 V. It can be seen from figure 4(b) that the emission peak of the EL spectra shift from that of the PL one (593 nm) to 615 nm with enlarged FWHM (90 nm). Red-shift of the EL spectra is likely caused by the aggregation of dots resulted from the partial detachment of organic surface ligands after the several purification before the spin-coating process for device fabrication [17]. Furthermore, the compact film of solvent and the dielectric dispersion are also attributable to the red-shift of EL [32]. As the curves shown in figure 4(b), the FWHM of the EL spectrum is wider than that of the solution PL one. I-III-VI QDs usually exhibit much wide line widths whose origin is still not fully understood. Both sample heterogeneities including size polydispersity and random positioning of the emitting center are considered to be account for the broad emission of PL. It is still remained unclear whether the observed wide FWMH is an intrinsic optical property [13, 14, 34]. During the process of QD solution transferring to QD film, solvent evaporation and ligand detachment caused by spinning, annealing or other handling will increase the dot concentration and lead to the dot aggregation. Therefore, intensive size inhomogeneous and distribution of positional heterogeneity of emitting centers within a QD solid in a dot film may be reasons for the widening of the FWHM of the AgInS2/ZnS based QLED, compared to that of the PL of dot solution.

4. Conclusion

In summary, we synthesized emission tunable AIS QDs by using of a hot-injection method. By adjusting the ratio of In and Ag precursor, the emission wavelength of AIS QDs can be tuned from 603 to 868 nm. Therein, QDs peaked at ~666 nm exhibited a highest PL QY of 57% and were chosen as cores to synthesize core/shell AIS/ZnS QDs. The PL QY of the final AIS/ZnS QDs was measured to be 72%, enhanced by 26.3% compared to that of the core dots. QLED based on the AIS/ZnS QDs with a conventional device structure exhibited a maximum luminance of 1120 cd m⁻², and highest EQE of 1.25% and a current efficiency of 0.331 cd/A. With the development of chemical strategies for synthesis core/shell I-III-VI QDs, and explore more matched materials and device structure, QELDs based on the heavy-metal-free QDs are expected to find practical application in the field of display and illumination.
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