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Mg-Doped ZnO Nanoparticle Films as the Interlayer between the ZnO Electron Transport Layer and InP Quantum Dot Layer for Light-Emitting Diodes

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ABSTRACT: Because of the wide emission spectrum tunability that ranges from the visible region to the near-infrared, InP-based colloidal quantum dots (QDs) show great promise for use in the next-generation full-color displays and solid-state lighting. The performance-improved InP QD-based light-emitting devices (QLEDs) were fabricated by using Mg-doped ZnO nanoparticles (ZnMgO NPs) as an interlayer between the ZnO electron transport layer and active InP QD layer. It is found that ZnMgO NPs can reduce electron injection and suppress exciton quenching, which are attributed to the improvement of charge balance in the devices. We successfully demonstrated higher maximum current efficiencies of 5.46 and 5.91 cd/A than the references (2.31 and 2.36 cd/A) without the ZnMgO NP layer in highly efficient red and green QLEDs, respectively. These results signify an effective approach to improve heavy-metal-free QLEDs for commercial applications.

INTRODUCTION

Because of their excellent characteristics, such as high luminance efficiency, high color saturation, solution-progress fabrication, and large-area production, quantum dot light-emitting diodes (QLEDs) have become one of the most interesting research hotspots in display and solid-state lighting fields during the past 30 years. Up to now, the external quantum efficiencies (EQEs) over 20% of red, green, and blue QLEDs based on CdSe core–shell quantum dots (QDs) have been obtained.1−5 Highly efficient QLEDs were obtained relying on the use of heavy-metal cations such as cadmium,6−9 lead,10,11 and mercury,12−15 which make up the core or the shell or the core/shell of colloidal QDs. However, there are growing concerns regarding the risks that these materials pose to our health as well as the environment. It is necessary to develop high-performance heavy-metal-free QLEDs, which can be applied into livelihood and commercial field. Previous studies have already reported a few demonstrations of QLEDs based on heavy-metal-free QDs, such as CuInS/ZnS QDs,16,17 and silicon QDs.18,19 Among the possible materials, InP QDs have been paid special attention because of their wide emission, which can, in principle, be tuned throughout the whole visible and near-infrared range by changing their size.20,21 InP QDs show great promise for use in the next-generation full-color displays and solid-state lighting. It is a challenge to achieve high-performance QLEDs based on InP QDs.

Recently, great progress of QLEDs based on InP QDs has been achieved through the fast development of synthesis strategy (thick shell and alloy-intermediate shell),22−26 device architecture (conventional27,28 and inverted29,30), and interfacial engineering. Though good QLEDs have been obtained,30,31 the luminance and efficiency are still lower than those of Cd-based QLEDs. Considering that InP QDs possess energy levels with alternative emitting materials (valence band maximum (VBM): 3.5−4 eV and conduction band minimum (CBM): 5.5−6 eV), and organic–inorganic hybrid device structures are employed. In order to enhance the electroluminescence (EL) efficiency of InP QLEDs, approaches to improve charge injection and transport balance, especially, the fraction of injected charges that form excitons must be applied into all solution-processed QLEDs.

Since reported 10 years ago, ZnO nanoparticles (NPs)32 and doped ZnO NPs33,34 show excellent electron transport properties, such as high mobility, suitable energy level, and solution-processed deposition, which can be used as an electron transport layer (ETL) in QLEDs. In addition, recent studies show that the strong electron injection ability of ZnO NP layer can cause unbalanced carrier injection and result in excess electrons in the emitting layer. In general, the excess electrons may cause many problems, for example, a reduction
of the fraction of charges that form excitons, trion emission formed by charging QDs, a drop of EL performance, or a decrease of device lifetime. One way to solve the above problems is in virtue of the reduction of excess carriers injected into the QD layer and forming efficient exciton recombination by incorporating interlayers into QLEDs. This strategy has been previously demonstrated with a thin poly(methyl methacrylate) insulating layer sandwiched between ZnO NP ETL and QD emitting layer or double aluminium oxide (Al₂O₃) insulating layers around QDs for high-efficiency and long lifetime QLEDs. Allowing for QLEDs based on InP QDs, in 2013, a thin conjugated polyelectrolyte layer (poly[(9,9-bis(3-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-octylfluorene)]) was used as an interfacial dipole layer in inverted green QLEDs to reduce the electron injection barrier between the cathode and QDs via the vacuum level shift. The bright, efficient, and environmentally friendly InP QLEDs show a maximum EQE of 3.46% and a luminance of 3900 cd/m², respectively.

Generally speaking, inserting an interlayer in the QLED structure is a quite helpful method to modulate the carrier migration and enhance the EL performance of the device. However, most interface optimized QLEDs were fabricated based on an insulating layer or organic polymer layer, there are a few reports focusing on the metal oxide modification layer. Especially, for InP QLEDs, there are few reports on Mg-doped ZnO (ZnMgO) NPs that are used as an interlayer. For the purpose of improving the EL properties, in this work, we use ZnMgO NPs as an interlayer between ZnO NP ETL and InP-emitting layer to suppress exciton quenching and reduce the electron current, in consequence, obtaining a better charge balance in the device. The best performance device with ZnMgO NPs shows a 2.36-fold enhancement of current efficiency (CE, 5.46 cd/A) than the reference (2.31 cd/A) without the interlayer. Luminance over 5000 cd/m² is achieved for the red device. This strategy was also used in green InP QDs to realize a 2.5 times higher CE (5.91 cd/A) for the green device than reference (2.36 cd/A).

EXPERIMENTAL DETAILS

Materials. TFB was purchased from Luminescence Technology Group. Chlorobenzene (99.8%) and hexane (99%) were purchased from Sigma-Aldrich. Zinc acetate dehydrate (99%) was purchased from Xilong Chemical Co., Ltd (Guangdong, China), magnesium acetate was acquired from Aladdin Chemical Reagent Company Ltd. (China), potassium hydroxide was acquired from Tianjin Chemical Reagent Factory (Tianjin, China), and normal butanol (99%) was purchased from Alfa Aesar. Methanol (99%) was obtained from Sinopharm Chemical Reagents (Shanghai, China). The InP/ZnSe/ZnS core–shell QDs were synthesized under the help of Mesolight Inc. Detailed synthetic information of nanoparticles is provided in the Supporting Information. All materials were used as received without any further purification.

Fabrication of QLEDs. The custom-made ITO electrodes on glass with a sheet resistance of ~15 Ω/□ were treated with the UV−ozone method for 15 min. PEDOT:PSS (Baytron PVPAl 4083, filtered through a 0.22 μm filter) was spin-coated onto ITO electrodes at 2000 rpm for 40 s. Then, the PEDOT:PSS-coated substrates were transferred into a nitrogen-filled glovebox (O₂ < 1 ppm, H₂O < 1 ppm). TFB (8 mg mL⁻¹, chlorobenzene), QDs (6 mg mL⁻¹, hexane), ZnMgO NPs (20 mg mL⁻¹), and ZnO NPs (40 mg mL⁻¹) were deposited layer-by-layer by spin-coating on the PEDOT:PSS layer. The TFB, ZnMgO NP layers were baked at 150 °C for 30 min and 120 °C for 10 min. The QD layer was spin-coated at 3000 rpm for 30 s. The ZnO NPs were spin-coated at 1000 rpm for 40 s. Finally, Al electrodes (100 nm) were deposited using a thermal evaporation system through a shadow mask to form an active device area of 1 mm² under a high vacuum of 1 × 10⁻⁴ Pa. The thickness of each layer of device C: 35 nm PEDOT:PSS, 35 nm TFB, 20 nm InP QDs, 20 nm ZnMgO NPs, 65 nm ZnO NPs, and 100 nm Al. The thickness of multiple layers in the electron-only device: ITO/ZnO NPs (60 nm)/QDs (20 nm)/ZnO NPs (60 nm)/Al and ITO/ZnO NPs (60 nm)/QDs (20 nm)/ZnMgO NPs (20 nm)/ZnO NPs (40 nm)/Al.
Characterization. The cross-sectional scanning electron microscope (SEM) measurements were performed on a field-emission scanning electron microscopy instrument (S4800, Hitachi). Transmission electron microscopy (TEM) images were recorded with a transmission electron microscope (JEM-2100F, JEOL) operating at 200 kV. Atomic force microscope (AFM) measurements were conducted using a scanning probe microscope (SPM-9700, Shimadzu) in the tapping mode. Ultraviolet photoelectron spectroscopy (UPS) was measured using the Thermo ESCALAB 250 surface analysis system. The X-ray diffraction (XRD) patterns were taken on a Rigaku D/MAX-2500 diffractometer (Cu Kα, λ = 1.54 Å). The PL spectra were measured with a fluorescence spectrophotometer (F-7000, Hitachi) at an excitation wavelength of 440 and 360 nm for red and green QDs, respectively. The PL decay curves are showed in Figure 1c, as we all know, lifetime is determined not only by radiative decay but also by nonradiative recombination progress. The time-resolved PL spectra of InP/ZnS QDs exhibit a decay with a dual channel form, while the average lifetime (53.2 ns) of QDs in solution is naturally decreased when they remain in the solid state. An average lifetime reduction to 47.21 ns is observed on a 20 nm thick QD film on glass, and detailed information of PL exponential decays is collected in Table S1. As the device structure diagram shown in Figure 1d, the optimized multilayer structure of QLED is: an indium tin oxide (ITO) as an anode, a poly (ethylenedioxythiophene):polystyrene sulphonate (PEDOT:PSS) as a hole-injecting layer (HIL), a poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine) (TFB) as a hole transport layer (HTL), InP QDs as the emitting layer (EML), ZnMgO NPs as the interlayer, ZnO NPs as ETL, and Al as the cathode. Hence, the cross-section SEM image of representative QLED is exhibited in Figure 1e, which shows that the interfaces of the multiple layers are distant contact.

For the purpose of reducing the excess carriers that are injected into the QD layer and forming efficient exciton recombination by incorporating the interlayer, Mg-doped ZnO NPs were used in this work by increasing the injection barrier as the energy-level diagram of device, as illustrated in Figure 1f. The higher CBM level attributes to form an injection barrier when electrons are injected from ZnO to ZnMgO. Compared with the previous report,38,39 the Zn0.85Mg0.15O NP film was used as the interlayer in our work to investigate the ZnMgO interlayer effect on the device performance. Atom fraction of used ZnMgO NPs is 15%, which was shown in energy-dispersive analysis of X-ray (Figure S1).

Figure 2a shows the XRD patterns of the as-prepared ZnO and ZnMgO NPs. It can be observed that the diffraction peaks of ZnO and ZnMgO NPs are in agreement with JCPDF card, 36-1451, which indicates that ZnO NPs have a hexagonal wurtzite structure, and ZnMgO NPs have an archetypal wurtzite-type ZnO structure. No visible shift in reflection peak positions by MgO alloying was observed. It may due to the fact that Mg2+ was incorporated into the ZnO lattice without...
appreciable strain caused by the ionic radii of Mg$^{2+}$ (0.57 Å) being smaller than the ionic radii of Zn$^{2+}$ (0.60 Å). ZnMgO NPs have more broad diffraction peaks than ZnO NPs, suggesting that the size of ZnMgO NPs is smaller than that of ZnO NPs, just as illustrated in surface morphology images (Figure 2b,c). Consequently, the surface roughness of ZnO NP layer (3.82 nm) is larger than that of the ZnMgO NP layer (1.61 nm). The smooth surface morphology of ZnMgO NP films is considered as particularly important for the high performance of solution-processed optoelectronic devices. SEM images of ZnO and ZnMgO NP film are provided in Figure S3a,b, and a relative smooth ZnMgO NP film is observed, which is in agreement with the 3D AFM images in Figure S3c,d.

The $(\alpha h \nu)^2 - h \nu$ plots converted from UV-abs spectroscopy (Figure S4) and UPS of ZnO and ZnMgO NPs are measured and demonstrated in Figure 2d,e, respectively, to investigate the band gaps and energy levels of different NPs. As shown on $(\alpha h \nu)^2 - h \nu$ plots, the band gaps of ZnO and ZnMgO NPs are 3.32 and 3.44 eV, respectively. In Figure 2e, it can be seen that the high-binding energy cutoff $(E_{\text{cutoff}})$ and the onset energy in valence-band edge $(E_{\text{onset}})$ regions change with the content of dopant. The VBM is determined, according to the equation of $VBM = 21.2 - (E_{\text{cutoff}} - E_{\text{onset}})$, which is $-7.49$ and $-7.0$ eV for ZnO and ZnMgO NPs, respectively. The CBM can be calculated based on the band gap and VBM, which is $-4.17$ and $-3.56$ eV for ZnO and ZnMgO NPs, respectively. As exhibited in the energy level diagram of multiple layers in the QLED (Figure 1f), there exists a 0.61 eV injection barrier when electrons are injected from ZnO to ZnMgO. The interlayer could block the interfacial charge transfer and reduce the electron current, which can result in a better charge balance in QLED.

As demonstrated in Figure 3a, the PL spectra of ZnO and ZnMgO NPs show a wide emission in the visible region. Because of the larger band gap, the peak of visible emission is blue-shifted from 547.8 nm for ZnO NPs to 531.2 nm for ZnMgO NPs. The intensity of visible emission reflects the defect concentration of ZnO and ZnMgO NPs. By the Mg doping, the defect emission is suppressed. In addition, the intragap states located inside the band gap of ZnO could act as charge recombination sites, which trap holes and quench excitons because of the well-aligned defect level with the VBM of QDs. To investigate the effect of incorporation of ZnMgO NP interlayer, the time-resolved and steady-state PL spectra of two samples with structures of glass/ZnO NPs/QDs and glass/ZnO NPs/ZnMgO NPs/QDs were tested. In the time-resolved PL spectra (Figure 3b), we can see that the average exciton lifetime of QDs on the glass/ZnO NP substrate shows a significant drop compared with QDs directly
The enhancement of EL efficiency is probably because of the reduction of electron injection, which thus reaches the charge balance. To verify this hypothesis, electron-only devices with or without the ZnMgO NP layer were fabricated, and their J−V characteristics are measured and shown in Figure 4e. The total thickness of the NP layer was kept at the same value, in order to exclude the influence of increased device thickness on J−V characteristics. Detailed device fabrication information and thickness of electron-only devices is provided in the experimental part. As demonstrated in Figure 4e, devices with the ZnMgO NP layer indeed exhibit a remarkably lower electron current than the reference. As the above discussion (Figure 2), because of the higher CBM level of ZnMgO NPs, ZnMgO NPs can effectively block the injection of electrons and thereby reduces the electron current. Furthermore, the lower electron mobility of ZnMgO also contributes to the reduction of electron current. As shown in Figure S6, mobility of different NPs was achieved by fitting the space charge-limited current region with Child’s law, and an electron mobility of 0.36 × 10⁻⁵ cm² V⁻¹ s⁻¹ is obtained for ZnMgO NPs, which is lower than that of ZnO NPs (2.78 × 10⁻⁴ cm² V⁻¹ s⁻¹). To sum up, the reduced electron current of devices with the ZnMgO NP layer is caused by: (1) the higher CBM level, which can effectively block the injection of electrons into the active layer, and (2) the lower electron mobility, which can slow down the pace of electron transport from ETL to the emitting layer. Allowing for what discussed in Figure 3, the reduced defect concentration of ZnMgO NPs, exciton quenching can be effectively suppressed, which is also benefit for the improvement of EL efficiency. In conclusion, these conditions make devices with ZnMgO NPs reach a better charge balance as well as a better EL performance.

The Commission International de l’Eclairage (CIE) property of device C is shown in Figure S9. The red EL emission corresponds to CIE 1931 color coordinates of (0.66, 0.32). EL spectra and images of device C at different driving voltages are shown in Figure 4f. As bias voltage increases, there is no remarkable variation in the peak wavelength and FWHM of EL spectra. Detailed EL characteristics are summarized in Table 1. This strategy is also applied in QLEDs based on green InP QDs to verify if the ZnMgO interlayer could be applied in other color devices. The normalized PL spectrum of green QDs (peak @521 nm) and EL spectrum of green InP QLED (peak @526 nm) are shown in Figure S10. EL performance of the device with/without ZnMgO interlayer based on green InP QDs is illustrated in Figure S11. By the incorporation of the ZnMgO layer, green InP QLED reaches an enhanced CE from 2.36 to 5.91 cd/A, which means a 2.50-fold efficiency improvement.

**Table 1. Summary of Peak Wavelength (λmax) and FWHM of EL Spectra, Driving Voltage at 200 mA/cm², Maximum CE (CEmax), and Maximum EQE (EQEmax) of Devices A–D**

<table>
<thead>
<tr>
<th>device</th>
<th>EL λmax (nm)</th>
<th>fwhm (nm)</th>
<th>driving voltage (V)</th>
<th>CE (cd/A)</th>
<th>EQE (max) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>633</td>
<td>45</td>
<td>4.13</td>
<td>3.91</td>
<td>1.48</td>
</tr>
<tr>
<td>B</td>
<td>633</td>
<td>45</td>
<td>4.27</td>
<td>3.91</td>
<td>1.50</td>
</tr>
<tr>
<td>C</td>
<td>633</td>
<td>45</td>
<td>4.52</td>
<td>5.46</td>
<td>3.56</td>
</tr>
<tr>
<td>D</td>
<td>633</td>
<td>45</td>
<td>5.15</td>
<td>2.81</td>
<td>1.80</td>
</tr>
</tbody>
</table>

Because of the electric field-induced Stark effect and the interdot interactions, the trace of EL spectrum has 4 nm red-shift compared with that of the PL spectrum. In general, the current density is influenced not only by the hole/electron injection barrier but also by the thickness of the transport layer. As J−V characteristics presented in Figure 4b, the driving voltage increases as the thickness of interlayer increase. For example, at a current density of 200 mA/cm², the thickness of ZnMgO NP layer increases from 0 to 30 nm, the driving voltage increases from 4.13 to 5.15 V. From the L−V curves, it is obtained that the turn-on voltage (Vturn at luminance of 1 cd/m²) is 1.9, 1.9, 2.0, and 2.3 V for the device without the ZnMgO NP layer (device A), with the 10 nm ZnMgO NP layer (device B), 20 nm ZnMgO NP layer (device C), and 30 nm ZnMgO NP layer (device D), respectively. Additionally, the relatively thin devices (A and B) reach higher current density than the thick devices (C and D). The relatively high current density makes device A and B reach higher luminance than device C and D. For the QLEDs with the ZnMgO NP modification layer, although the luminance reaches a similar level during the whole driving voltage region, the current density is lower than that without the interlayer, implying a higher CE. This is confirmed by the CE and EQE as a function of current density, which are demonstrated in Figure 4c,d, respectively. By inserting a ZnMgO NP layer, a quite high CE of 3.91 cd/A is obtained for device B at a luminance of 230 cd/m². At a current density of 4.62 mA/cm², device C reaches a highest CE of 5.46 cd/A. However, when the thickness increased to 30 nm, the luminance is quite lower than that of the device B and C, resulting in a reduction of current efficiency. The EQE of device C reaches a highest EQE of 3.56%, which is 1.74-fold higher than that of the device without the ZnO NP layer (2.0%, Figure S5) and 2.40-fold higher than that of device without the ZnMgO NP layer (1.48%).

**CONCLUSIONS**

In a word, we have designed and fabricated red and green organic–inorganic hybrid structure QLEDs by using cadmium-free red and green InP QDs as the emitting layer. We found that incorporation of Mg-doped ZnO NPs as an interlayer between ZnO NP ETL and active InP QD emitting layer is a quite helpful way to enhance the device EL performance. The reduced electron current of devices with the ZnMgO NP layer is caused by: (1) the higher CBM level, which can effectively block the injection of electrons into the active layer, and (2) the lower electron mobility, which can slow down the pace of electron transport from ETL to the active layer. In addition, because of the reduced defect concentration of ZnMgO layers...
This work highlights the potential of ZnMgO approach to improve heavy-metal-free QLED performance. The CEs of QLEDs are lower than the previously reported best results because of the relative low PL QY of QDs (Table S5), we believe that this work offers an effective approach to improve heavy-metal-free QLED performance. This work highlights the potential of ZnMgO film as the interlayer in constructing solution-process, high-performance organic—inorganic hybrid QLEDs and moves a significant step toward the transparent and flexible application of InP-based electroluminescent devices.

- **ASSOCIATED CONTENT**

  **Supporting Information**

  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00351.

  Synthesis of InP/ZnSe/ZnS QDs, ZnO NPs, and ZnMgO NPs. The EDX spectrum of ZnMgO NP film, TEM image of ZnMgO NPs, fitted results of PL exponential decay of red QDs and multilayer samples, SEM images and 3D AFM images of ZnO NPs and ZnMgO NPs on glass, UV-abs spectroscopy of ZnO and ZnMgO NPs, EL performances of red QLEDs with different ETLs, summary of maximum luminance ($L_{\text{max}}$), CE$_{\text{max}}$, and EQE$_{\text{max}}$ of the red device with different ETLs, current density–voltage ($J$–$V$) characteristic of the electron-only device with a structure of Al/NPs (40 nm)/Al, EL performances of QLEDs with different spin-coating speeds of the QD layer and different concentrations of the ZnMgO NP layer, CIE property of device C, normalized PL and EL spectra of green QLED, EL performances of green QLEDs, summary of $L_{\text{max}}$, CE$_{\text{max}}$, and EQE$_{\text{max}}$ of the green device with (w/) or without (w/o) the ZnMgO NP layer, and summary of InP QLEDs EL performance of reported works and this work (PDF)

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