Surface engineering of ZnO nanoparticles with diethylenetriamine for efficient red quantum-dot light-emitting diodes

Dandan Zhang, Yan-Hua Liu, Lianqing Zhu

yhliu@suda.edu.cn (Y.-H.L.)
lqzhu_bistu@sina.com (L.Z.)

Highlights

Develop a simple and feasible surface engineering strategy to modify ZnO NPs

The DETA ligand passivates the surface defects and reduces the intervals of ZnO NPs

An impressive EQE of 23.7% is achieved for the inverted QLEDs
Surface engineering of ZnO nanoparticles with diethylenetriamine for efficient red quantum-dot light-emitting diodes

Dandan Zhang,1 Yan-Hua Liu,2,3,* and Lianqing Zhu1,*

SUMMARY

Due to the outstanding electron injection/transport capability of ZnO nanoparticles (NPs), quantum-dot light-emitting diodes (QLEDs) are commonly constructed by employing a hybrid device structure with ZnO electron-transporting layer and organic hole-transporting layer. However, the emission quenching of quantum dots and excessive electron injection induced by ZnO NPs also limits the device efficiency and operational stability. Here, diethylenetriamine (DETA) molecules as the ligands are introduced to modify the surface of ZnO NPs, which not only passivate the surface defects of ZnO but also suppress the overwhelming electron injection in the QLED. As a result, the device based on the DETA-modified ZnO NPs exhibits a peak external quantum efficiency of 23.7%, corresponding to an enhancement factor of 129% in comparison with that of the device with as-synthesized ZnO as the electron-transporting layer. The easy and feasible strategy may also be applicable to other photoelectric devices, such as solar cells and photodetectors.

INTRODUCTION

Colloidal quantum-dot light-emitting diodes (QLEDs) have been intensively investigated as next-generation display technologies due to their unique properties, such as tunable color emission, narrow spectral bandwidth, high photoluminescence (PL) efficiency, and solution processability for ease of mass production (Dai et al., 2014; Li et al., 2018; Yang et al., 2015, 2020; Zhang et al., 2020). With the rapid development of colloidal QD synthesis (Dai et al., 2014; Li et al., 2018; Yang et al., 2015) and optimization of device architectures (Fu et al., 2018; Lee et al., 2019; Shen et al., 2019; Won et al., 2019; Zhang et al., 2018), the performance of QLEDs has been improved greatly, achieving the impressive external quantum efficiencies (EQEs) of 28.7%, 23.9%, and 19.8% for red, green, and blue emissions, respectively (Li et al., 2019a; Song et al., 2019; Wang et al., 2017). However, the device operational lifetime and shelf stability are still a central challenge for the practical applications of QLEDs so far. Therefore, further efforts are needed to optimize both the materials and device structure.

To date, hybrid QLEDs with ZnO nanoparticles (NPs) as the electron-transporting layer (ETL) and organic/polymer films as hole-transporting layers have been proved to be the most efficient device structure (Ho et al., 2013; Li et al., 2020). However, the electron mobility of solution-processed ZnO NPs is always higher than hole mobility of commonly used organic HTLs, leading to electron accumulation at the QD/ETL interface and thus the QD charging. Besides, the defects on the surface of ZnO NPs including the oxygen vacancies, zinc vacancies, zinc interstitials, and oxygen interstitials (Schmidt-Mende and MacManus-Driscoll, 2007; Yadav et al., 2007) will also result in the exciton quenching at the QD/ZnO interface. Therefore, to improve the QLED performance, additional functional layers between ZnO ETLs and QD emissive layers have been added as a physical spacing layer (Cao et al., 2017; Ding et al., 2017; Ji et al., 2013; Moon et al., 2019; Pan et al., 2018), which can hinder the interactions between QDs and ZnO NPs. Additionally, surface modification of ZnO NPs has also been proposed to effectively passivate the defects in ZnO and thus enhance the device performance (Li et al., 2019b; Sun et al., 2018; Wang et al., 2019).

Recently, di-n-propylamine treatment has been demonstrated to be an effective way to control the surface ligand density of perovskite quantum dots (PQDs), even for underpurified PQDs with high surface ligand density (Wang et al., 2020). As we know, the defects of ZnO nanocrystals including hydroxyl groups,
carboxylate groups, and dangling bonds can be removed by forming zinc ethanedithiolates (Dai et al., 2017). Herein, we propose a simple and feasible approach to optimize the surface states of ZnO NPs by eliminating CH$_3$COO$^-$ groups with diethylenetriamine (DETA) molecules (hereafter named as D-ZnO). We demonstrate that the surface defect density of ZnO NPs is decreased obviously after replacing CH$_3$COO$^-$ groups with DETA molecules, suppressing the emission quenching at QDs/ZnO interfaces and leading to an improved charge carrier injection balance. As a result, the inverted red-emitting QLED device based on D-ZnO ETL achieves a maximum external quantum efficiency (EQE) of 23.7%, which is 29% higher than that of the control device with normal ZnO (N-ZnO) ETL. Furthermore, the operational lifetime is also improved, which mainly arises from the decrease of accumulated electrons at QDs/ETL interface and suppression of thermal-induced degradation in QDs or/and ZnO.

RESULTS AND DISCUSSION

Characterization of the ZnO NPs modified by DETA

Figure 1 depicts the modification mechanism of DETA molecules used as the ligands to replace the CH$_3$COO$^-$ groups outside ZnO NPs. The DETA molecules can effectively passivate the surface defects of ZnO NPs (this will discussed in detail in the following text) and decrease the separation between ZnO NPs. Therefore, it is expected that D-ZnO can suppress the emission quenching effect induced by surface defects of ZnO NPs, and thus enhancing the device performance. Simultaneously, reduced separation between ZnO NPs is beneficial to form a compact ZnO film, which can improve the stability of ZnO ETL, as well as the device operation stability. Moreover, short-chain DETA ligands can also reduce the distance between ZnO NPs and QDs, which is beneficial for the electron injection from ZnO to QDs.

The successful modification of DETA for ZnO NPs is demonstrated by X-ray photoelectron spectroscopy (XPS), thermal gravity (TG), and Fourier transform infrared spectroscopy (FTIR) measurements. The C 1s region of two samples is shown in Figure 2A, two peaks of C 1s are located at about 288.0 and 284.5 eV corresponding to C=O and C-C, respectively. It should be mentioned that the measurement conditions are same for the two samples in Figure 2A, so the intensity of the peaks may reflect the relative contents of respective elements in the samples. Both the intensity of C-C and C=O peaks of N-ZnO were higher than that of D-ZnO, which may indicate the reduction of CH$_3$COO$^-$ content in D-ZnO samples. Moreover, as obtained in Figure 2B, the -CH$_3$ content is reduced by comparing the two curves, which should be due to the replacement of CH$_3$COO$^-$ by DETA. However, the specific change cannot be got directly from the FTIR spectra since it can only show the relative content changes of different materials.

To further evaluate the modification of ZnO by DETA, thermal-gravimetric analyses were carried out and the results are shown in Figure 2C. Before 100°C, the weight loss for N-ZnO sample mainly originates from the volatilization of absorbed water and solvent. When the temperature further increases, Zn(OH)$_2$ groups will be lost during heating as previously reported (Bai et al., 2015). It is worth noting that a more obvious weight loss could be observed before 100°C during TG process for D-ZnO samples, which should be attributed to that the DETA can be lost before 100°C due to the weak binding interaction of -NH groups.
on the ZnO surface. When the temperature is higher than 300°C, the CH3COO- begins to decompose. So the change of CH3COO- content can be estimated by the weight change from 300°C to 800°C. The weight loss ratio is 8% for N-ZnO while it is only 4.6% for D-ZnO sample, this result may indicate the reduction of CH3COO- in D-ZnO, which further demonstrates that the CH3COO- groups have been replaced with DETA molecules in D-ZnO.

TEM images of ZnO NPs before and after DETA modification are shown in Figure 3; the samples for TEM measurements is prepared by dropping the ZnO (with different ligands) solution with the same concentration. It can be clearly seen that the ZnO NPs possess better dispersity after introducing DETA as ligands. Although ZnO NPs remain easy to aggregate due to the relatively weak interactions between Zn NPs, the improvement is obvious when DETA is used as the ligands. In other words, the DETA can effectively bind with ZnO surface, avoiding the agglomeration of ZnO NPs. It is well known that good dispersity of ZnO dispersion solution is the prerequisites to form a dense and smooth ZnO NP film, so D-ZnO is benefit to improve QLED performances.

**Electrical performance of the QLEDs**

To assess the effect of the DETA-modified ZnO on the performance of QLEDs, inverted red-emitting QLEDs were fabricated. Firstly, the DETA-modified ZnO layer was optimized by changing the DETA concentration from 0.5 to 1.5 μL/mL in the ZnO dispersion solution. Correspondingly, QLEDs based on D-ZnO with different DETA concentrations were fabricated. In addition, the as-synthesized N-ZnO was also used to build QLEDs as the control device. Figure 4A shows the luminance-voltage-current density (L–V–J)
characteristics of these devices. It could be clearly seen that the current density is decreased obviously with increasing DETA concentration in the ZnO dispersion solution while the luminance remains almost identical for devices without DETA and with DETA of 0.5 and 1.0 μL/mL. Further increase of DETA concentration (1.5 μL/mL) results in the reduction of device luminance. This might originate from the insulating nature of DETA molecules, which decreases the electron transport capabilities across the ZnO films. However, the turn-on voltage and luminance of devices based on D-ZnO ETL are identical to that of the control device, implying that the electron injection from ZnO NPs to QDs becomes more efficient even though the amount of injected electrons is decreased. These results indicate that the properly reduction of electron injection into QDs emission layer does not affect the amount of excitons formed in the QDs, indicative of more efficient exciton formation probability in devices based on D-ZnO ETLs. In other words, the decreased current density for devices based on D-ZnO with suitable DETA concentration can result in an improved charge injection balance, especially under low driving voltage. As a result, these devices exhibit higher efficiency than the control device as shown in Figure 4B. A more obvious enhancement for the device efficiency is found under low driving voltage with luminance less than 5,000 cd/m². Especially, the maximum EQE value reaches 23.7%, corresponding to an enhancement factor of 129% compared to that of the control device.

The device operational stability is also enhanced dramatically as shown in Figure 4C. During the operational stability characterization process, the QLED devices based on N-ZnO and D-ZnO ETLs were driven under the same current density of 20 mA/cm². Along with the operating time, the driving voltage is gradually increased due to the degradation of functional layers in the devices. However, the increased extent of the driving voltages for the device based on D-ZnO ETL is much slower than that of the control device, indicative of better stability of DETA-modified ZnO NPs and also the QD/ZnO NPs interface. Moreover, the device based on D-ZnO ETLs exhibits better stability with T90 (T90 is defined as the time for the device luminance decreases to 90% of the initial luminance) is around 100 h with the initial luminance of around 3,500 cd/m², much higher than that of the control device (~30 h). Additionally, the operating voltage of the device based on D-ZnO ETL increases rather slowly in comparison with that of the control device, which is attributed to the significantly reduced electron accumulation at ZnO/QDs interface of the device based on D-ZnO ETL. This is in consistent with the results shown in Figure 4. The impedance Cole-Cole plots are shown in Figure 4D. At a 4.5 V driving voltage, a single semi-circle can be seen in the impedance plots, which could be modeled by an equivalent circuit containing a parallel capacitor Cpe, shunt resistance Rsh, etc.
and serial resistance $R_s$. The serial resistance value is almost identical, and the device based on D-ZnO ETL exhibits a larger $R_p$, which indicates that the D-ZnO hinders the electron injection/transport across the device.

The modification effect of ZnO NPs by DETA molecules is also demonstrated by the photoelectrical measurements as shown in Figure 5. The $J$–$V$ properties of the electron-only devices with a structure of ITO/ZnO (80 nm)/Al (100 nm) confirm that the introduction of DETA modification significantly reduces the current density of ZnO NPs, which indicates that the electron transport across the ZnO NP film is decreased owing to the decrease of surface defects. As shown in Figure 5B, the decreased PL emission intensity in D-ZnO NPs also provides evidence that the defects of ZnO NPs are reduced after introducing DETA ligands. The PL decay of QDs on the ZnO film with and without DETA ligands as well as on the glass substrate were also measured using the excitation wavelength of 375 nm, and the results are shown in Figure 5C. Compared with the PL decay of QDs on glass substrate, a faster decay behavior is observed for QDs on N-ZnO film, which is due to the quenching effect induced by the defects of ZnO (Chen et al., 2021; Sun et al., 2017, 2020). In comparison, the PL decay of QDs in D-ZnO film is slightly slower, and the lifetime is about 11.23 ns, which is higher than that of N-ZnO (8.97 ns). These results further demonstrate the passivation of defects on ZnO NPs by the DETA ligands. The UV photoelectron spectroscopy (UPS) measurements were also carried out to assess the influence of DETA on the work function of ZnO. It could be seen from Figure 5D that the conduction band level of D-ZnO samples is lower than that of N-ZnO samples. However, the barrier for electron injection from ZnO to QDs is still negligible as shown in the inset of Figure 5D. Therefore, the decrease of the current density of the DETA-containing devices does not come from the effect of reduced conduction band energy level, but could be attributed to the passivation of surface defects on ZnO NPs by surface modification of DETA molecules.

Photoluminescence properties of the ZnO NPs
To further evaluate the effects of DETA on the QD emission, temperature-dependent PL spectra of QDs were measured and the results are shown in Figure 6. The PL spectra of QDs on different substrates all present a redshift and decreased PL intensity with elevated temperature from 100 K to 280 K, which is due to
the temperature-dependent bandgap shrinkage of QDs as reported in the literature (Lu et al., 2014; Valerini et al., 2005). The evolution of relative PL intensities of QDs on different substrates is plotted in Figure 6D as an inverse function of $k_B T$. Here, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. It could be seen that the PL spectrum of QDs on N-ZnO is significantly temperature dependent, exhibiting a rapid decreased intensity under high temperature. In contrast, the QD emission is protected at high temperature while contacting with D-ZnO, similar to the case on the inert glass substrate. The decrease of PL intensity of QDs on glass with increasing temperature should be owing to the scattering effect of multiply phonons (de Mello Donegà et al., 2006; Qian et al., 2011). The larger decrease of PL emission may arise from the exciton thermal quenching induced by surface defect states on ZnO NPs. These results indicate that the defects on the ZnO surface have been effectively passivated by DETA molecules, hindering the interaction between QDs and ZnO NPs.

Conclusion

In summary, we have developed an efficient and feasible strategy to improve the performance of QLEDs by surface engineering of ZnO NPs. The DETA ligand can not only passivate the defects on the surface of ZnO NPs but also alleviate the overwhelming electron injection into the device. As a result, an impressive EQE near 24% is achieved for the inverted QLEDs. Moreover, benefiting from the balanced charge injection, electron accumulation at QDs/ZnO interface is dramatically decreased, hence prolonging the operational lifetime of the QLED based on D-ZnO ETL. All the results demonstrate that our proposed ZnO surface engineering is an easy and feasible strategy to enhance the device performance, including efficiency and operational lifetime. We believe that this strategy could also be applied to the other color QLEDs, as well as other photoelectric devices, such as solar cells and photodetectors.

Limitations of the study

In this work, the DETA is used as the ligand of ZnO nanoparticles to passivate the defect on the surface of ZnO NPs and reduce the separation between ZnO and QDs. The device performance is highly improved with DETA-modified ZnO as the electron-transporting layer. However, we optimize the QLED performance by the feed ratio of DETA into the ZnO NPs dispersion. Thus, the exact extent of the effect of DETA on the defects of ZnO NPs is a little unclear. The addition of DETA inevitably changes the viscosity of the ZnO dispersion, which will affect the formation of ZnO electron-transporting layer obtained by spin coating.
technology. Therefore, more efforts are needed to uncover the micro-mechanism of DETA in improving the device performance.

**STAR METHODS**

Detailed methods are provided in the online version of this paper and include the following:

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**AUTHOR CONTRIBUTIONS**

Conceptualization, D.D.Z, Y.H.L., and L.Q.Z.; Methodology, D.D.Z., Y.H.L., and L.Q.Z.; Investigation, D.D.Z., Y.H.L., and L.Q.Z.; Writing, D.D.Z.; Funding Acquisition, D.D.Z., Y.H.L., and L.Q.Z.; Supervision, Y.H.L. and L.Q.Z.

**DECLARATION OF INTERESTS**

The authors declare no competing interests.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Zinc acetate dihydrate | Sigma-Aldrich | CAS: 5970-45-6 |
| Tetramethylammonium hydroxide | Sigma-Aldrich | CAS: 75-59-2 |
| 4,4'-N,N'-dicarbazolyl-biphenyl | Lum-Tech. | CAS: 58328-31-7 |
| Molybdenum oxide | Lum-Tech. | CAS: 1313-27-5 |
| Ethanol | Aladdin | CAS: 64-17-5 |
| Ethyl acetate | Aladdin | CAS: 141-78-6 |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Yan-Hua Liu (yhliu@suda.edu.cn).

Materials availability
This study did not generate new unique reagents.

Data and code availability
- Data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this work paper is available from the lead contact upon request.

METHOD DETAILS

Preparation of DETA modified ZnO NPs
A typical synthesis method of ZnO NPs (Yang et al., 2015) was employed in our experiment. The solutions of zinc acetate dihydrate and tetramethylammonium hydroxide in ethanol were mixed and stirred for 1 h in ambient air, and then it was washed and dispersed in ethanol for device preparation. The concentration of ZnO NPs in ethanol is 30 mg/mL. To modify the surface of ZnO NPs, diethylenetriamine (DETA) was added into the N-ZnO ethanol dispersion with a concentration of 0.5, 1.0, and 1.5 mL/mL, forming D-ZnO samples.

Device fabrication
The inverted QLED device consists of glass/indium-tin-oxide (ITO)/ZnO (~40 nm)/QD layer (~25 nm)/HTL (60 nm)/MoO3 (7 nm)/Al (100 nm). For device fabrication, patterned ITO coated glass substrates were first ultrasonically cleaned in sequence with acetone, ethanol, and deionized water each for 15 min, and then were dried by N2 gas flow. A UV ozone treatment for 9 min was performed before spin-coating the functional layers. ZnO NP dispersion was filtered through a 0.45 μm nylon filter and spin-coated in a N2-filled glove box at 2500 rpm for 1 min on the ITO substrates with film thickness of around 40 nm, followed by a baking process at 90°C for 30 min. Then, the QD emissive layer was fabricated on ZnO ETL by spin-coating the QD dispersion (20 mg/mL in toluene) at 2000 rpm for 1 min, and then baked at 100°C for 30 min. After that, the substrate was transferred into the interconnected high-vacuum evaporation chamber. The samples during all the spin-coating and transfer processes were not exposed in air to avoid the effect of water and oxygen. To finish the device fabrication, CBP (60 nm), MoO3 (7 nm), and Al (100 nm) were thermally deposited under a base pressure below 4 x 10^-4 Pa.
Characterization
The transmission electron microscope (TEM) images of ZnO NPs were obtained through FEI Talos F200X microscope. The PL spectra of ZnO NPs were obtained by using an FM-4 type fluorescence spectrophotometer (JY company, French). The steady-state and time-resolved PL spectra of QDs were measured by FLS 920 spectrometer (Edinburgh, British). PLQYs of QDs were measured in a nitrogen atmosphere by C9920-02G type fluorescence spectrophotometer (HAMAMATSU, Japan) with an integrating sphere. All the X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) measurements were conducted by using Kratos AXIS Ultra DLD. The EL performance of QLEDs was tested with a computer controlled programmable power source (Keithley model 2400) and a luminance meter/spectrometer (Photo Research PR670). The EQE values were calculated by taking into account the angular distribution of EL intensities.