Enhancing performance of inverted quantum-dot light-emitting diodes based on a solution-processed hole transport layer via ligand treatment

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Abstract: The performance of inverted quantum-dot light-emitting diodes (QLEDs) based on solution-processed hole transport layers (HTLs) has been limited by the solvent-induced damage to the quantum dot (QD) layer during the spin-coating of the HTL. The lack of compatibility between the HTL's solvent and the QD layer results in an uneven surface, which negatively impacts the overall device performance. In this work, we develop a novel method to solve this problem by modifying the QD film with 1,8-diaminooctane to improve the resistance of the QD layer for the HTL's solvent. The uniform QD layer leads the inverted red QLED device to achieve a low turn-on voltage of 1.8 V, a high maximum luminance of 105 500 cd/m^2, and a remarkable maximum external quantum efficiency of 13.34%. This approach releases the considerable potential of HTL materials selection and offers a promising avenue for the development of high-performance inverted QLEDs.

Key words: quantum dots; quantum-dot light-emitting diodes; inverted structure; ligand treatment

1. Introduction

Colloidal quantum dots (QDs) have garnered significant interest in next-generation displays and lighting[1–3] owing to their outstanding advantages, such as narrow emission linewidth[4, 5], size tunable emission wavelength[6, 7] and low-cost solution processing[8–12]. In the past few decades, the performance of quantum-dot light-emitting diodes (QLEDs) has been significantly improved through various means including the improvement of material synthesis[13–15] and device structure design[16–18]. To date, the external quantum efficiency (EQE) of red, green, and blue QLED devices has been significantly improved, with values of 33.1%[19], 28.7%, and 21.9%[20], respectively. Moreover, the lifetime of red and green QLEDs have met the standard for the display industry[21–23].

Nowadays, two conventional architectures are employed for QLED devices, the normal structure and the inverted structure. The normal QLED is structured as a substrate/anode/hole injection layer (HIL)/hole transport layer (HTL)/QDs/electron transport layer (ETL)/cathode, while the inverted QLED comprises substrate/cathode/ETL/QDs/HTL/HIL/anode[23, 24].

Many published works have been centered on normal QLEDs[13, 19, 20, 25–27] and the champion QLEDs adopted the normal structure. Meanwhile, all QLEDs with long lifetime regard the Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl))diphenylamine)] (TFB) or its derivant as HTL material[20, 22, 26, 28]. However, the normal architecture presents challenges in integration with low-cost n-type metal oxide or amorphous silicon-based thin-film transistors (TFTs). The direct connection between the cathode of inverted QLEDs and the drain of TFTs makes the inverted structure a better choice for the display industry[1, 16]. In addition, TFB is incompatible in inverted devices directly, because when the TFB spins on the QD layer, the non-orthogonal solvent will severely erode the QD layer, resulting in a dramatic reduction in device performance.

To prevent the QD EML from being disrupted when fabricating the HTL, several strategies have been implemented. Liu *et al.* dissolved the HTL in orthogonal solvents such as 1,4-dioxane[1]. However, most of the device performances are unideal and TFB exhibits poor solubility in this solvent. Some groups reported the addition of a protective layer such as polyethylenimine ethoxylated (PEIE) between the QD EML and HTL to protect the QD layer[29, 30]. In addition, some ligands and cross-linkers, such as hexamethyldisilazane (HMDS) and 6-mercaptohexanol, are used to modify the surface of the QD film[31, 32]. However, the interlayer and cross-linkers materials used are typically electrically insulating to impede
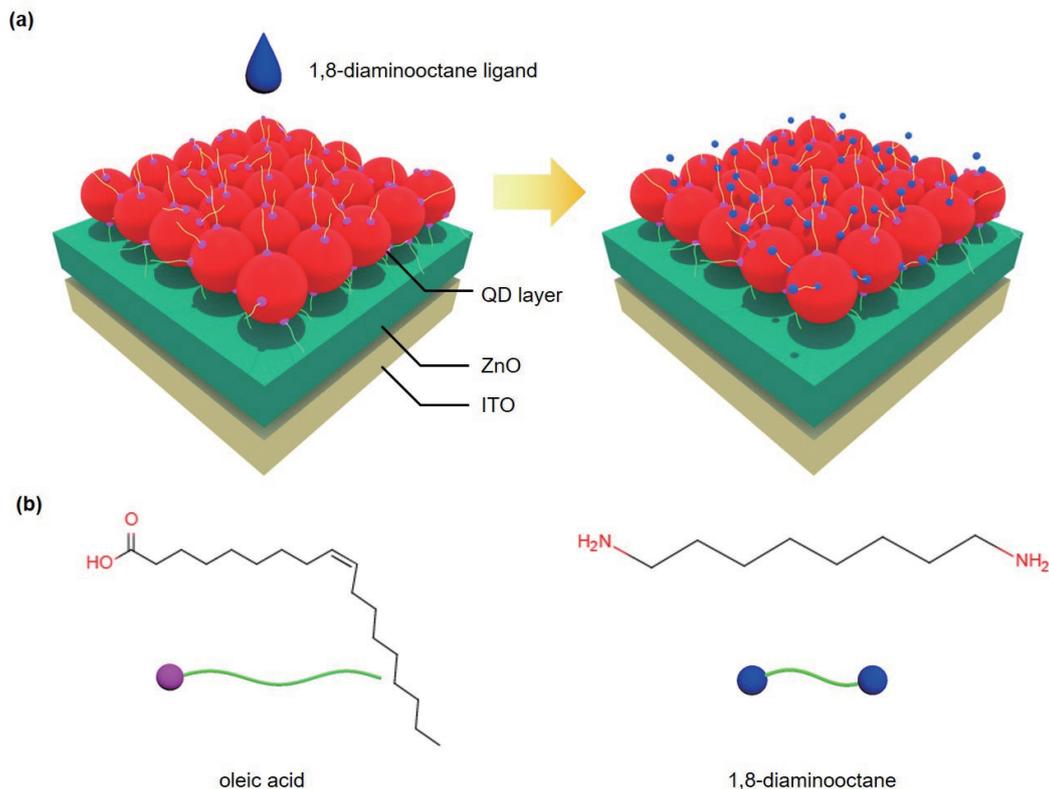
Fig. 1. (Color online) (a) Schematic illustration of the 1,8-diaminooctane ligand treatment process, (b) chemical structure (top) and graphical sketch (bottom) of the oleic acid and 1,8-diaminooctane ligand. The purple and blue balls represent the carboxyl and amine groups, respectively, and the green line is the carbon chain.

the carrier injection, thereby limiting the performance of QLEDs.

In order to achieve inverted QLEDs based on TFB with high performance, it is crucial to enhance the QD layer's resistance against TFB solvent, chlorobenzene (CB). In our study, a facile solid-film ligand treatment approach was employed to modify the surface of QD films, resulting in the enhanced resistance of the QD films to non-polar solvents such as CB. After ligand treatment, a uniform and smooth TFB film was formed on the undamaged QD layer. Remarkably, the inverted red QLED device with a low turn-on voltage of 1.8 V, a maximum luminance of 105 500 cd/m², and a maximum EQE of 13.34% was achieved. These results represent significant improvements over untreated QLED devices, thereby underscoring the potential of this work to promote further research interest in developing practical applications for QLEDs.

2. Result and discussion

Inspired by bifunctional ligands during the deposition of multiple QD layers[33−35], we developed a simple solid-film ligand treatment method in the process of inverted QLEDs. As shown in Fig. 1(a), the QD layers are treated by 1,8-diaminooctane ligands via spin-coating. This ligand acts as a cross-linking molecule thanks to the amino functional groups at both ends of the octane alkyl chain[33]. It adsorbs onto the QD surface and forms strong anchors among QDs[36] (Fig. 1(b)). Additionally, the partial substitution of long-chain ligands such as oleic acid with short-chain ligands can enhance the charge transport capability[37, 38].

The UV-vis absorption spectra show that the first exciton absorption peaks at around 617 nm (Fig. 2(a)), indicating that

this treatment has little impact on the energy gap of the QD layer. Fig. 2(b) demonstrates that the photoluminescence (PL) intensity of the QD layer after ligand treatment is slightly lower than that of the untreated QD layer. Additionally, the photoluminescence quantum yield (PLQY), PL peak, and full width at half maximum (FWHM) of the QD film are similar, as shown in Table S1. These results suggest the ligand treatment will not lead to a decrease in the PL performance of the QD layer, which is the premise for realizing high performance devices. The PL image of QD films before and after ligand treatment, as illustrated in the inset of Fig. 2(b), reveals that the ligand treatment shows no damage to the evenness of QD layer. Time-resolved PL results of QD films are shown in Fig. 2(c). The PL decay of the QD films before and after treatment is essentially the same, which suggests that this method does not cause additional surface traps to QDs. These results indicate that the ligand treatment does not significantly damage the QD layer and retains its excellent luminescent properties. As for the resistance to the solvent CB, shown in Fig. 2(d), the ligand-treated QD film can withstand rinsing with CB, and the PL intensity is mostly retained compared to the untreated QD film. These observations suggest that the incorporation of 1,8-diaminooctane does not significantly damage the QD layer, but improves its tolerance to CB.

To illustrate the impact of ligand treatment and CB rinsing on the film morphology, SEM and AFM measurement were conducted, as shown in Fig. 3 and Fig. S1. The pristine QD film shows the smooth and dense surface with low roughness of 1.87 nm (Figs. 3(a) and 3(c)). As expected, after rinsing with CB, the film becomes discontinuous, and some noticeable voids appear on the surface due to the dissolution of CB
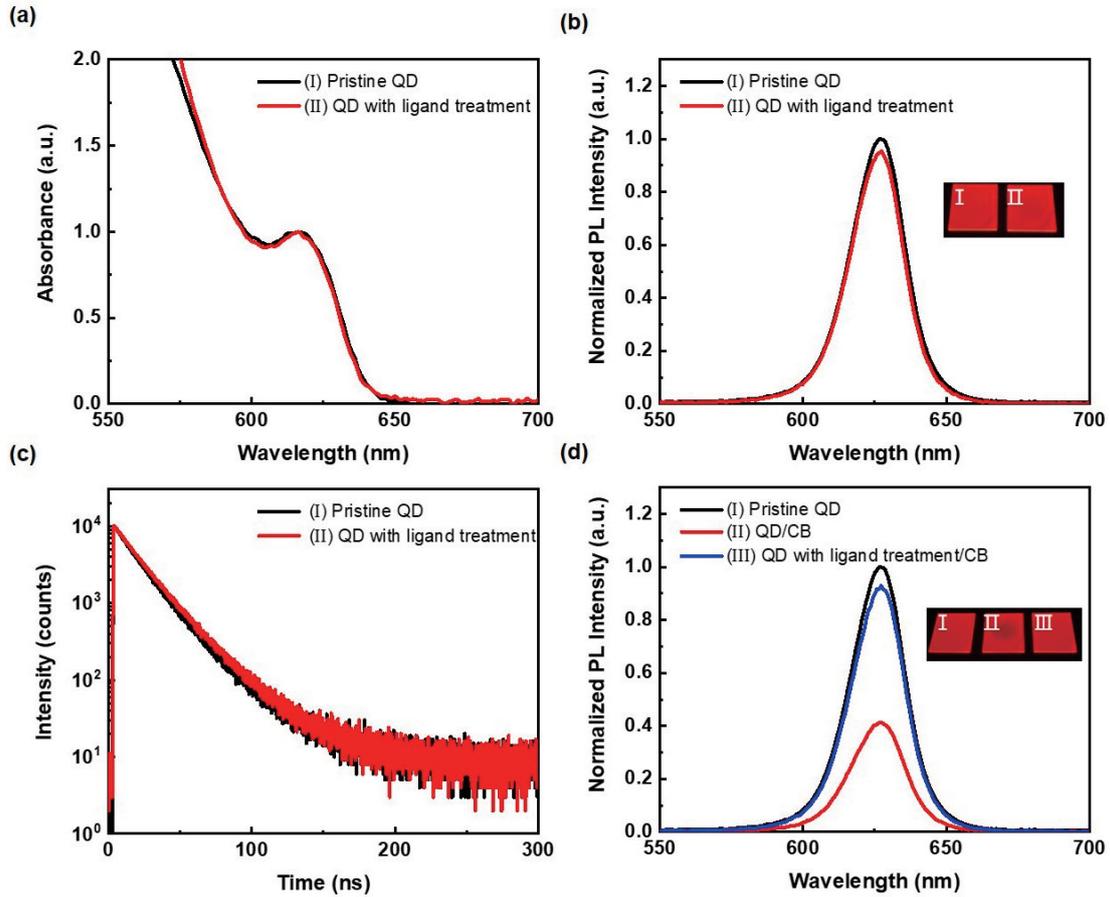
Fig. 2. (Color online) Characterization of the QD films. (a) UV-vis absorption spectra, (b) PL spectra and (c) time-resolved PL decay of the QD films before and after ligand treatment. The inset of (b): the corresponding PL image of the QD films under 365 nm LED excitation. (d) The PL spectra of the pristine and ligand-treated QD films rinsed with CB. The inset of (d): PL image (under 365 nm) of corresponding PL image of the QD films.
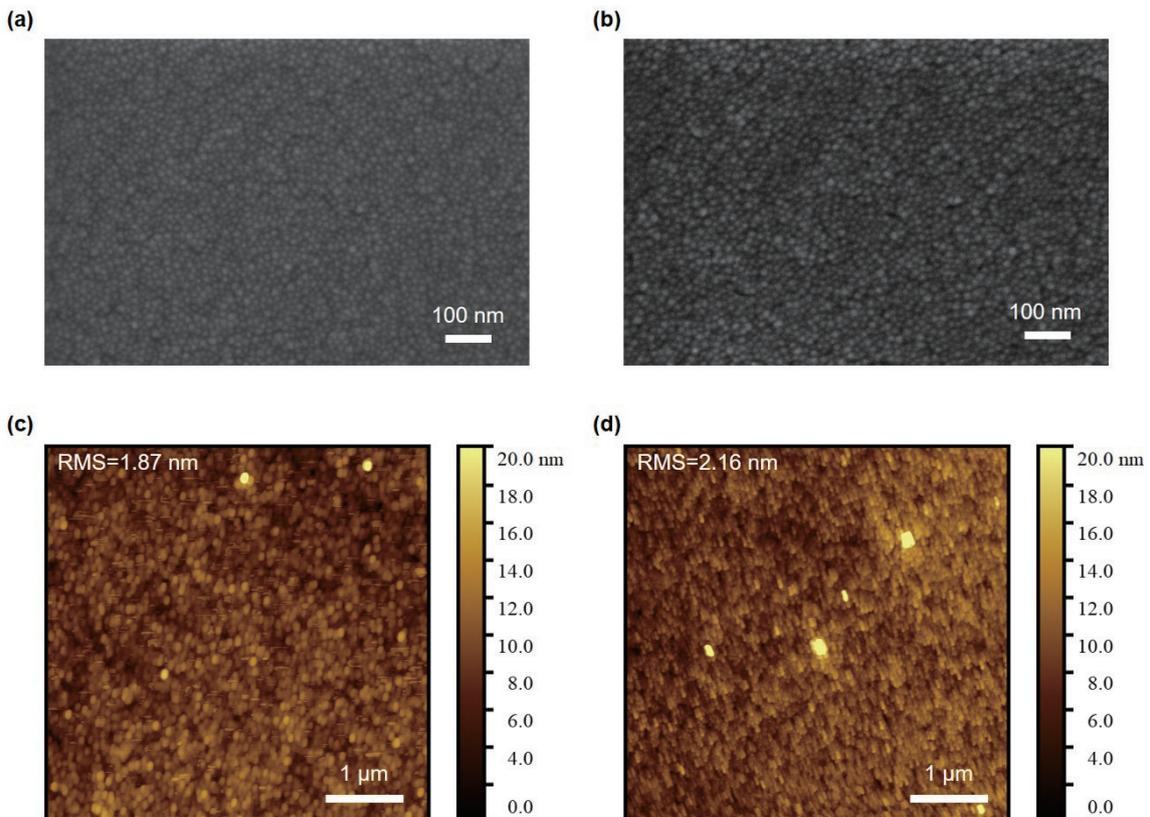
Fig. 3. (Color online) SEM images of the (a) pristine QD film and (b) ligand-treated QD film. AFM images of the (c) pristine QD film and (d) ligand-treated QD film.

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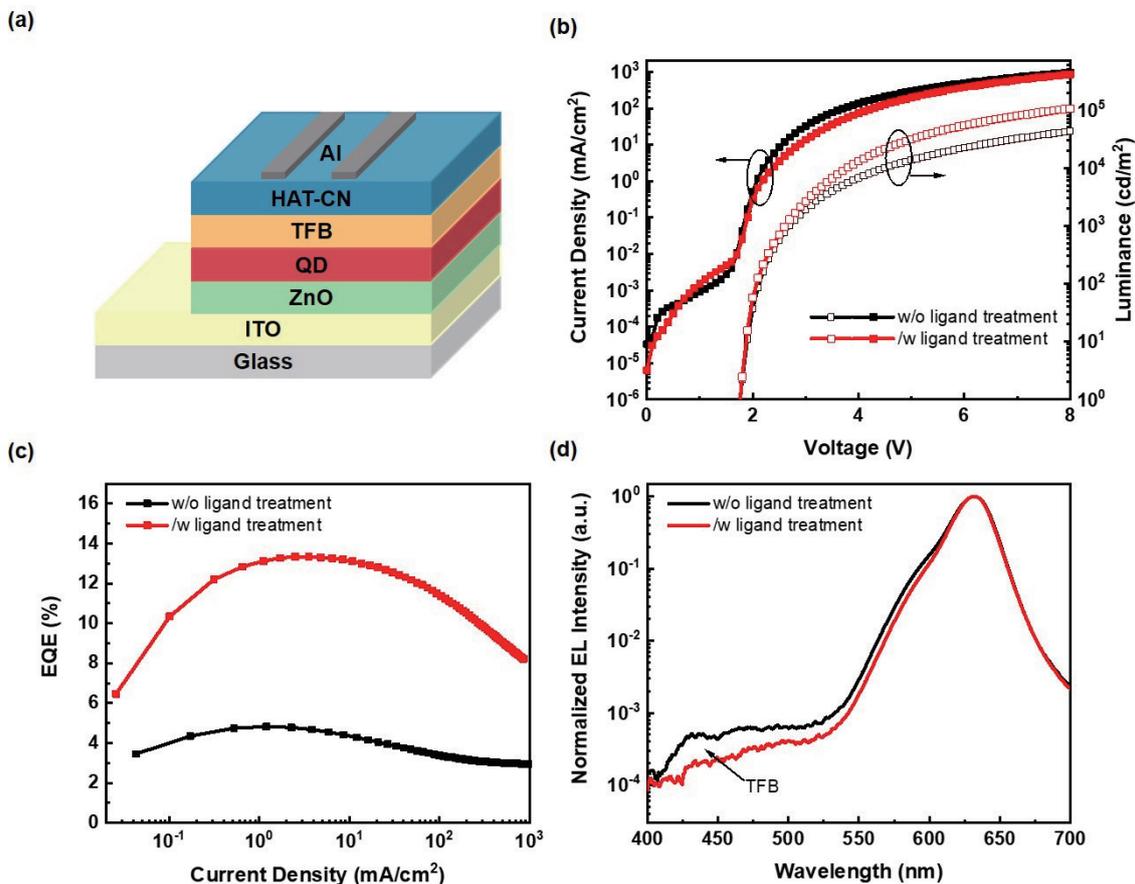
Fig. 4. (Color online) Device characteristics of inverted QLED. (a) Device structure, (b) J–V–L characteristics, (c) EQE–J characteristics, and (d) EL spectra of the inverted device (at 8 V).

Table 1. The device characteristics of inverted QLEDs.

Method	V_{on} (V) (at 1 cd/m²)	$V_{driving}$ (V) (at 100 cd/m²)	EQE (%)		L_{max} (cd/m²)
			100/1000/10 000 cd/m²	Max	
w/o ligand treatment	1.8	2.1	4.83/4.16/3.15	4.83	42 980
/w ligand treatment	1.8	2.2	12.84/13.31/12.04	13.34	105 500

to the QD layer (Fig. S1(a)). The AFM image reveals the presence of distinct bumps, which further suggests that the rinsing of CB inflicts serious damage to the QD layer (Fig. S1(c)). In contrast, after the ligand treatment, the film surface has no significant voids and exhibits a similar roughness and density as the pristine film (Figs. 3(b) and 3(d)). The improved resistance of the QD film with ligand treatment to CB is further confirmed by the surface morphology (Figs. S1(b) and (d)). The roughness of the ligand-treated QD film has increased compared to the pristine QD film, but the surface remains dense, and the size of the cracks and voids is smaller than that of the pristine QD rinsed with CB. These results indicate the protective role of ligand treatment on QD film during device fabrication.

To demonstrate the effect of ligand treatment on the performance of inverted QLED, two types of QLEDs, with and without ligand treatment, were fabricated. The architecture of the inverted QLED is illustrated in Fig. 4(a). The device consists of stacked layers of ITO/ZnO/QD/TFB/HAT-CN/Al. The ZnO is used as the ETL. TFB and HAT-CN are the HTL and HIL, respectively. The current density–luminance–voltage (J–V–L) and EQE–J curves for the two devices are shown in Figs. 4(b) and

4(c), respectively. Remarkably, the device with ligand treatment demonstrates a significantly improved performance, as indicated by the data summarized in Table 1. As shown in Fig. 4(b), the leakage current of the untreated device is larger than the ligand-treated device, which can be attributed to the increased electron leakage channels induced by the uneven surface of the QD film (Fig. S1(a)). The turn-on voltage of the ligand-treated device is similar to that of the untreated device, at 1.8 V, which indicates that the ligand treatment does not hinder carrier injection. The ligand-treated device achieves a much higher brightness of 105 500 cd/m² at 8 V compared to the untreated device's 42 980 cd/m². Additionally, the EQE is increased by a factor of 2.76 after ligand treatment, reaching a maximum value of 13.34%. The above results suggest the ligands treatment approach is highly effective for fabricating inverted QLEDs based on solution-processed HTL. The electroluminescence (EL) spectra of two QLEDs under 8 V are presented in Fig. 4(d). Both the EL emissions are centered at 630 nm with a narrow FWHM of 27 nm. However, the parasitic emission from the TFB (blue region, EL emission spectrum of TFB is shown in Fig. S2) is observed in the EL spectrum of the device without ligand treatment
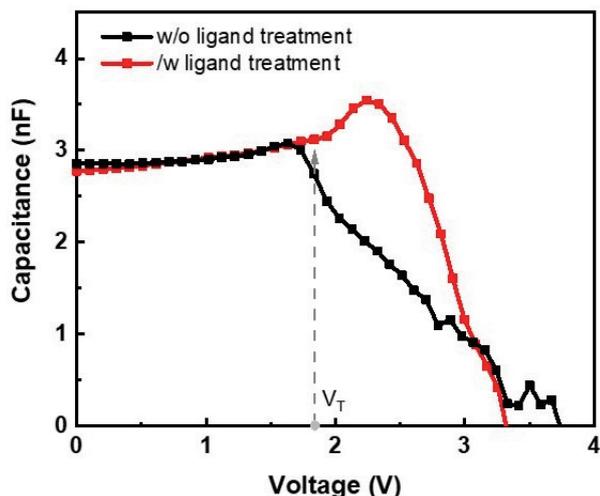
Fig. 5. (Color online) Capacitance–voltage characteristics of the inverted devices, f = 1 kHz.

(Fig. 4(d) (arrows)). Thus, these results also indicate that the untreated QD film is severely dissolved and eroded during the HTL layer deposition, leading to excessive electron leakage into the HTL layer and causing a further reduction in device efficiency and performance[20]. The ligand treatment, which reduces the damage to the QD from CB and the electron leakage problem, offers an effective solution for fabricating inverted QLEDs.

The operational stability of QLEDs is also significantly improved by the implementation of ligand treatment. At an initial luminance of 1000 cd/m², the ligand-treated device has an operational lifetime T_{50} of 583 hours greater than the untreated device (T_{50} = 442 h) (Fig. S3). By applying the equation $L_0^n T_{50}$ = constant[39] (L_0 and n are the initial luminance and acceleration factor) with n = 1.8[40–42], the T_{50} lifetime for the ligand-treated device is estimated to be 36 785 h at 100 cd/m², whereas the T_{50} lifetime for the untreated device is estimated to be only 27 888 h.

The capacitance–voltage (C–V) provides valuable insights into carrier dynamics in QLEDs[35, 43–46]. The C–V characteristics of both the untreated and ligand-treated devices are shown in Fig. 5 at the frequency of 1 kHz. The device capacitance is predominantly governed by the geometrical capacitance at 0 V. The ligand-untreated device has a slightly higher geometrical capacitance (2.86 nF) compared to the treated device (2.78 nF). Statistical analysis of geometrical capacitance exhibits similar results (Fig. S4) across different frequencies. The higher geometrical capacitance of untreated devices may be due to the thinning of the QD layer during the TFB spin-coating. As the voltage increases, electrons gradually inject and accumulate in the device, resulting in capacitance rise[43]. For the ligand-treated device, there is a capacitance peak (3.54 nF) at 2.2 V due to the electron accumulation at the QD/HTL interface[47, 48]. Afterward, the capacitance drops sharply, which is attributed to the effective-enough recombination of electrons and holes. However, for the untreated device, the capacitance begins to drop at 1.6 V and does not exhibit an obvious peak. This indicates a low level of charge accumulation in the untreated device, since numerous leakage paths are formed during the TFB fabrication, as observed by the morphology results shown in Fig. S1.

3. Conclusion

In conclusion, this study developed a ligand-treatment approach on QD films to prevent damage to the QD layer during TFB layer deposition. After the treatment of QD film with a 1,8-diaminooctane ligand, the inverted QLED possesses higher efficiency, higher brightness, and longer operational lifetime than the untreated QLED. These findings firmly indicate that the treatment of QD film with ligands is a simple and effective strategy for fabricating high-performance inverted QLED. We expect this study to provide a feasible solution for inverted QLED.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/1674-4926/44/9/092603.

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