Eco-Friendly Solvent Substitution for Enhanced Performance in All Solution-Processed QD-LEDs†

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Abstract

Anisole (Ani) is proposed as an eco-friendly alternative to chlorobenzene (CB) for dissolving PVK in QLEDs. Replacing CB with Ani improved PVK film smoothness, reduced operating voltages, and enhanced efficiency, demonstrating anisole's potential as a sustainable, high-performance solvent for QLED applications.

Author Keywords

QLED; Quantum dot; green solvent; Eco-friendly.

1. Introduction

Quantum-dot (QD) are promising light sources, compared to the organic light emitting diode (OLED), due to several advantages such as high color purity and quantum yield, facile tunable wavelength, solution processability. Given the efficient materials consumption and simple fabrication process, the all-solution-processed quantum-dot light-emitting diodes (QLEDs) are good candidates for next-generation display and lighting applications. [1-8] However, the QD and solvents such as Cd-based materials and toluene, chlorobenzene (CB) are high toxicity and environmental risks.[9] Thus, there is much research to replace the Cd-based QD with eco-friendly QD with high performance and color purity.[10] As a result, the QLED with eco-friendly QD has achieved high performance and color purity.[11]

In the perspective of the amount of materials consumption, solvents are used more than the QD materials. Considering materials consumption and the effectiveness for human and environmental hazards, replacing the harmful solvent to eco-friendly solvent should not be ignored. However, comparing the amount of research about developing eco-friendly QD materials, only a few research about adopting the eco-friendly solvent for QLED are reported.[12]

To address these issues, this study investigates replacing CB, a widely used but toxic and volatile solvent for PVK in QLEDs, with greener alternatives.[3] Using Hansen solubility parameters (HPSs), solvents which are capable of dissolving PVK effectively while maintaining critical orthogonality in the solution process can be identified.[13] Among these, greener solvents were filtered, ensuring smooth film formation, reduced operating voltages, and improved efficiency, paving the way for sustainable QLED fabrication.[3]

2. Experimental

Materials: PEDOT: PSS (Al40383) was purchased by Clevios™ P AI 4083, Heraeus, Germany. PVK and Zinc oxide nanoparticles (ZnO NPs) was purchased by Sigma-Aldrich, USA. Green QDs (CZO-530T) were purchased by Zeus, Republic of Korea.

Device Fabrication: All layers except the electrode were fabricated by solution process with spin coating method in the glove box of ambient dry air condition. Patterned ITO glasses were washed with ethanol in an ultrasonic bath and rinsed with deionized water. The multilayered QLED is consecutively deposited with hole injection layer (HIL, PEDOT:PSS), hole transport layer (HTL, PVK), emission layer (EML, Cd-based QD), electron transport/injection layer (ETL/EIL, ZnO NPs). The Al electrode was deposited about 100nm by using thermal evaporation with a rate of 0.1nm/sec under high vacuum conditions (1.0×10-6 Torr).

3. Results & Discussion

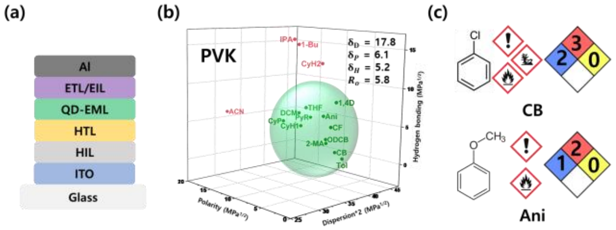

Figure 1. (a) Normal structure QD-LED, (b) the HSPs of various solvents and PVK in the Hansen space. (c) Human and environmental hazardous comparison between the CB and Ani based on NFPA and EHS.

The normal structure of the QLED device is illustrated in Figure 1(a). The device consists of multiple layers with solution process. Thus, the solvent orthogonality adjacent layer should be considered in various structures such as normal, inverted, and tandem. [14] Figure 1(b) demonstrates the solubility parameters of various solvents in a 3D Hansen plot, which evaluates their compatibility with PVK, a HTL material. The three axes represent dispersion forces (x-axis), polarity (z-axis), and hydrogen bonding (y-axis). The green sphere indicates the ideal solubility range for PVK. Among the tested solvents, anisole (Ani) is located within this green region, signifying its high compatibility with PVK. This contrasts with other solvents such as IPA or ACN, which are outside the region, demonstrating limited suitability. In Figure 1c, according to NFPA hazard ratings, anisole has lower health (1 vs. 2) and flammability (2 vs. 3) risks, indicating reduced harm to human health and lower fire hazards.[15] Additionally, CB is associated with greater environmental concerns, as reflected by its GHS hazard symbols, which include warnings for toxicity, flammability, and environmental damage.[3] In contrast, anisole lacks the environmental hazard symbol, underscoring its eco-friendly nature.[16] This makes anisole a more sustainable and safer solvent choice, while maintaining its compatibility and effectiveness in the QLED fabrication process. These results indicated Ani as a promising eco-friendly alternative to traditional solvents like CB.

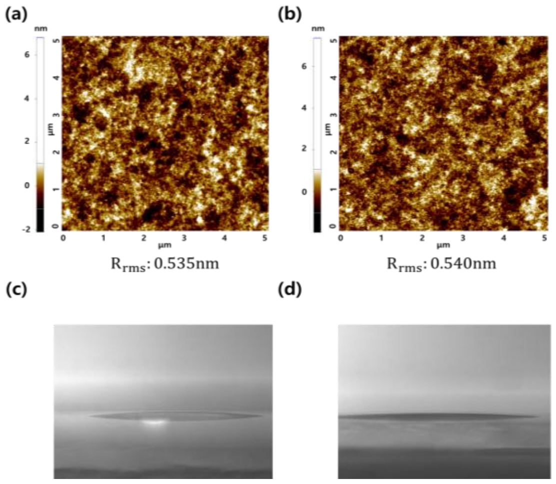

Figure 2. (a), (b) Surface morphology property of PVK thin film processed using CB and Ani solvent. (the structure is ITO/PEDOT: PSS/PVK(CB, Ani) (c), (d) CB and Ani solvent wettability characteristic on the PEDOT: PSS thin film.

To have smooth surface roughness is essential for high performance QLED. Thus, to evaluate the PVK morphology, atomic force microscopy (AFM) measurements were conducted for PVK thin films processed using CB and Ani on PEDOT: PSS thin film. In Figure 2a-2b, there are negligible differences in the root-mean-square roughness (R_{rms}) values of the PVK films (CB: 0.535nm, Ani: 0.540nm). Therefore, the Ani solvent can form high-quality and smooth PVK thin film. Before the deposit PVK thin film with Ani, the wettability property on PEDOT: PSS was conducted in Figure 2c-2d. The results revealed no notable difference in the contact angles between the two films, indicating that both CB and Ani create similar surface wettability and adhesion properties for PVK thin films.

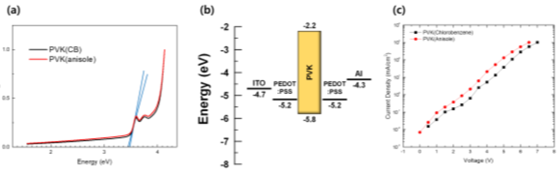

Figure 3. (a) Optical bandgap about PVK-CB and PVK-Ani by using UV-vis spectroscopy. (b) Schematic of energy band diagram of HOD. (c) The J-V curves of HODs for PVK-CB and PVK-Ani.

In Figure 3, UV-vis absorption measurements and hole-only devices (HOD) were fabricated to examine the hole injection characteristics. In Figure 3a, shows the UV-vis absorption spectrum and the Tauc plot used to measure the band gap of the materials. The band gap values were found to be approximately 3.5 eV, with similar results within the margin of error for both solvents. This indicates that the bandgap is not changed by changing the CB to Ani. Figure 4b-4c presents the corresponding schematic of energy band diagram and J-V characteristics of HOD. From the J-V curves, it is evident that the device using Ani exhibits better hole injection compared to the device using CB. Since QLEDs typically exhibit an electron-excess nature, improving hole injections can significantly enhance charge balance within the device, leading to better overall performance.

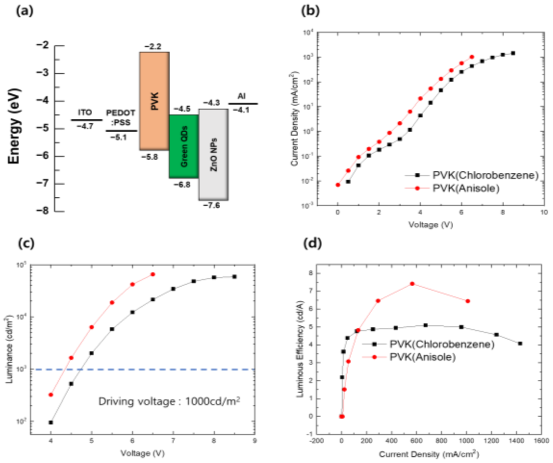

Figure 4. (a) Energy band diagram of the QLED normal structure. (b) J-V, (c) L-V, (the dashed line indicates the driving voltage at 1000 cd/m²) (d) luminous efficiency-J about the CB and Ani solvent used.

In Figure 4, the electro-optical property is investigated on the QLED normal structure. As shown in Figure 4a, it is the energy band diagram which has a high hole injection barrier than electron injection barrier for EML. The PVK-Ani QLED shows a higher current density than PVK-CB QLED in Figure 4b. Since the hole injection ability has improved, the PVK-Ani improved the current density. In Figure 3c, the driving voltage reduced from 4.74 V to 4.34 V. In Figure 3d, the luminous efficiency of PVK-Ani QLED increased 144% than PVK-CB QLED. Because of improvement of the hole injection ability, the charge imbalance which can attribute to the Auger recombination has been alleviated. Therefore, the eco-friendly Ani can be replaced by hazardous CB, while the QLED performance is improved.

4. Conclusion

In this study, it is investigated that replacing the harmful solvent with eco-friendly solvent. Firstly, the solvents are selected by using HSP theory, then the Ani is selected for eco-friendly solvent based on the NFPA and EHS in the filtered one. Secondly, through AFM and contact angle measurements, it is checked that the Ani can make the smooth PVK thin film. Finally, electro-optical analysis is conducted. From the UV-Vis and HOD analysis, the Ani can improve the hole injection ability. In that the electron-excess nature of QLEDs, the improvement of hole injection of PVK-Ani QLED alleviates the charge imbalance in EML. Therefore, the PVK-Ani QLED has higher performance than the PVK-CB QLED. From this study, it is confirmed that the harmful solvent can be replaced by an eco-friendly solvent. In addition, it is proven that the solvent can change the electro-optical properties of QLED. Thus, the proposed method and Ani is highly useful for fabricating eco-friendly and high performance QLED. Although this study has a lack of the mechanism about enhancing the improvement of hole injection ability, this study can provide valuable insights into the development of next-generation QLED and their practical applications.

5. Acknowledgment

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