Solution-processed WO$_3$ nanoparticle-based QLEDs are synthesized, which are highly promising for the next generation lighting and displays thanks to their narrow emission linewidth, tunable color emission spectral window across the visible to near-infrared range, and cost-effective fabrication techniques compatible with solution processed methods. As reported by H. V. Demir, X. W. Sun, and co-workers on page 247, the fully functional WO$_3$ interfacial layers deposited from WO$_3$ nanoparticle dispersions can be obtained by low annealing temperatures without further O$_2$-plasma treatment. The resulting WO$_3$ nanoparticle-based QLEDs also exhibit superior performance compared with the present PEDOT:PSS-based QLEDs.
Solution Processed Tungsten Oxide Interfacial Layer for Efficient Hole-Injection in Quantum Dot Light-Emitting Diodes

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Light-emitting diodes (LEDs) based on colloidal quantum dots (QDs) are highly promising for the next generation of lighting and displays thanks to their narrow emission linewidth,[1–4] tunable color emission spectral window across the visible to near-infrared range,[5–7] and cost-effective fabrication techniques compatible with solution processed methods.[8–12] Ever since the first demonstration of QD-based LEDs (QLEDs) 18 years ago,[13] rapid progress has been made in the device performances owing to the technological development and accumulation of relevant knowledge in materials and device architectures, i.e., understanding the underlying device physics,[14–16] designing more efficient device architectures,[17–20] and improving quantum dot properties by adjusting their composition and structure.[21–23] To date, QLEDs have emerged as an undeniable competitor to organic light-emitting diodes (OLEDs) for lighting and display applications. However, despite their apparent advantages, long-term stability of QLEDs is still a big concern for their practical applications.

Traditionally, polyethylene dioxythiophene:polystyrene sulfonate (PEDOT:PSS) is the most widely used buffer layer on an indium tin oxide (ITO) electrode for the fabrication of QLEDs. However, the aqueous PEDOT:PSS dispersion causes a side effect on the QLED stability due to its hygroscopic nature as well as acidic nature corroding the ITO electrode, resulting in the reduction of device lifetime.[24,25] Furthermore, compared with the inorganic material-based devices, the organic interfacial buffer layers have inferior thermal stability. Efforts to replace PEDOT:PSS with metal-oxides such as tungsten-, molybdenum-, nickel-, copper (I)-, rhenium-, or vanadium-oxides (WO3, MoO3, NiO, Cu2O, ReO3, or V2O5) have gained significant importance in the recent years.[26–31] In particular, highly n-doped WO3 and MoO3 exhibiting remarkably deep lying electronic states and efficient hole-injection into organic materials have been demonstrated.[32–35] However, their unique electronic properties have so far been primarily achieved using thin films made by high-cost thermal evaporation under vacuum, which presents disadvantages due to the cost issues and incompatibility with roll-to-roll scalable manufacturing. Additionally, it has been demonstrated that metal-oxide nanoparticles (NPs) as the interfacial buffer layers are often more efficient as compared to their bulk counterparts. For example, ZnO nanoparticle films as the electron transporting layers (ETLs) prepared by a sol–gel method have been introduced, resulting in all-solution-processed QLEDs with the maximum brightness values of 31 000 cd m−2, 68 000 cd m−2 and 4200 cd m−2 for red, green and blue devices, respectively, which are among the highest reported thus far.[36] Recently, Meyer’s group reported the preparation of solution-processed MoO3 nanoparticle films where the MoO3 was spin-coated on ITO from a suspension containing MoO3 nanoparticles and a block copolymer dispersing agent in xylene.[30] However, the films require an extra O2-plasma treatment to remove the polymeric dispersing agent to facilitate hole injection in the device and the...
resulting surface of MoO$_3$ nanoparticle film was relatively rough. Therefore, as such, in-depth studies focusing on solution-processed inorganic interfacial buffer layers is of critical importance for improving the QLED performance.

Here we report a highly efficient, stable QLED using solution-processed WO$_3$ nanoparticles as the hole injection layer. The preparation of the WO$_3$ nanoparticle layer described here is simple and cost-effective employing cheap and commercially available WO$_3$ nanoparticles and ethanol as a solvent and utilizing a low-temperature process under ambient conditions (annealing temperature can be as low as 80 °C and without requiring the O$_2$-plasma treatment). This treatment temperature is much lower than that of PEDOT:PSS (120–150 °C). At the same time, the overall performance for WO$_3$ nanoparticle-based QLED is superior compared to that of the present PEDOT:PSS-based QLEDs using the same device architecture. The WO$_3$ nanoparticle-based QLEDs with a maximum brightness of 30,006 cd/m$^2$, an external quantum efficiency (EQE) of 3.32%, and a peak current efficiency of 10.75 cd A$^{-1}$ have been achieved. Besides, the device lifetime has been also improved remarkably compared to that of PEDOT:PSS-based QLEDs, which marks as a further step towards the practical application of the QLED technology.

The standard structure of QLEDs is given as a multilayer structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/Poly[N,N′-bis(4-butylphenyl)-N,N′-bis(phenyl)benzidine] (poly-TPD)/QDs/2, 2′, 2″- (1, 3, 5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBi)/LiF/Al. The CdSe/ZnS core-shell structured QDs prepared according to a previous reported literature were used for the emissive layer.[3] The poly-TPD and TPBi layers were chosen as the hole transport layer (HTL) and the electron transport layer (ETL), respectively.

In our case, the WO$_3$ nanoparticle layer spin-coated on ITO was used to replace PEDOT:PSS as the HIL. The device structure is schematically presented in Figure 1a. The atomic force microscopy (AFM) image of the close-packed thin film of WO$_3$ nanoparticles on ITO with an average particle size of 7 nm (annealed at 100 °C in the glove box) is shown in Figure 1b. The surface roughness (RMS) of the film made from a 2 wt% of WO$_3$ ethanol solution is only 2.8 nm, indicating that the nanoparticle film has a smooth surface. To confirm the electronic structure of the as-prepared WO$_3$ nanoparticle film, the ultraviolet photoelectron spectroscopy (UPS) spectra including the magnified regions of the photoemissioncut-off and valence band are given in Figures 1c and 1d. The photoemission onset is found at 16.05 eV from the photoemission cut-off in Figure 1c. This corresponds to a work function (WF) of 5.15 eV in agreement with the WF values of WO$_3$ reported in literature, which can range from 4.7 to 6.4 eV depending on the film preparation conditions.[37] Figure 1d displays the zoom-in spectra of the density of states near the oxide valence band edge and the ionization energy (IE) of the WO$_3$ film that is determined to be 2.7 eV with respect to the Fermi level. According to the schematic energy level diagram of the device depicted in Figure 1e, it can be observed that the electrons can easily be injected from the Al to the QD layer. However, the case is quite different for the hole injection.[24,34,36] Owing to the deep lying electronic states of WO$_3$ nanoparticle interface layer, efficient hole injection can be proceeded via electron extraction from the highest occupied molecular orbital (HOMO) level of poly-TPD into the conduction band of WO$_3$ nanoparticles. For n-doped WO$_3$ or MoO$_3$, the hole injection from ITO to the organic semiconductors results from electron extraction from the highest occupied molecular orbital (HOMO) level.
of organic semiconductors through the WO₃ or MoO₃ conduction band, and then into ITO. For our case, owing to the deep lying electronic states of WO₃ nanoparticle interface layer, the energy barrier for the injection of electrons from the HOMO level of to the conduction band of WO₃ nanoparticles is quite small, and the efficient hole injection can be proceeded via electron extraction from the HOMO level of poly-TPD into the conduction band of WO₃ nanoparticles.

**Figure 2** presents the output performance of an optimized WO₃ nanoparticle-based QLED. The device is fabricated with QDs of 4 monolayers-equivalent thickness (~20 nm) and a WO₃ nanoparticle film of 2 monolayers-equivalent thickness (~14 nm). The electroluminescence (EL) spectrum of the QLED was recorded at the bias voltage of 12 V, showing a characteristic QD EL peak centered at ~518 nm with a full-width-at-half-maximum (FWHM) of ~30 nm. It should be noted here that there is a weak emission in the blue-wavelength region due to the residual emission from poly-TPD. The emission from poly-TPD indicates the presence of the LUMO of poly-TPD through defects of the QD layer to suppress the excess electrons for improving the charge balance of device. The LUMO of TCTA is 2.4 eV [38] and the relatively high energy barrier of 0.8 eV between the LUMO of TCTA and that of TPBi can block electrons to reach the poly-TPD layer in the device effectively. **Figure 3a** shows the EL spectra for the device with TCTA utilized as an EBL under different driving currents. It can be observed that the blue emission of poly-TPD is hardly found even when the driving current is just 40 mA, which indicates the better device stability for the WO₃ nanoparticle-based QLED.

**Figure 4** shows the operating stability of the resulting unencapsulated WO₃ nanoparticle-based QLED in comparison with the optimized PEDOT:PSS-based QLED. Under a continuous current driving condition corresponding to an initial luminance of 1000 cd/m², it can be clearly observed that using WO₃ nanoparticles to replace PEDOT:PSS as the HILs in QLEDs can drastically improve device stability. The unencapsulated WO₃ nanoparticle-based QLED displays a half-lifetime of ca. 6530 s, showing an approximately two-fold lifetime enhancement as compared to that of PEDOT:PSS-based QLED. The significant improvement in the device stability can be attributed to the fact that WO₃ nanoparticles are highly stable when compared to organic materials and can therefore act as a protection layer for organic materials.
In summary, we have demonstrated an efficient QLED using solution-processed WO$_3$ nanoparticle film instead of using PEDOT:PSS as the anode interfacial buffer layer. The WO$_3$ nanoparticle-based QLEDs show enhanced performance as compared to the PEDOT:PSS-based QLEDs. The EQE of 3.32% reported here is the highest value for green QLEDs using a non-inverted structure and the brightness of 30 006 cd/m$^2$ matches that of the best QLEDs with organic materials used as HTLs/HILs. Moreover, with the incorporation of the WO$_3$ nanoparticles, the unencapsulated device exhibits a significant improvement in the device stability and the lifetime is increased by approximately two-folds at an initial brightness of 1000 cd/m$^2$ as compared to that of PEDOT:PSS-based QLED. Meanwhile, since the solution-processed preparation method of WO$_3$ nanoparticle film used in our work is very simple and can be achieved at low annealing temperatures, it is suitable for application in flexible devices where the flexible substrates such as plastics often cannot withstand high annealing temperatures. These results indicate that WO$_3$ nanoparticles are promising solution-processed buffer layer materials and offer a practicable platform for the realization of high-performance, stable and large-area commercial QLEDs using a low-cost manufacturing process.

Table 1. List of figure-of-merits to compare the device performance using WO$_3$ nanoparticles (A) and PEDOT:PSS (B) as HILs.

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<tr>
<td>A</td>
<td>3.8</td>
<td>30 006 (@50 mA)</td>
<td>3.32</td>
<td>9.75</td>
<td>6.8</td>
<td>6530</td>
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<tr>
<td>B</td>
<td>4.2</td>
<td>25 202 (@40 mA)</td>
<td>3.02</td>
<td>8.74</td>
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Sulphur (S) was injected into the flask swiftly, and the octylphosphine (TOP) dissolving 0.15 mmol of selenium (Se) and ZnS QDs with a chemical-composition gradient were prepared. For PEDOT:PSS based QLEDs, we rotated the reaction flask and the reactor was then filled with nitrogen and heated up to 300 °C. At the elevated temperature, 1.6 mL of tri-n-octylphosphine (TOP) dissolving 0.15 mmol of selenium (Se) and 4 mmol of sulphur (S) was injected into the flask swiftly, and the reaction mixture was maintained at 300 °C for 10 min for the QD growth. To purify the synthesized QDs, the reaction mixture was cooled down to room temperature, and the QDs were extracted by the addition of acetone and methanol, followed by centrifugation. The CdSe-ZnS core-shell QDs were readily dispersed in toluene.

Fabrication of QLED Devices: The patterned ITO substrates were cleaned by sonication sequentially in detergent, de-ionized water, acetone, and isopropyl alcohol. The WO₃ anode buffer layer was cleaned by sonication sequentially in detergent, de-ionized water, acetone, and isopropyl alcohol. The CdSe-ZnS core-shell QDs were readily dispersed in toluene. The CdSe-ZnS core-shell QDs were readily dispersed in toluene. The CdSe-ZnS core-shell QDs were readily dispersed in toluene.

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Experimental Details

Synthesis of CdSe-ZnS Core–Shell QDs: Green-emitting CdSe-ZnS QDs with a chemical-composition gradient were prepared according to a modified method reported in the literature. For a typical preparation of green-emitting QDs, 0.1 mmol of cadmium oxide (CdO), 4 mmol of zinc acetate (Zn(Acet)₂), 5 mL of oleic acid (OA) were loaded in a 50 mL 3-neck flask, heated to 150 °C under vacuum to form cadmium oleate (Cd(OA)₂) and zinc oleate (Zn(OA)₂). Then 20 mL of 1-octadecene (1-ODE) was added to the reaction flask and the reactor was then filled with nitrogen and heated up to 300 °C. At the elevated temperature, 1.6 mL of tri-n-octylphosphine (TOP) dissolving 0.15 mmol of selenium (Se) and 4 mmol of sulphur (S) was injected into the flask swiftly, and the reaction mixture was maintained at 300 °C for 10 min for the QD growth. To purify the synthesized QDs, the reaction mixture was cooled down to room temperature, and the QDs were extracted by the addition of acetone and methanol, followed by centrifugation. The CdSe-ZnS core-shell QDs were readily dispersed in toluene.

Fabrication of QLED Devices: The patterned ITO substrates were cleaned by sonication sequentially in detergent, de-ionized water, acetone, and isopropyl alcohol. The WO₃ anode buffer layer was spin-coated on the O₂-plasma treated ITO substrate from diluted 1.25 wt% of WO₃ ethanol solution at 5000 rpm for 60 s and annealed at 80–110 °C for 30 min. The 2 wt% of poly-TPD (50 nm) in chlorobenzene was also spin-coated on the WO₃ layer at 4000 rpm for 60 s, followed by thermal annealing at 150 °C for 30 min in a nitrogen glove box. The QD layer was then deposited on the ITO/WO₃/poly-TPD layer by spin-coating the QD dispersion (QDs were dispersed in toluene with 15 mg/mL) at a rate of 1000–4000 rpm for 60 s, and cured at 90 °C under N₂ atmosphere for 30 min. The TPBi (35 nm), LiF (0.5 nm), and Al (190 nm) layers were thermally deposited under a base pressure of ~2 × 10⁻⁴ Pa. WO₃ dispersion in ethanol (2.5 wt%) was purchased from Nanograde GmbH (product no. 4035). For PEDOT:PSS based QLEDs, we followed the same procedure and only the WO₃ layer was replaced by PEDOT:PSS layer (40 nm) which was spun on the ITO substrate at 4000 rpm for 60 s and annealed at 150 °C for 30 min.

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Instrumentation: AFM (Cypher AFM, Asylum Research) was used to image the WO₃ nanoparticle film. UPS was performed using X-Ray Photoelectron spectroscopy (XPS) (VG Escalab 220i XL) with a He I (21.2 eV) gas discharge lamp. The electroluminescence (EL) spectra of the fabricated devices were measured using a PR650 Spectra Scan spectrometer, while the luminescence-current density-voltage (L-J-V) characteristics were obtained simultaneously, by connecting the spectrometer to a programmable Keithley 236 source measurement unit. All measurements were carried out at room temperature under ambient conditions.


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