Highly Stable and Scalable Blue QD-LED via an Evaporated TiO₂ Thin Film as an Electron Transport Layer

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Quantum dot-based light-emitting diodes (QD-LEDs) have excellent optical properties; however, their limitations of stability, reproducibility, and scalability due to the solution process are the major drawback. Herein, blue QD-LEDs fabricated with the conventional vacuum process using an e-beam-evaporated TiO₂ thin film as an electron transport layer (ETL) are demonstrated. GdZnS/ZnS-based blue LEDs with a TiO₂ thin film are fabricated under ambient conditions. They exhibit maximum external quantum efficiencies of 3.53% and a peak luminance of 2847 cd m⁻². These values are retained, which minimizes performance degradation under high potential bias. In addition, the optimized evaporated TiO₂ thin film has a negligible red shift (0.5 nm) of the peak wavelength between the photoluminescence spectrum and electroluminescence spectrum with stable full-width at half-maximum changing by less than 2 nm at high voltage. Finally, a blue QD-LED is fabricated on a scalable emission area of 2 × 2 in. with a patterned cathode accompanied by an evaporated TiO₂ thin film, which allows to perform conventional photolithography. A highly stable and reproducible vaporized inorganic thin film as the ETL supports the multilayer architecture to minimize the process damage.

1. Introduction

The interest in semiconductor colloidal quantum dots (QDs) is growing as their tunable bandgaps and functionalized characteristics receive considerable attention for the potential use in various applications such as field-effect transistors, biosensors, solar cells, and light-emitting diodes (LEDs).[1] Particularly, their uniqueness, making them prosperous quantum dot-based light-emitting diodes (QD-LEDs).[4] However, this recent progress in solution-processed multilayer QD-LEDs has restricted the fabrication diversity, specifically the patterning techniques of conventional photolithography.

Because of undergoing the solution phase during QD synthesis, the fabrication of QD-LEDs has been mainly developed using solution processes such as spin coating. Although spin coating is attractive owing to the easy control of composition and low cost, reproducibility and scalability of QD-LEDs cannot be ensured because the suitability of the solvent of the subsequent layer for the lower layer has to be considered and multiple processes with chemicals are required.[5] Hence, for the conventional structure (anode–hole transport layer (HTL)–emission layer (EML), QDs)–electron transport layer (ETL)–cathode), the deposition of an ETL via spin coating onto QDs can cause many issues such as dehydration, lack of reproducibility of electroluminescence (EL) performance, and instability of the device. To overcome the above limitations, physical vapor deposition (PVD) can be used instead of the spin-coating process for forming ETLs by introducing a metal oxide thin film. E-beam evaporator is one of the most common PVD equipment owing to its high scalability, reproducibility, simple deposition mechanism, and minimum side effects such as plasma or heating.[6]

Here, we report highly stable and scalable blue QD-LEDs accompanied by a physically vaporized TiO₂ layer as the ETL for the bottom emission-hybrid architecture. TiO₂, a wide-bandgap (3.9 eV) semiconductor, is a suitable candidate for the ETL because of the high electron mobility (μ_e ∼ 1 cm² V⁻¹ s⁻¹), excellent thermal stability with low sensitivity to oxygen and humidity, and unique optical characteristics such as high index...
ratio and excellent waveguide properties.[7] It is well-known that blue QD is the most sensitive QD because of the small particle size and large energy bandgap, which can be easily influenced by numerous surrounding conditions such as pinholes during spin-coating deposition and impurities at the interface. By introducing a high-vacuum deposition technique, we overcame these limitations and demonstrated a high-performance device, while scaling up the device size for fabrication innovation using the conventional photolithography method. Herein, the optimization results were analyzed to obtain high device performance based on the thickness of the evaporated TiO₂ thin films. The stability of the device performance, such as luminance and efficiency, was found to depend on the film thickness significantly in the high-potential range. The performance of a blue QD-LED with 40 nm TiO₂ as the ETL achieves the maximum luminance of 2847 cd m⁻², a stable external quantum efficiency (EQE) of 3.53%, and a narrow full-width at half-maximum (FWHM) of 26.75 nm; the devices were fabricated entirely under ambient conditions except for the ETL. Unlike the evaporated thin film of TiO₂, the conventional photolithography process was not applicable to the top of solution-processed ZnO nanoparticles (NPs) as the ETL because of the previous-layer damage by the penetration of pinholes between the NPs. The ETL using a highly dense TiO₂ thin film empowers the utilization of the conventional photolithography steps, which require multiple wet-chemical processes. We also demonstrated a 2 × 2 in. blue QD-LEDs with a pixelated size of 100 × 100 μm. The improved device performance and sophisticated fabrication techniques confirm a notable accomplishment in terms of stability, reproducibility, and scalability for QD-LEDs applications. Furthermore, this study highlights the potential usage of patterned scalable blue QD-LEDs as self-emissive full-color displays or backlight units associated with color filters for display applications.

2. Results and Discussion

A synthesis procedure of CdZnS/ZnS QDs was adopted with a similar modification as the method described in the literature[8] to enhance their fabrication stability for expanding applications of the most sensitive blue QDs because of their intrinsically small particle size. The structure of CdZnS/ZnS core shell is well-known to provide high photoluminescence quantum yield (PLQY) and stability by preventing mismatching of unsaturated bonds and dangling bonds on the QD surface.[9] By adopting their properties, the one-pot synthesis method was optimized and simplified by eliminating redundant steps; hence, multiple and complex shell growth processes are not necessary, which enables the improvement in reproducibility and scalability. Figure 1a shows the schematic diagram of the experimental setup used in this study for the synthesis of blue QDs. The synthesis starts with mixing and heating to form Cd-oleate and Zn-oleate by preparing mixed solvents of oleic acid (OA) in 1-octadecene (ODE) with CdO and Zn acetate (Zn(Ac)₂) at 140 °C. After increasing the temperature to 300 °C under N₂ flow, S precursor in ODE was quickly injected for the core formation. Because the reactivity of Cd to S is much faster than that to Zn, the amount of Zn precursor was larger than that of Cd to achieve a reaction balance and form the CdZnS alloyed core. Next, the second part of another S precursor in OA was injected at a slow rate of 1 mL min⁻¹ for the thick-ZnS shell growth onto the CdZnS core. Different conditions of shell growth were applied to obtain the PLQY as a function of the amount and concentration of S in OA and the volume of the injection rate. Experimental results show that a large amount of S and a slow injection rate promote the thick-shell growth. Furthermore, additional insertion of OA rather than ODE or tri-n-octylphosphine along with S for the second injection was found to promote high PLQY and good stability of QDs.[8b] The consequential QDs were rinsed for an hour at 310 °C and cooled down to room temperature under ambient conditions. Next, in the purification step, QDs were separated from the precursor, and isolated QDs were dissolved in hexane for further device fabrication. The detailed experimental information is provided in the Experimental Section.

The absorption and PL spectra of the resulting CdZnS/ZnS core–shell-structured QDs are shown in Figure 2a with a pure blue light emission at around 448 nm with an FWHM of 24 nm. This featureless nature in the absorption spectrum is not caused by the inhomogeneity of QDs but originates from the alloyed CdZnS core nucleation and the gradient structure due to the diffusion of Zn atoms during the shell growth; thus, the purity required for the QD emission can still be satisfied.[8a] Further, the PLQY of the CdZnS/ZnS QDs is measured as high as 83% (Figure 2b and Figure S1, Supporting Information), which is comparable to the literature report.[8] The high PLQY of the QDs is due to the gradient structure of the interface between the core and the shell, as well as the efficient passivation of thick ZnS shells.

Figure 1. Schematics of the a) one-pot synthesis process of CdZnS/ZnS QDs, b) solution process of QD-LEDs, and c) e-beam evaporation of a TiO₂ thin film.
As for the comparison of the shell growth, the larger concentration of S introduced in the second injection increases the PLQY of the QDs (Figure 2b). The excess S added into the solution preserves the shell growth completely and leads to the thick shell of the CdZnS/ZnS QDs. In addition, we found out that a slow injection rate was also effective for obtaining high PLQY (Figure 2b). A slow injection rate can avoid possible ZnS isolated core formation at a high temperature of 310 °C and makes all Zn and S precursors transfer for the shell formation. Such a thick shell can not only keep a high PLQY of the QDs in the solution but also benefit for the EL in the QD close-packed film of the QD-LEDs by suppressing the nonradiative fluorescence resonance energy transfer (FRET) process.[10]

To study the effect of the evaporated TiO2 thin film as the ETL on the blue QD-LEDs in terms of stability, reproducibility, and scalability, the most conventional hybrid structure including organic layers of hole injection layer (HIL) and HTL and an inorganic layer of ETL (indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)/poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′-(N-(4-sec-butylphenyl)diphenylamine) (TFB)/blue QDs/TiO2/Al) was introduced, as shown in Figure 1b,c. Herein, all fabrication processes of the blue QD-LEDs were conducted in an ambient atmosphere, specifically to confirm the stability during the fabrication process. Figure 3a shows the layered structure and the energy band diagram of the QD layer fabricated in this study. A TiO2 thin film was deposited by an e-beam evaporator under a high vacuum ($5.0 \times 10^{-7}$ torr) above the spin-coated blue QDs (EML). To reduce the damage of the blue QDs, TiO2 thin films were deposited at room temperature without the post-annealing process. In Figure 3b, the X-ray diffractometer (XRD) analysis was performed by comparing the as-deposited TiO2 thin films with the annealed one. The diffraction peaks of the TiO2 thin film after annealing at 600 °C were well indexed with the polycrystalline anatase phase (JCPDS# 21–1272), whereas the as-deposited one indicated the amorphous state. The scanning electron microscopy (SEM) image of the as-deposited TiO2 thin films shows a smooth surface morphology, which is close to amorphous TiO2 (Figure 3c). Even though the device configuration is for the bottom emission, the transmittance of the ETL is important for the light not to be absorbed in the ETL because the light passes the ETL twice by reflecting on the cathode electrode. As shown in Figure 3d, the average transmittance of the amorphous TiO2 thin film was $\approx 87.5\%$ in the visible region with respect to the reference glass.

To compare the EL properties of evaporated TiO2, QD-LEDs with the conventional structure of ZnO NPs for the ETL were fabricated using our blue QDs. The entire solution process was carried out in an ambient atmosphere. As shown in Figure 4, the maximum values of the luminance, current efficiency, and EQE characteristics of the device were 5895 cd m$^{-2}$, 1.71 cd A$^{-1}$, and 3.42%, respectively (Table 1). In addition, the Commission

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**Figure 2.** a) Absorption and PL spectra (inset) of CdZnS/ZnS in hexane and snapshot image of CdZnS/ZnS QDs under UV irradiation (inset). b) PLQY as a function of the amount of S precursor in OA with different injection rates for ZnS shell formation.

**Figure 3.** a) Energy level diagram of the layers in blue QD-LEDs. b) XRD patterns of the as-deposited and annealed TiO2 thin films. c) The surface morphology of the as-deposited TiO2 thin film via SEM. d) Optical transmittance spectra of the as-deposited TiO2 thin film via a UV-vis spectrometer in visible range.
Internationale de l’Eclairage (CIE) coordinate is (0.16, 0.05), which is close to the edge of spectral locus and matches with the EL spectra of the corresponding blue color (EL = 452.2 nm). The current density increases as the biasing voltage is increased to 10 V. Moreover, the abrupt decrease in the EQE from 3.42% to 1.08% was observed when the luminance increased from 5.2 V (20 nm TiO2), 6.4 V (40 nm), and 7 V (80 nm) (Table 1). Their efficiency dropped from 1.78% to 0.91% for 20 nm TiO2, from 2.06% to 1.65% for 40 nm TiO2, and from 3.53% to 2.06% for 40 nm TiO2. Equivalent trends of the Auger ionization were found in Figure 5c in terms of efficiency, albeit QD-LED with 40 nm TiO2 is found to be the most optimized device.

The blue QD-LEDs with the TiO2 thin films were fabricated and characterized under ambient atmosphere (relative humidity: 50–60% and room temperature: 20–22 °C) without encapsulation, and this condition should be considered for understanding the device performance. Compared to the highest recorded performance of blue QD-LEDs from the previous literature,[13] these devices exhibit the stability despite the ambient atmosphere. Particularly, the optimized 40 nm TiO2-accompanied QD-LED outperforms the ZnO NP-accompanied one in terms of stability by reducing the decreases in the efficiency and luminance at higher potential. The efficiency drop was from 3.53% to 2.06% (40 nm TiO2 QD-LED) and from 3.42% to 1.08% (ZnO NP QD-LED). The lower efficiency drop can be due to oxygen and moisture traps at the interface during the solution process when depositing the HTL, HIL, and QD layer. This can be solved by facilitation improvements.

To verify evaporated TiO2 thin films in blue QD-LEDs as new candidates for the ETL, further, we optimized the EL properties of the blue QD-LEDs as functions of the TiO2 thickness. Figure 5a,b shows the J−V and L−V curves as functions of the thickness, where 20 nm TiO2 exhibits higher current density and luminance in the low-voltage range of 3–7 V because of the high probability of creating pinholes, which leads to the leakage currents. Hence, the turn-on voltage was the lowest because of the higher current density at low voltage; however, the efficiencies were the lowest, as shown in Figure 5c–e. In contrast, the QD-LEDs with 80 nm TiO2 demonstrated the most stable device performance in terms of efficiency fluctuation because of blocking the leakage currents. As the luminance increases, the EQE, current density, and power density do not decrease dramatically, as compared to the 20 and 40 nm TiO2-based QD-LEDs. The stabilities in terms of efficiency are enhanced with the trade-off of the decreased luminance of the 80 nm thick TiO2 thin film, as compared to the 20 and 40 nm TiO2 layers. In addition, the QD-LED with 40 nm TiO2 shows comparable current density to the 80 nm TiO2 device except that its luminance and efficiencies are outstanding among the others. The peak luminance for all conditions is 2252, 2847, and 1982 cd m–2 for 20, 40, and 80 nm, respectively, at 10 V (Table 1). Moreover, the TiO2 thickness of 40 nm shows the highest device performance in terms of efficiency (Figure 5c–d). The maximum values of the EQE are 1.78% at 5.2 V (20 nm), 3.53% at 6.4 V (40 nm), and 2.06% at 7 V (80 nm) (Table 1). Their efficiency dropped from 1.78% to 0.91% for 20 nm TiO2, from 2.06% to 1.65% for 80 nm TiO2, and from 3.53% to 2.06% for 40 nm TiO2. Equivalent trends of the Auger ionization were found in Figure 5c in terms of efficiency, albeit QD-LED with 40 nm TiO2 is found to be the most optimized device.

Table 1. EL performance of QD-LEDs with ZnO NPs and evaporated TiO2 thin films as the ETLs.

| ETL           | V1 at 1 cd m–2 [V] | Lmax [cd m–2] | EQEmax [%] | CEmax [cd A–1] | PEmax [lm W–1] | FWHMmax [nm] |
|---------------|-------------------|---------------|------------|----------------|----------------|--------------|
| ZnO NPs       | 3.1               | 5895 (at 8.2 V) | 3.42 (at 5.6 V) | 1.71 (at 5.6 V) | 1.00 (at 5.2 V) | 28.07        |
| TiO2 thin film |                   |               |            |                |                |              |
| 20 nm         | 3.3               | 2252 (at 10 V)  | 1.78 (at 5.2 V) | 0.41 (at 5.2 V) | 0.27 (at 4.4 V) | 26.75        |
| 40 nm         | 4.3               | 2847 (at 10 V)  | 3.53 (at 6.4 V) | 0.90 (at 6.4 V) | 0.48 (at 5.6 V) |              |
| 80 nm         | 4.6               | 1982 (at 10 V)  | 2.06 (at 7 V)   | 0.47 (at 7 V)   | 0.24 (at 5.8 V) |              |
luminance of the 40 nm TiO₂ QD-LEDs increases without a single drop until 10 V. The device may be further enhanced by optimizing the electrical properties of the TiO₂ thin film by applying various annealing conditions. Furthermore, the high-vacuum deposition technique can improve reproducibility by eliminating pinholes, which are difficult to control during the spin-coating process, and by eliminating impurities, oxygen, and moisture at the interface between the QD layer and the ETL. Therefore, stable electron and hole carriers are introduced to an impurity-free and clean interface to be injected for the QD-LED operation. To compare the stability and reproducibility of the TiO₂ thin film-based QD-LEDs with those of the ZnO NP-based one, the EQEs of four QD-LEDs based on each ETL layer were statistically analyzed (Figure S2, Supporting Information). The standard deviation of the EQE max of the TiO₂ thin film-based QD-LEDs (0.11–0.15) is significantly lower than that of the ZnO NP-based one (0.50), which confirms the superior stability and reproducibility of the device performance of the evaporated ETL-embedded QD-LEDs, as compared to the devices fabricated using solution-processed ZnO NPs as the ETL (Figure S2e, Supporting Information). The CIE coordinate of the evaporated TiO₂-embedded blue QD-LED is (0.16, 0.02) indicating (Figure 5f) an extremely close point toward the edge of spectral locus, as compared to the blue QD-LED with ZnO NPs.

To investigate the stable EL properties of evaporated TiO₂ as the ETL further, the distinguished EL spectra of the blue QD-LEDs with ZnO NPs and the TiO₂ thin films were characterized by comparing the shifts of the peak wavelength. In the PL spectra (dashed line), the peak wavelength is 448.0 nm, and it is shifted to 452.2 nm for the EL spectra, denoted with solid lines with different colors for different potential values. A noticeable red shift of 4.2 nm is observed to substantiate the FRET behavior, which commonly occurs under nonradiative recombination. Nonetheless, the EL spectra of the blue QD-LEDs with the TiO₂ thin films as the ETL demonstrate only a 0.5 nm shift of the peak wavelength from 448.0 nm of the PL spectra to 448.5 nm of the EL spectra (Figure 6b). It is assumed that if a dense thin film is formed above blue QDs rather than NPs, nonradiative recombination can be restrained onto the interfaces. This confirms that QD-LEDs accompanied by evaporated TiO₂ thin films as the ETL can emit light with the intrinsic QD color properties. Moreover, their FWHM have critical optical properties on color rendering. Without exploiting the optical concavity structure, a wide and unsteady FWHM will limit the high sensitivity when presenting a wide color gamut. As the bias voltage is increased from 5 to 10 V, the FWHM for ZnO NPs increases from 24.71 to 28.07 nm by 3.36 nm, and the FWHM for TiO₂ is increased from 25.39 to 26.76 nm by 1.36 nm.

Furthermore, to confirm the effect of the evaporated thin film above QDs on the stability, the surface morphology of ZnO NPs and TiO₂ thin films was analyzed using atomic force microscopy (AFM; Figure 4c,d). The solution-processed ZnO NP film on the top of blue QDs has a root-mean-square (RMS) roughness value of 1.89 nm with peak heights of 16.9 nm. In contrast, the evaporated TiO₂ film has a low RMS roughness of 0.67 nm with peak heights of 6.1 nm. The evaporated TiO₂ film demonstrates a smooth and uniform surface, as compared to the solution-processed ZnO NP film. Moreover, the

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**Figure 5.** EL performance of QD-LEDs with evaporated TiO₂ thin films with different thickness of 20, 40, and 80 nm as the ETL. a) Current density versus applied voltage (J–V) curve. b) Luminance versus applied voltage (L–V) curve. c) EQE, d) current efficiency, and e) power efficiency as functions of luminance. f) CIE coordinates and photo image (inset) of the blue EL QD-LEDs.
SEM-acquired surface morphologies of ZnO NPs (Figure S4, Supporting Information) illustrate the difficulties of uniform deposition of the ETL on the top of QDs for the solution process. The aggregation NPs, either QDs or ZnO NPs, can generate pinholes, which result from the direct contact with the Al electrode. This undesirable structure generates leakage currents, which lead to the unexpected behavior of the devices such as efficiency degradation. The used deposition technique affects the interface and coverage of the ETL, whose parameters are crucial for achieving uniform and stable QD-LED devices.

Finally, blue QD-LEDs with a 2 × 2 in. square size were fabricated and characterized under ambient conditions. Blue QDs are well-known sensitive materials with many limitations caused by the conventional fabrication process. Hence, utilizing the solution process with ZnO NPs for the ETL is highly restrictive to complement photolithography steps defining the electrodes as the previous layers can be easily damaged by the developer (strongly alkaline solution) or photoresist (PR) remover (acetone). However, because of the evaporated TiO₂ thin film as the ETL, the conventional photolithography process can be implemented in the QD-LED fabrication process. The EL emission is shown in Figure 7. A schematic illustration of the patterning process of the Al electrode using photolithography and lift-off is shown in Figure 7a, which involves reiterating the process of wet-chemical steps such as coating PR, developing UV-exposed areas, and rinsing PR by acetone. The image reversal PR of AZ5214E is used in the lift-off process for 100 µm grating patterns with a 300 µm gap over 2 × 2 in. square (see Figure S4, Supporting Information); the defined area is perpendicular to the anode. Hence, the light is only illuminated from the 100 × 100 µm square (Figure 7d), which is sandwiched between the anode and cathode electrodes (Figure 7b).

3. Conclusions

We synthesized CdZnS/ZnS core/shell blue QDs possessing a high PLQY of 83% with a narrow spectral bandwidth of 24 nm at a peak wavelength of 448 nm at room temperature. This simple synthesis enhanced the highly stable and reproducible characteristics of blue QDs, which can be utilized in the fabrication of QD-LEDs outside of the glovebox under a harsh condition of unrestricted oxygen and moisture under ambient conditions. Highly stable blue QD-LEDs were achieved by employing evaporated TiO₂ thin films as the ETL. They showed the following high-performance characteristics: the maximum luminance up to 2847 cd m⁻², a peak EQE of 3.53%, and a narrow FWHM of 26.75 nm. These results show remarkable qualities in terms of fabrication under ambient conditions, not inside of the glovebox. Particularly, stable device performance was observed with the evaporated TiO₂ thin films by delivering carriers without either energy transfer to undesired particles or excessive carrier aggregation for ionization effects. Furthermore, vacuum deposition of the TiO₂ thin films as the ETL allowed for the conventional photolithography process for further investigation of patterning techniques for full-color.
4. Experimental Section

Synthesis of CdZnS/ZnS QDs: In a typical synthetic procedure, 0.5 mmol of CdO and 5 mmol of Zn(Ac)₂ were added to a mixture solvent containing 4 mL of OA and 10 mL of ODE in a three-neck reector. After degassing under vacuum at 140 °C for 30 min, the reaction temperature was further increased to 300 °C under N₂ flow. At this temperature, 0.8 mmol of S powder in 2 mL of ODE was quickly injected into the reaction flask, and the temperature was then raised to 310 °C. After the core formation for 8 min, 7 mmol S powder in 10 mL OA was slowly introduced into the reactor (1 mL/min) to overcoat ZnS shells onto CdZnS cores. The temperature was kept for 1 h for annealing the QDs and then was decreased to room temperature naturally. The resulting QDs were precipitated with the addition of an excess of 60 mL ethanol and centrifugation (8000 rpm, 10 min). After discarding the supernate, the QDs were purified twice by the dispersion/precipitation process with a solvent of hexane/ethanol (20/60 in mL) under the same centrifugation condition. Finally, the purified QDs were re-dispersed into hexane. After removing insoluble QDs and impurities, the QD solutions were kept in refrigerator (4–8 °C) for a long-time storage.

Fabrication of QD-LEDs: All steps were performed in ambient air (RH: 50–60% and room temperature: 20–22 °C) at the cleanroom of 1000 level university facility. Patterned ITO substrates were cleaned by ultrasonication in acetone and isopropyl alcohol and then treated with oxygen plasma for 5 min. The cleaned and patterned ITO substrates were spin-coated with PEDOT:PSS at 4000 rpm for 30 s and then annealed at 150 °C for 30 min under ambient conditions. Subsequently, the resulting substrates were spin-coated with TFB at 2000 rpm for 30 s and then annealed at 130 °C for 30 min under ambient conditions. The synthesized blue QDs were spin-coated at 4000 rpm for 30 s and then annealed at 100 °C for 5 min. Next, TiO₂ thin films were deposited onto the blue QDs via an e-beam evaporator (ULVAC, ei-S), using the commercially available TiO₂ (99.999%) evaporation pellets. The substrates were located in parallel 70 cm away from the crucible and rotated at 7 rpm to obtain the thickness uniformity. The base pressure and growth rate were, respectively, 5 × 10⁻⁷ torr and 1 Å s⁻¹, and the thin film thicknesses were finely controlled by means of a deposition controller (ULVAC, CRTM-9000) with a gold-coated quartz crystal microbalance. The electron gun voltage was 10.0 kV, and the current was 120–130 mA. It is worth noting that the substrate was not additionally heated during the deposition. The patterning process was performed after the lift-off process to deposit Al onto specific areas. A PR (AZ5214, Microchem) was spin-coated at 4000 rpm for 45 s, soft baked at 95 °C for 1 min, and exposed to a 25 mJ UV-I line source. Hard baking was carried out at 105 °C for 2 min, and another flood exposure to 250 mJ.

Figure 7. a) Schematic illustration of the solution process using a spin coater for the HIL, HTL, and EML, PVD for the ETL, and photolithography for the patterned cathode electrode. b–d) Photographs of 2 × 2 in. of the blue QD-LED with 100 × 100 µm size of the patterned electrode.
under an MA/BA6 mask aligner. AZ 351B with water in a ratio of 1:4 was used to remove the desired area of the PR to deposit electrodes. Finally, Al electrodes were deposited using an e-beam evaporator under a high vacuum (<5 × 10⁻⁶ torr). The completed sample was again immersed into acetone for 1 min to remove the PR and undesired metal electrodes. The final active device areas were 4.5 mm².

Characterization: EL spectra, current density/voltage (J–V), and luminance/voltage (V–L) characteristics were obtained using photonic multichannel analyzer PMA-12 (Hamamatsu Photonics K.K.) coupled with a source meter (Keithley 2400) as the voltage and current source unit. Particularly, PMA-12 is a compact spectral characterization instrument based on an optical fiber, which can deliver the high sensitivity spectra to the system. An integrating sphere unit facilitated the accurate measurements of luminous efficiency of LEDs. The measurements had the specification that the wavelengths from 350 to 1100 nm were covered, which included the visible-light range for red, green, and blue of the primary colors from QDs with a resolution lower than 2.5 nm and a pixel size from 24 µm to 2.93 mm.

The atomic structure of the TiO₂ thin films was investigated using a Bruker D8 Advance XRD. The system uses Cu Kα (λ = 1.54 Å) radiation. It was operated in the reflection mode with a 2θ scan from 20° to 70° with a step of 0.02°. The unique XRD patterns from the samples were analyzed by comparing them with the reference JCPDS cards. SEM (FEI Magellan 400) was used to determine the morphology of the TiO₂ thin films using a field emission gun of 15 kV working at a distance of 4 mm. Room-temperature UV-vis absorption spectra were measured to obtain the absorption of CdZnS/ZnS QDs and the transmittance of the TiO₂ thin films using an Agilent Technology Cary 7000 UV–vis–near-infrared spectrometer. PL spectra and absolute PLQY were measured using a spectrophotometer coupled with an integration sphere (Hamamatsu, Quantaurus-QY plus), and the excitation wavelength was set to 370 nm.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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