Blue Light Emitting Diodes based on Bright Quasi-Type-II ZnO@1-Aminopyrene Hybrid Quantum Dots with a Long Operation Life

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Non-toxic heavy metal, low-cost indium-free blue emissive quantum dots (QDs) are critical for the realization of self-emissive electroluminescent quantum dot (ELQD) light-emitting diode (LED) displays. A facile and effective hybridization of ZnO QDs with functionalized polyaromatic hydrocarbons (f-PAHs) to synthesize a very bright and stable blue-light emissive quantum-dot LED (QLED) using non-toxic quasi-type-II ZnO@1-Aminopyrene hybrid QDs is reported. The optimized QLEDs of ITO/PEDOT:PSS/TFB/ZnO@1-Aminopyrene/TPBi/LiF/Al demonstrate very bright deep blue-light electroluminescence of 3379 cd m⁻² centered at λ = 441 nm with a full-width-at-half maximum of 41.7 nm and CIE 1931 color coordinates of 0.17 and 0.09, a luminous efficacy of 3.32 cd A⁻¹, power efficiency of 2.45 lm W⁻¹, external quantum efficiency of 2.35%, and a remarkably long lifetime T₅₀ of >17 830 h at 100 cd m⁻².

1. Introduction

According to the forecast on future flat-panel display technology, a self-emissive electroluminescent quantum dot (ELQD) light-emitting diode (LED) display is highly expected

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for next generation flexible displays as well as for flat panel displays with color filters (organic LED and liquid crystal display (LCD)) or on-chip (LCD and microLED) type displays.^[1-3] This is because QDs may offer high internal quantum efficiency (IQE) and ultranarrow full-width at half maximum (FWHM) which provide very wide color purity and gamut displays. It is also solution processed, thus potentially opening a route to low-cost large-sized display manufacture. To implement ELQDs displays, high-resolution pixel manufacturing methods along with highly efficient and stable blue-emissive QDs need to be developed together.

Regarding blue-emissive QDs, Cd(Zn)Se(S) alloyed quantum-dot LEDs (QLEDs)^[4-7] showed a blue electroluminescence (EL) of ≈437–477 nm, external quantum efficiency (EQE) of \approx 1.7–19.8%, brightness of \approx 2250–62 600 cd m⁻², and lifetime T_{50} (time required for the brightness to decrease to 50% of the initial value, h@100 cd m⁻²) of \approx 16–10 000 h. However, the use of Cd-contained QDs in electrical and electronic products is strictly restricted according to the directive on the Restriction of Hazardous Substances (RoHS)^[8] due to environmental harm and health issues. As an alternative to excellent CdSebased QLEDs, QLEDs based on InP, ZnSe, CuInS2, and lead halide perovskites, etc., have also been widely studied, among which InP and ZnSe are considered as promising candidates. InP/GaP/ZnS//ZnS QLEDs exhibited an EL of 488 nm, a record brightness of 3120 cd m⁻², and EQE of 1.01%.^[9] However, for application to pure blue lighting QDs, InP QDs still have some difficulties: They need to be fabricated to a size smaller than 1 nm in diameter and to overcome poor color purity (known as FWHM \geq 35 nm). Among a number of ZnSe_{1-x}Te alloyed QDs,^[10,11] optimized ZnTeSe/ZnSe/ZnS core-shell-shell QLEDs with double emitting layers showed blue emission tuned at 457 nm by Te doping, an EQE of 20.2% with brightness of 88 900 cd m^{-2} , which is close to the theoretical limit, and the longest lifetime, $T_{50} = 15\ 850\ h.^{[12]}$ The limitations of the use of ZnSe due to its wide band gap of 2.7 eV for the growth of QDs that emit pure blue color can be overcome by alloying it with zinc telluride (ZnTe), which has a band gap as low as 2.25 eV. Te is a rare and mildly toxic element. The oxidative tendency of Tecontaining compounds reduces its chemical stability, resulting in lower emission efficiency. Moreover, alloying creates a vulnerable heterogeneity of the core due to the difference in the ionic radius between Se and Te, which increases the FWHM (\approx 27–36 nm) of the ZnTeSe ODs core twice as much as those (≈11–20 nm) of the ZnSe core QDs, and consequently deteriorates the purity of color.^[13] As an alternative to using ZnSeTe material to overcome these potential shortcomings of Te, II-VI ZnO QDs are good candidates as they are environmentally friendly and abundant in nature. ZnO metal oxide for semiconductors (II-VI) has been of interest for optoelectronic applications due to its wide band gap (\approx 3.3 eV), large exciton binding energy (60 meV) at room temperature, high electron mobility ($\approx 205 \text{ cm}^2 \text{ Vs}^{-1}$), large optical gain (300 cm⁻¹), and fast saturation velocity ($\approx 3.2 \times 10^7$ cm s⁻¹).^[14–16] Intrinsic defects causing visible emissions such as oxygen vacancies (Vo's) or Zn interstitials (Zni's) are known to mostly exist at the surface of ZnO QDs.^[17,18] Visible emissions from ZnO QDs have been reported to be well controlled by hybridization with fluorophores such as anthracene $\left(C_{14}H_{10}\right)^{[19]}$ or nanocarbons such as graphene quantum dots (GQDs),^[20–22] C₆₀,^[23] graphene oxide (GO),^[20] and reduced GO (rGO).^[24-26] The proximity of the electronic energy levels of the organic material with the defect levels of ZnO QDs at the interface of organic/inorganic heterojunction structures facilitates efficient resonant energy transfer through non-radiative (NR) transition of electron excitation and/or the charge transfer. Blue luminescence from ZnO QDs was lately realized by the synthesis of type-I ZnO@GO hybrid QDs,[27] which showed only an enhanced blue emission from the inner ZnO core by means of charge transfer from the lowest unoccupied molecular orbital (LUMO) of GO to the conduction band (CB) of ZnO QDs irrespective of the excitation wavelength without green or yellow emission.

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In this study, we introduced an interesting and facile manufacturing method in which ZnO QDs are hybridized with functionalized polycyclic aromatic hydrocarbons (f-PAHs) to produce ZnO@f-PAHs hybrid QDs. In addition to abundance, PAHs as organic molecules to be hybridized have the advantage that their electronic structure can be accurately predicted through density-functional-theory (DFT) calculation depending on the number of benzene rings and the type of functional groups. Functionalization of PAHs with S, O, N, Se, and P are inevitably necessary for forming chemical bonds with ZnO QDs. Accordingly, it becomes possible to predict the energy levels related to the resonant energy transfer and/or charge transfer at the interface of ZnO@f-PAHs hybrid QDs, which means that the visible emissions from ZnO@f-PAHs can be well modulated. To synthesize the blue-light emissive quasi-type-II ZnO@1-PyNH₂ hybrid QDs, we selected 1-Aminopyrene (1-PyNH₂), which consists of 4 benzene rings and contains only an amine (-NH₂) functional group, which is a molecule with the simplest structure among f-PAHs. We precisely determined the electronic energy levels of the CB and the valence band (VB) and the intrinsic defect levels in ZnO QDs and those of LUMO and highly occupied molecular orbital (HOMO), which were induced by amine functional groups of 1-PyNH₂ using an ultraviolet photoemission spectroscopy (UPS), photoluminescence (PL) and photoluminescence excitation (PLE), UV-vis absorption spectroscopy, and DFT calculation using Gaussian 09 package.^[28] ITO/ PEDOT:PSS/TFB/ZnO@1-PyNH2/TPBi/LiF/Al **QD-LEDs** achieve a deep blue EL at 441 nm with 1931 Commission Internationale de l'Eclairage (CIE) color coordinates of 0.17 and 0.09, a luminance of 3379 (cd m⁻²), a luminous efficacy (LE) of 3.32 cd A⁻¹, an EQE of 2.35%, and a longer average lifetime $T_{50} = 17$ 830 h than ever reported to date at an initial brightness of 100 cd m⁻².

2. Results and Discussion

2.1. Surface Chemistry of ZnO@1-PyNH₂ Hybrid QDs

Figure 1a graphically illustrates that hydroxyl bondings of Zn-OH on the surface of ZnO QDs react with the amino groups (-NH₂) of 1-Aminopyrene to form Zn–NH through dehydration. From the FT-IR spectrum of ZnO QDs (Figure 1b), the existence of hydroxyl (-OH) as well as acetoxy $(-O-C=O-CH_3)$ groups on the surface of ZnO QDs is confirmed by the observation of absorption peaks at 1556 and 1402 cm⁻¹ (COO⁻), and at 3400–3200 cm⁻¹ (OH). The occurrence of absorption peaks at 1490 and 1330 cm⁻¹ corresponding to C-N bonding of TMAH indicates the remains of the basis product of TMAH within ZnO QDs, even after they are washed with acetone. These peaks almost disappear after 1-PyNH2 molecules react with the ZnO QDs in DMF through heating at 100 °C, as shown in Figure 1b. In the case of ZnO@1-PyNH₂ hybrid QDs, the aromatic C-H stretching mode (2919 and 2850 cm⁻¹), aromatic C=C bond (1630 and 1530 cm⁻¹), N-H stretching mode (960 cm⁻¹), and Zn-N (459 cm⁻¹) are clearly observed and the O-H stretching mode and C-N bond of TMAH disappear.

The wide scan of survey and core-level XPS spectra (Figure S1a-e, Supporting Information) of ZnO QDs and ZnO@1-PyNH2 core-shell QDs were taken and fitted with Gaussian sub-peaks. Their atomic compositions and relative chemical bonding ratios are also calculated (Tables S1 and S2, Supporting Information). C1s XPS peaks (Figure S1b, Supporting Information) for ZnO QDs can be fitted into three subpeaks at binding energy (BE) = 284.67, 286.28, and 288.21 eV, which correspond to C-CH₃ and N-CH₃/OH-CH₃ of TMAH, and the acetoxy group of $O-C(-CH_3)=O$, respectively. C1s of 1-PyNH₂ is also resolved into C-C/C-CH₃ (284.67 eV), C-N (285.30 eV),^[29,30] and a satellite peak $(\pi \cdot \pi^*)$ at BE = 290.60 eV. The C1s peak of ZnO@1-PyNH2 hybrid QDs is resolved into four sub-peaks at $C-C-C/C-H/C-CH_3$ at BE = 284.69 eV, $C-N_{arom.}$ at BE = 286.11 eV, $O-C(CH_3)=O$ at BE = 288.74 eV, and π - π ^{*} satellite at BE = 289.88 eV. Figure 1c shows the Zn2p core-level XPS peak of ZnO QDs and ZnO@1-PyNH₂ hybrid QDs. The spin-orbit splitting of Δ_{SO} = 23.09 eV between Zn2p^{1/2} (1044.02 eV) and Zn2p^{3/2} (1020.93 eV) for ZnO QDs is the same as that for $\Delta_{SO} = 23.09$ eV of ZnO@1-PyNH₂ hybrid QDs, but Zn2p of the ZnO QD peak is blue-shifted as $\Delta E =$ 0.82 eV in ZnO@1-PyNH₂ hybrid QDs, which means that electrons are transferred from the inner ZnO (donor) core to the outer 1-PyNH₂ (acceptor) molecules. As shown in Figure 1d, the O1s core-level XPS peak for ZnO QDs is resolved into lattice O as Zn-O at BE = 529.51 eV, hydroxyl Zn-OH at BE = 530.61 eV, and carboxylate in $O-C(CH_3)=O$ at BE = 531.66 eV, and that for ZnO@1-PyNH2 hybrid QDs is fitted into three subpeaks of Zn-O at BE = 529.88 eV, Zn-OH at BE = 530.98 eV,







Figure 1. a) Schematic diagram of chemical reaction between ZnO and ZnO@1-PyNH₂ hybrid QDs (Photographic images of ZnO QDs (yellow) and ZnO@1-PyNH₂ hybrid QDs (blue) irradiated by UV lamp (λ = 325 nm)). b) FT-IR spectra of ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ hybrid QDs. c) Zn2p, d) O1s, and e) N1s core-level XPS spectra of ZnO QDs and ZnO@1-PyNH₂ hybrid QDs.

and O–C(CH₃)=O at BE = 531.92 eV. N1s peaks in Figure 1e derived from CH₃-N at the surface of ZnO QDs are observed at BE = 402.77 eV, which disappear after the QDs are washed in acetone and that from C–NH_{2(arom.)} (arom. = aromatic) bond of 1- PyNH₂ appears at BE = 399.57 eV. The N1s peak of ZnO@1-PyNH₂ consists of only one peak derived from the C–NH_{arom}–Zn bond at BE = 400.17 eV as a result of the chemical reaction between the amine group (-NH₂) of 1-PyNH₂ and the -OH group of ZnO QDs accompanied by a dehydration process.

2.2. Crystalline Structure

Figure 2a presents XRD patterns of ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ hybrid QDs XRD peaks observed at 2 θ values of 31.74°, 34.24°, 36.2°, 47.64°, 56.5°, 62.86°, 68.08°, 66.3°, 67.9°, and 69.1° can be respectively indexed to different planes (100), (200), (101), (102), (101), (102), (110), (103), (200), (112), and (201) of crystalline ZnO with a wurtzite structure (JSPDF File No. 79–2205). Due to the microcrystalline-like structure, many sharp diffraction peaks are detected in 1-PyNH₂ molecules. In the case of ZnO@1-PyNH₂ hybrid QDs, most XRD

peaks of inner ZnO core QDs are not significantly suppressed. Figure 2b shows HR-TEM images of ZnO QDs (upper) and ZnO@1-PyNH₂ (below) hybrid QDs with a statistical distribution and average size of about 8.45 nm and about 12.42 nm, respectively. Figure 2c also presents HRTEM and selected area diffraction (SAD) patterns of ZnO@1-PyNH₂ hybrid QDs. The inner ZnO core has a distorted hexagonal shape and the black lines indicated by arrows outside 1-PyNH₂ molecules are clearly seen outside the inner ZnO QDs in Figure 2c. The lattice spacing of 0.244 nm corresponds to the interplanar distance of the (101) crystal plane of wurtzite ZnO. TEM diffraction images of polycrystalline ZnO@1-PyNH2 hybrid QDs in Figure 2c are identical to the XRD results. Figure 2d shows EDX-elemental mapping images that explicitly illustrate the C, O, and Zn atoms of ZnO@1-PyNH2 hybrid QDs, in which the mapping image of the Zn atom is almost identical to that of O and similar to that of C.

2.3. Optical Properties

Using the UV-vis absorption spectra (Figure S3, Supporting Information) of ZnO QDs, 1-PyNH₂ molecules, and

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Figure 2. a) XRD pattern of ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ hybrid QDs. b) HRTEM images of ZnO QDs and ZnO@1-PyNH₂ hybrid QDs. c) Closer views of HRTEM image for ZnO@1-PyNH₂ hybrid QDs taken from hexagon marked in white circle (Yellow arrows indicate the outer 1-PyNH₂ attached outside the inner ZnO QDs) and the image of SAD. d) EDX images of ZnO@1-PyNH₂ hybrid QDs.

ZnO@1-PyNH₂ hybrid QDs, the corresponding Tauc plot $((\alpha h v)^2 \text{ vs } h v)$ in **Figure 3** are obtained using Equation (1).

$$\alpha h v = A (h v - E_g)^{\frac{1}{2}} \tag{1}$$

where α is an absorption coefficient, *h* is Plank's constant, *v* is the photon frequency, *A* is a constant relating the effective mass associated with the valence and conduction bands, *E*_g is the optical band gap. In the Tauc plot, the band gap (*E*_g) for ZnO QDs is determined as 3.3 eV by extrapolating the linear part until it intersects with the h*v* axis. The band gap of QDs is theoretically described in Equation (2), which was derived from



Figure 3. Tauc plot obtained from UV–vis absorption spectrum of ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ hybrid QDs.

the effective mass approximation (EMA) models^[31,32] considering the quantum confinement, the Coulomb interaction, and the spatial correlation between the electron and the hole.

$$E_{(g,\text{QD})} = E_{(g,\text{bulk})} + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.78e^2}{4\pi\varepsilon_o\varepsilon_r R} - 0.248E_{\text{Ryd}}^*$$
(2)

where $E_{(g,QD)}$ and $E_{(g,bulk)}$ (= 3.37 eV) are respectively the bandgaps of QDs and bulk ZnO; *R*,*h*, ε_r = 3.7, and E_{Rvd}^* are the QDs' radius, Plank's constant, dielectric constant at the optical frequency, and bulk exciton binding energy (60 meV), respectively; $m_{e}^{*} = 0.24m_{e}$ and $m_{h}^{*} = 0.59m_{e}^{[33]}$ are the effective mass of electrons and holes, respectively. From the above Equation (2), the band gap for ZnO QDs with R = 4.225 nm is estimated as E = 3.32 eV, which is well coincident with a Tauc band gap of 3.3 eV and close to the 3.21 eV obtained from the excitonic emission captured from near band edge (NBE) emission at 386 nm of PL spectra which is usually lower by as much as the exciton binding energy of 60 meV from the CB. This lies within the range of the previous band gaps of 3.4 and 3.28 eV of ZnO QDs synthesized at 50 and 100 °C, respectively.^[34] The band gap of 1-PyNH₂ is 2.94 eV and that of ZnO@1-PyNH₂ hybrid QDs shows two edges, 2.94 and 3.18 eV, which are ascribed to the outer 1-PyHN₂ molecules and the inner ZnO QDs, respectively.

Figure 4 presents spectral-dependent PL (SDPL) for ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ hybrid QDs. As the excitation wavelength (λ_{ex}) increases from 300 nm, a broad yellow luminescence (YL) with FWHM \cong 96 nm centered at 562 nm (2.20 eV) gradually increases and shows the maximum at $\lambda_{ex} = 380$ nm (3.26 eV), but it decreases until 400 nm (3.10 eV). The PL peak excited at $\lambda_{ex} = 360$ nm (Figure S4, Supporting Information) can be further resolved into three visible emission





Figure 4. SDPL of a) ZnO QDs, b) 1-PyNH₂, and c) ZnO@1-PyNH₂ hybrid QDs. PLE spectra of d) ZnO QDs, e) 1-PyNH₂ at $\lambda_{Det} = 440$ nm, and f) ZnO@1-PyNH₂ hybrid QDs at $\lambda_{Det} = 430$ nm with Gaussian fitting.

sub-peaks centered at 463 (2.67 eV), 541 (2.29 eV), and 585 nm (2.12 eV) with a weak NBE emission at 386 nm (3.21 eV) as well as a violet emission at 412 nm. The YL almost disappears at a $\lambda_{\rm ex}$ longer than 400 nm, but instead only the blue emission at around 460 nm is observable for $\lambda_{\rm ex} \approx$ 410–430 nm. This implies that the threshold excitation wavelength ($\lambda_{\rm th}$) or energy ($E_{\rm th}$) for YL is $\lambda_{\rm th}$ <400 nm ($E_{\rm th}$ >3.1 eV). This result coincides with the former $\ensuremath{\mathsf{result}}^{[34]}$ in which YL in ZnO QDs could only be produced by the super- E_{σ} (above E_{σ}) process and were related to the electrons photo-excited above the $E_{th}>3.1$ eV through an optically detected electron paramagnetic resonance (ODEPR) study. These results indicate that YL and BL directly depend on the excitation wavelength and have different luminescence centers. The excitation energy (E_{ex}) of YL should be larger than 3.10 eV (λ_{ex} = 400 nm), which energy region corresponds to shallow donor levels like Zn interstitial (Zn_i) located within 0.3 eV below CB, while BL can only be observed at an excitation energy of less than $E_{\rm ex}$ <3.02 eV (410 nm) and which is referred to as the sub- $E_{\rm g}$ excitation energy.^{[35]} It is noteworthy that $E_{ex} \approx 410-430$ nm ($\approx 2.88-3.02$ eV) exceeds the energy for generating visible emission, but GL or YL is not detected in the PL spectra. The PLE spectra in Figure 4c for ZnO QDs reveal that the detection wavelengths (λ_{Det}) of 535 and 580 nm, which are close to the visible emission sub-peaks of 541 and 585 nm, are derived by excitation from an energy level of only 375 nm (3.30 eV), which corresponds to CB. However, the BL of λ_{Det} = 465 nm, which is close to 463 nm, is derived by the energy levels of both 375 and 430 nm (2.88 eV) and more dominantly by the latter lower energy level. Considering the excitation energy level of 430 nm, it is very natural that the BL of 463 nm (2.67 eV) is due to the electronic transition from the energy level of 2.88 eV (430 nm) to the energy level of 0.21 (= 2.88 - 2.67) eV above from the VB, which is well known as a deep acceptor of the Zn vacancy (V_{Zn}) .^[36–38] This shallow donor of 2.89 eV located below ~0.5 eV from CB was in particular assigned as extended Zn interstitial (ex-Zn_i),^[39] and the shallow acceptor located at around ≈ 0.3 eV from VB is also well known as a Zn vacancy (V_{Zn}).^[40,41] The shallow acceptor at 0.21 eV is very close to the V_{Zn}^{-} of 0.18 eV calculated by a theoretical calculation.^[38] As a consequence, the YL of 535 (2.31 eV) and 580 nm (2.13 eV) correlates to the electronic transition from CB (-3.45 eV) or $\text{Zn}_{i} \approx -3.65 \text{ eV}$ to deep levels at 0.99 (= 3.3 - 2.31) or 0.97 (= 3.1 - 2.13) eV, which in a previous study^[34] was known as the intrinsic defect of a doubly ionized Zn vacancy (V_{Zn}^{2-}) rather than an oxygen vacancy (V_O). The BL of 463 nm (2.67 eV) originates from the electronic transition from ex-Zn_i (2.89 eV) to V_{Zn}^{-} (0.21 eV). The SDPL for 1-PyNH₂ in Figure 4b shows one prominent BL peak centered at around 440 nm. For the BL of λ_{Det} = 440 nm in PLE (Figure 4e), two excitation energy levels, 308 (4.02 eV) and 426 nm (2.91 eV), are observed. Moreover, for the PLE, the UV-vis absorption spectrum of 1-PyNH₂ (Figure S3, Supporting Information) also shows two distinctive absorption edges crossed by the x-axis at around 312 (3.97 eV) and 425 nm (2.91 eV). These two absorption edges can be well interpreted in terms of DFT calculation of pyrene and 1-PyNH₂. Figure 5a presents the HOMO and LUMO energy diagram of a single pyrene and 1-PyNH₂ as calculated by DFT (Gaussian packet 09). The HOMO and LUMO (Table S34, Supporting Information) of pyrene with 4-aromatic rings consist of soly P_z orbital from the π -electron, and the energy gap is estimated at



Figure 5. a) Pyrene and 1-PyNH₂ molecular frontier orbitals and their energies calculated by DFT. b) Suggested electronic energy level diagram of 1-PyNH₂.

3.84 eV. When the amino group (-HN₂) combines with pyrene, S, P_x , and P_y orbitals other than the Pz orbital contribute to the populations of HOMO (HOMO+1) and LUMO (LUMO-1). The relative atomic compositions of 1-PyNH₂ are changed to C:N = 93.84%:6.16% for LUMO and C:N = 96.47%:3.53% for LUMO-1 and C:N = 87.36%:12.64% for HOMO and C:N = 91.64%:8.36% for HOMO+1 (Table S45, Supporting Information). Compared to pyrene, the energy levels of HOMO and LUMO in 1-PyNH₂ shift ≈ 0.23 and ≈ 0.52 eV toward the high energy side, respectively. DFT calculations qualitatively support the existence of non-bonding (π, π^*) states related to C=NH₂ in 1-PyNH₂ between the HOMO and LUMO of pyrene. The electronic states induced by O, N, and S doping in carbon dots have been induced in the order of, and related to, the π^{\star} and π orbitals of C=O, C=N, and C=S from LUMO and HOMO, respectively.^[42-44] Therefore, LUMO of 1-PyNH₂ may result from the π^* orbitals of C=NH₂ and the π^* orbital of C=C bonds. Similarly, HOMO consists of the non-bonding π orbitals of C=NH₂ and the π orbital of C=C. The absorption edge E = 3.97 eV of 1-PvNH₂ (Figure S3, Supporting Information) is qualitatively close to E = 3.55 eV between HOMO (-5.052 eV) and LUMO (-1.497 eV) calculated by DFT with the B3LYP exchange-correlation functional and yields a deviation of 0.42 eV. Moreover, the reference energy levels of π (C=C) (-6.38 eV), non-bonding (n state) C=N π (-5.32 eV), and π^* (C=C) (-2.41 eV) LUMO (-2.41 eV) are determined by using UPS as below. By analogy with DFT and UPS results, the absorption edges at both 3.97 and 2.91 eV can be assumed as the π (C=C) (-6.38 eV) – π^* (C=C) (-2.41 eV) transition and as non-bonding (n state) C=N π (-5.32 eV) – π^{*} (C=C) transition. Accordingly, two excitation energy levels of 308 nm (= 4.02 eV) and 426 nm (= 2.91 eV) in PLE of 1-PyNH₂ are consistent with 3.97 and 2.91 eV extracted from UV-vis absorption spectra. From the above, energy levels of 1-PyNH₂ can be depicted as in Figure 5b and the BL peak at 440 nm (= 2.82 eV) can be successfully ascribed to the electronic transition both from the π^* (C=C, π^*) to the nonbonding (C=N, π) state or from the non-bonding (C=N, π^*) state to the π (C=C) state. The SDPL for ZnO@1-PyNH₂ hybrid QDs in Figure 4c also shows one BL peak centered at around 430–435 nm with FWHM = 40 nm. From the fitting of PLE for ZnO@1-PyNH₂ hybrid QDs in Figure 4f, the PLE spectrum for $\lambda_{\text{Det}} = 430$ nm is fitted by four excitation energy levels of 283 (4.38 eV), 318 (3.89 eV), 365 (3.39 eV), and 404 nm (3.06 eV).

The variations of internal photoluminescence quantum yield (PLQY) (Figure S5, Supporting Information) are investigated at the different absorptance of ZnO QDs, 1-PyHN₂, and ZnO@1-PyNH₂ hybrid QDs in ethanol excited by $\lambda = 365$ nm (Table S56, the Supporting Information). The PLQY of ZnO@1-PyNH₂ hybrid QDs shows the values of approximately \approx 40–60% similar to those of 1-PyNH₂ at the absorptance lower than 60%, but increases up to more than 90% while that of 1-PyNH₂ hardly changes at the absorptance higher than 60%. On the other hand, as the absorptance decreases from 93.8% to 9.2% the PLQY of ZnO QDs increases gradually from 7.9% to 16.5% Therefore, it is so natural to infer this conclusion that the increment in PLQY of ZnO@1-PyNH₂ hybrid QDs will be intrinsically associated with the additional contribution of the inner ZnO QDs instead of the outer 1-PyNH₂ molecules.

2.4. Electronic Energy Levels

Figure 6a,b shows UPS spectra of ZnO QDs and 1-PyNH₂. Based on the UPS experiment, the work function (ϕ) of ZnO QD and 1-PyNH₂ are determined by the values of 3.49 and 4.28 eV, as shown in Figure 6c by extrapolating the cutoff curve of the kinetic energy of secondary electrons using the relation $\phi = h\nu - (E_{\text{cutoff}} - E_{\text{F}})$, where hv = 21.22 eV (corresponding to the He I UV resonance line). Moreover, VB is also acquired using the relationship VB = $21.22 - (E_{cutoff} - E_{onset})$, where E_{onset} is the energy onset in the VB region. The energy level of VB is estimated as 3.26 eV for ZnO QDs and 2.1 and 1.04 eV for 1-PyNH₂. Thus VB for ZnO QDs is assumed as -6.75 eV and HOMO for 1-PyNH₂ is also defined as having two energy levels at -6.38 and -5.32 eV from E_{vac} . From the UV–vis absorption spectrum (Figure S3, Supporting Information) and corresponding Tauc's plot (Figure 3), those energy levels can be regarded as both the π (C=C)-state and non-bonding (C=N, π)-state respectively. From the UPS, SDPL, and PLE spectra, an Anderson electronic energy diagram can be plotted as shown in Figure 6c. From





Figure 6. UPS spectra of a) ZnO QDs and b) ZnO@1-PyNH₂ hybrid QDs. c) Anderson electronic energy level diagram of ZnO@1-PyNH₂ hybrid QDs. d) Variations of normalized PL intensity of ZnO QDs and ZnO@1-PyNH₂ hybrid QDs.

Figure 4, the YL of ZnO QDs can be defined as the electronic transitions for shallow donors (Zn_i) located at around -3.65 to -3.72 eV to deep acceptor V_{Zn}²⁻ or deep donor of oxygen vacancy (V_0) at -5.85 eV and BL as that from shallow donor ex-Zn_i at -3.87 eV to deep acceptor V_{Zn}⁻ at -6.54 eV, which means that both YL and BL are coincident with the former result.^[34] The above energy level diagram suggests that GL (≈510 nm, 2.4 eV) is generated from the electronic transition from CB (-3.45 eV) to deep acceptor V_{Zn}^{2-} or V_o at -5.85 eV. Compared to the PLE of 1-PyNH₂ and ZnO QDs in Figure 4d,e, the resolved excitations of 283 (4.38 eV) and 365 nm (3.39 eV) in Figure 4f are considered to be related to those of ZnO QDs denoted as the dotted lines A and C, and those of 318 (3.89 eV) and 404 nm (3.06 eV) of 1-PvNH₂ denoted as the dotted lines B and D. Considering the electronic energy levels of ZnO@1-PyNH₂ hybrid QDs, the π (C=C)-state and π^* (C=C)-state of 1-PyNH₂ have higher energy than CB and VB of ZnO QDs and thus ZnO@1-PyNH₂ hybrid QDs can be classified as quasi-type-II core-shell QDs, whereas the previously reported ZnO@GO hybrid QDs^[27] is classified as type-I core-shell QDs. More specifically, the CB (-3.45 eV) of ZnO QDs is slightly higher than that (-3.47 eV) of the non-bonding (C=N, π^{*})-state, which is slightly higher than those (\approx -3.65–3.72 eV) of Zn_i and that (-3.87 eV) of ex-Zn_i of ZnO QDs. Therefore, the BL from ZnO@1-PyNH₂ hybrid QDs is clearly described by the following processes: photo-excited electrons above the π (C=C)-state of 1-PyNH₂ are either transferred to CB of ZnO QDs (I) or radiatively transited to the nonbonding (C=N, π)-state (-5.32 eV) (IV). Transferred electrons into CB of ZnO QDs will be successively transferred to the adjacent non-bonding (C=N, π^{\star})-state (-3.47 eV) through non-radiative transition (II), and finally to the π (C=C)-state (-6.38 eV) through radiative transition (III). Similar radiation (III) can be also generated by electronic relaxation from LUMO (C=C, π^*) (-2.41 eV) to the non-bonding (C=N, π^*) state (-3.47 eV) through non-radiative (NR) transition and then subsequently to the non-bonding (C=N, π)-state (-5.32 eV). Figure 6d shows the variations of the normalized PL intensity of ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ hybrid QDs with the change of λ_{ex} . As λ_{ex} increases, the YL of ZnO QDs has a significant intensity only in the wavelength of $\lambda_{ex} \approx 360-400$ nm and shows a sharp peak with the maximum intensity at λ_{ex} = 380 nm. The BL of ZnO QDs emerges at a longer $\lambda_{\rm ex}$ than 400 nm and its intensity increases as λ_{ex} increases from 410 to 430 nm. After having the maxima once at λ_{ex} = 310 nm, the BL intensity of 1-PyNH₂ decreases and maintains a minimum value in the range of $\lambda_{ex} \approx 340-410$ nm, and then abruptly increases at longer than λ_{ex} = 410 nm. The BL intensity of ZnO@1-PyNH₂ hybrid QDs has a broad peak and the maxima at λ_{ex} = 360 nm. Unlike



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Figure 7. TRPL a) at the emission wavelength of 560 nm for ZnO QDs excited at 365 nm, b) at the emission wavelength of 440 nm for 1-PyNH₂ excited at 400 nm, and c) at the emission wavelength of 430 nm for ZnO@1-PyNH₂ excited at 365 and 400 nm.

ZnO QD or 1-PyNH₂, it does not increase even after λ_{ex} = 410 nm. The variation of intensity obtained by subtracting the normalized YL intensity of ZnO QDs from the normalized BL of ZnO@1-PyNH₂ is denoted as a red dotted line and shows two maxima at λ_{ex} = 360 and 400 nm and one minima at 380 nm. That obtained by subtracting the normalized BL intensity of 1-PyNH₂ from the normalized BL of ZnO@1-PyNH₂ hybrid QDs is denoted as a pink dotted line and shows two minima at 310 and 420 nm. Two maxima at $\lambda_{ex} = 360$ and 400 nm indicate that the enhancement of the BL intensity results from the hybridization of ZnO QDs with 1-PyNH₂. Since λ_{ex} = 360 and 400 nm are similar to the subpeaks at 371 nm (C) and 404 nm (D) in PLE of Figure 4f, the increase in BL intensity centered at $\lambda_{ex} = 360$ nm is surely due to the charge transfer both from CB of ZnO QDs to non-bonding (C=N, π^*)-state of 1-PyNH₂, which has been frequently observed in inorganic/organic hvbrid materials.^[19,45] There is no observation of any GL, YL, and BL with 460 nm (2.89 eV) in ZnO@1-PyNH₂ also confirms the charge transfer of all excited electrons in CB of the inner ZnO QD core into the outer 1-PyNH₂ outer shell through the Zn-NH_(arom.)-C bond.

2.5. Time-Resolved Photoluminescence

Figure 7(a)–(c) presents the TRPL spectra for ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ hybrid QDs respectively. Monoor bi-exponential fit is applied to extract the amplitude and the decay time. In Table R1, the best-fitted values of the amplitude and the decay time are summarized.

As shown in **Table 1**, the yellow emission at 560 nm excited at the excitation wavelength $E_{xc} = 365$ nm can be fitted by biex-

Table 1. The best-fitted values of the amplitude and the decay time of TR-PL for ZnO QDs, 1-PyNH₂, and ZnO@1-PyNH₂ QDs are summarized.

	E _{xc}	Em	τ [ns]	А	$ au_{Av}$ [ns]	χ^2
ZnO QDs	365 nm	560 nm	$ au_1 = 81$ $ au_2 = 1860$	$A_1 = 0.86$ $A_2 = 0.14$	1480	2.36
1-PyNH ₂	400 nm	440 nm	$\tau = 4.48$			1.68
ZnO@ 1-PyNH₂	365 nm	430 nm	$\tau = 4.31$			1.68
	400 nm	430 nm	$\tau = 4.31$			1.46

ponential fit as $\tau_1 = 81$ ns, $A_1 = 0.86$, and $\tau_2 = 1860$ ns, $A_2 = 0.14$ respectively. In general, the two components are usually assigned to trap-mediated recombination (shorter lifetime τ_1) and radiative recombination (longer lifetime τ_2). Accordingly, as suggested in the text τ_1 corresponds to non-radiative transition time of photoexcited electrons from conduction band (CB) to Zn interstitial trap and τ_2 corresponds to radiative transition time of electrons from Zn_i to deep levels of V_{Zn}^{2+} or V_o , which value of 1.86 µs is about 20 times longer than τ_1 and well consistent with 0.845 µs for yellow emission at 590 nm in ZnO QDs synthesized by solution-precipitation at room temperature.^[27]

2.6. Device Performance of ZnO@1-PyNH₂ QLEDs

Figure 8a presents the schematic cross-sectional view of ITO/ PEDOT:PSS/TFB/ZnO@1-PyNH2/TPBi/LiF/Al QLED device, where TFB and TPBi are used as a hole transport lyer (HTL) and an electron transport layer (ETL) respectively. Figure 8b shows an energy-level diagram of blue emissive QLEDs. The 1-PyNH₂ molecules chemically bonded with ZnO QDs play the role of ligands, which allows them to be well dispersed, which in turn will increase the uniformity of the emissive layer (EML). A deep blue EL peak positioned around 441 nm (Figure 8c) with a FWHM of about 41.7 nm (Figure S6a, Supporting Information) is observed with 1931 CIE coordinates of (0.17, 0.09) (Figure S6b, Supporting Information). The EL device shows a turn-on voltage at around 4 V and displays a current density of 156 mA cm⁻² and a luminance value of 3379 cd m⁻² at 9.6 V (Figure 8d). The current efficiency (CE), power efficiency (PE), and external quantum efficiency (EQE) were 3.32 cd A⁻¹, 2.45 lm W⁻¹, and 2.35% at 5.1 V, respectively (Figure 8e). This performance is much better than that of an earlier ZnO/TiO₂ blue emitter, in which blue emission could only be attained with a large bias voltage of 15 V. Moreover the performance of this QLED device is superior to the former type-I blue emissive ZnO@GO QD-LEDs with CIE 1931 (0.16, 0.11), which had a turn-on voltage lower than 3.5 V, a maximum luminance value of 1980 cd m^{-2} at 8.5 V, a CE of 2.53 cd A^{-1} , and a PE of 2.15 lm W⁻¹ at 4 V. The operational stability of the EL dives is evaluated by measuring the operational lifetime at three different initial brightness (Figure S7, Supporting Information). T_{50} at the initial brightness of 530, 980, and 1340 cd m⁻² is measured to be 2287, 1358, and 697 h, respectively (Figure S6a-c,

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Figure 8. a) Schematic cross-sectional diagram of ZnO@1-PyNH₂-based QD-LEDs. b) Electronic energy diagram. c) EL of ZnO@1-PyNH₂ QD-LEDs (Inset: Photographic images of EL devices with/without bias at 9 V.) d) Current density and luminance versus voltage (I-V-L) curves. e) LE (cd A⁻¹) and EQE (%). f) Expected lifetime T_{50} at the initial brightness of 100 cd m⁻².

Supporting Information), which is equivalent to 17 830 h at 100 cd m⁻² (Figure 8f), according to the empirical acceleration factor of n = 1.2 (Figure S7d, Supporting Information) based on the empirical formula $L_0^n \times T_{50}$ = constant, where L_0 is the initial brightness and *n* is the acceleration factor. A smaller value of n = 1.2 than n = 1.9 for ZnTeSe blue QDs^[12] implies slow degradation of the QLEDs.

3. Conclusion

ZnO QDs prepared by solution precipitation were chemically hybridized with 1-aminopyrene, one of the simple molecules among functionalized polyaromatic hydrocarbons (f-PAHs) through the bonding of Zn-NH_{amino}-C. The electronic structure of ZnO QDs@1-PyNH2 hybrid QDs is classified as quasi-type-II QDs. The YL observed in ZnO QDs disappeared and only deep BL in ZnO@1-PyNH₂ hybrid QDS was observed irrespective of the excitation wavelength in the range of 300-430 nm. This phenomenon can be well described by the charge transfer of photo-excited electrons from CB of ZnO to the adjacent LUMO level of anti-bonding (C=N, π^*)-states of 1-PyNH₂. Compared to 1-PyNH₂, PLQY of ZnO@1-PyNH₂ increases by more than 30% at an absorptance higher than 60%. The reason for the improved PLQY of $ZnO@1-PyNH_2$ as well as long operation lifetime of ZnO@1-PyNH2 EL device can be attributed to the following factors. First, the attached 1-PyNH₂ molecules effectively reduced the surface defects of the ZnO QDs and then suppressed non-radiative recombinations caused by interface defects. Second, the higher CB of the ZnO QDs caused the

carriers, especially the electrons, to be injected into the outer 1-PyHN₂. QLEDs based on an emissive layer (EML) of ZnO@1-PyNH₂ hybrid QDs achieved a brightness of 3379 cd m⁻², a blue emission centered at 441 nm with CIE color coordinates of (0.17, 0.09) belonging to the deep blue color of CIEy (y<0.1), and the outstandingly long operation lifetime $T_{50} = 17$ 830 h to date. Hybridization of ZnO QDs with f-PAHs is a facile and an effective method to design various luminescent QDs due to the advantages of not only the abundance of f-PAHs, but also the ease of band gap prediction by theoretical calculation and band gap control by changing the number of benzene rings and various gap states induced by functional groups.

4. Experimental Section

Materials: All reagents were purchased from commercial sources. Zinc acetate (99.99%), tetramethylammonium hydroxide pentahydrate (TMAH, \geq 97%), dimethyl sulfoxide (DMSO, \geq 99.7%), ethanol (\geq 99.5%, anhydrous), chlorobenzene (99.8%, anhydrous), and 1-Aminopyrene; C₁₆H₁₁N, \geq 97%) were purchased from Sigma-Aldrich.

Synthesis of ZnO Quantum Dots: ZnO QDs were prepared by a lowcost solution precipitation process using Zn acetate $(Zn(CH_2COOH)_2)$ and tetramethylammonium hydroxide (TMAH). Here, 5 μ m TMAH in 10 mL of pure ethanol (solution A) as a reducing agent and 3 μ m Zn acetate in 30 mL of DMSO (solution B) as a precursor were dissolved completely at room temperature for 30 min. Solution B was titrated slowly dropwise into solution A at a speed of 0.66 mL min⁻¹ for 1 h to produce ZnO QDs at 70 °C. The ZnO QDs were washed with excess acetone and the resultant ZnO QDs were collected via centrifugation in the solution at 12 000 rpm for 10 min, after which they were ultrasonically redispersed in pure 15 mL ethanol for use.



Synthesis of ZnO@1-Aminopyrene Core-Shell Quantum Dots: The 1-Aminopyrene (500 mg) was uniformly dispersed in 40 mL of DMF. The resultant ZnO QDs (1.2 g), as mentioned above, were dissolved in 300 mL of DMF, after which the 1-Aminopyrene solution was added while continually stirring to form a stable precursor. Subsequently, the mixed solution was heated to 120 °C and maintained at that temperature for 5 h to form ZnO@1-Aminopyrene hybrid QDs. This was subjected to repeated washing with toluene and acetone, and finally with ethanol. The final ZnO@1-Aminopyrene hybrid QDs were obtained by centrifugation and after drying the product at 70 °C overnight.

Structural and Optical Characterization: Crystalline structures of the synthesized ZnO and ZnO@1-Aminopyrene QDs were characterized by X-ray diffraction (XRD) as well as high-resolution transmission electron microscopy (HR-TEM). The XRD patterns were recorded using an X-ray diffractometer (Rigaku ATX-G) with Cu $K\alpha$ radiation of wavelength $\lambda = 1.5406$ Å in the scan range $2\theta = 20^{\circ}$ to 80° . TEM samples were prepared by dispersing QDs dry powders in deionized water to form a homogeneous suspension. HRTEM and diffraction pattern analyses were carried out using an FEI Super-Titan (TM80-300) STEM/TEM operating at 300 keV. The size distribution of ZnO and ZnO@1-Aminopyrene QDs was analyzed using Gatan Microscopy Suite Software (DigitalMicrograph, Ver.2.11.1404.0). FT-IR spectroscopy was carried out using a Perkin Elmer Spotlight 400N FT-NIR Imaging System. UV-vis absorption data were recorded by a PerkinElmer Lambda 18 UV-vis spectrometer with QS grade quartz cuvettes. PL and PLE data were recorded by a Hitachi F-7000 fluorescence system with QS-grade quartz cuvettes (3 mm x 10 mm x 19 mm). PLQY was measured by using ILF-835 (JASCO) integrating sphere at the excitation wavelength of λ = 365 nm. Time-resolved photoluminescence (TRPL) spectra were carefully measured by excitation with second-harmonic generation at 380 and 400 nm of 150 fs pulses from a mode-locked Ti:sapphire laser (Chameleon Ultra II, Coherent). The repetition rate was decreased to 97 kHz by a pulse picker. The generated photons were collected with a picosecond TRPL measurement system using a timecorrelated single-photon counting (TCSPC) setup together with a streak camera (C11200, Hamamatsu Photonics). For all measurements, the sample temperature was kept at room temperature. TRPL decays have been classically fitted with a sum of exponential decays A_i and τ_i (A_i and τ_i are respectively the amplitude and lifetime of component) as shown in Equations (3) and (4).

$$I(t) = \sum_{i} A_{i} e^{\frac{-t}{\tau_{i}}}$$
(3)

$$\tau_{\rm av} = \frac{\sum_i A_i \cdot \tau_i^2}{\sum_i A_i \cdot \tau_i} \tag{4}$$

DFT Calculation: The eigenstate energy and orbital contribution for both Pyrene and 1-Aminopyrene molecules were calculated using Gaussian 09 package.^[28] A Becke-style three-parameter exchange and Lee-Yang-Parr correlation hybrid functional were adopted with a split basis set of 6–311G (d).^[46] The electronic iteration and root-mean-square force on atoms were set to 1.0×10^{-5} Hartree and 3.0×10^{-4} Hartree, respectively, for the convergence conditions. In addition, the total energy minimum was calculated to determine the fully relaxed molecular structures, which was checked by vibrational frequency analysis. The density of state was simulated through a convolution of the Gaussian curve to the calculated eigenstate energy.

ZnO@1-Aminopyrene QD-Based Blue Electroluminescence Device: The multilayer-structured EL device was fabricated layer by layer using a spin-casting method and a vacuum evaporation method. Before the device fabrication step, the patterned ITO substrates were cleaned by sonication sequentially in acetone, methanol, and isopropyl alcohol. The ITO substrates were then rinsed with D.I. water and treated with O_2 plasma. The final step involved a PEDOT:PSS polymer in an isopropyl alcohol (2.39 wt.%) solution, which was mixed for 15 min and spincoated onto the ITO/glass as a hole injection layer (HIL). This was ADVANCED OPTICAL MATERIALS www.advopticalmat.de

then dried at 110 °C on a hot plate for 30 min. In a nitrogen glovebox, a poly-TFB polymer in a chlorobenzene (1 wt.%) solution was mixed for 15 min and spin-coated onto PEDOT:PSS/ITO/glass as a hole transport layer (HTL) and then dried at 90 °C for 40 min on a hot plate. ZnO@1-Aminopyrene QDs in an ethanol solution (20 mg mL⁻¹) were spin-coated onto the TFB/PEDOT:PSS/ITO/glass as an emissive layer (EML) for the EL device. The TPBi small molecules (40 nm) were deposited onto ZnO@1-Aminopyrene/poly-TFB (40 nm)/PEDOT:PSS (30 nm)/ITO/glass as an electron transport layer (ETL) using a thermal evaporator. In addition, a LiF and Al (1 nm/100 nm) cathode was deposited using the same method. The I-V-L characteristics of the device were measured using a SpectraScan PR-670 spectroradiometer and a Keithley 2400 source-measure unit.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

blue quantum-dot LEDs, excitation-independent emission, long operation lifetime, photoluminescence quantum efficiency, ZnO@1-PyNH₂ hybrid quantum dots

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- IDTechEx Research, Quantum Dot Materials and Technologies 2020–2030: Trends, Markets, Players, https://www.idtechex.com/ portal.v2/pages/forecast.ko.asp?articleid=22950&portaltopicid=102 (accessed: May 2021).
- [2] P. Palomaki, "What's Next for Quantum Dots?", https://www.displaydaily.com/article/display-daily/what-s-next-for-quantum-dots (accessed: April 2018).
- [3] https://en.wikipedia.org/wiki/Quantum_dot_display (accessed: June 2022).
- [4] H. Shen, Q. Gao, Y. Zhang, Y. Lin, Q. Lin, Z. Li, L. Chen, Z. Zeng, X. Li, Y. Jia, S. Wang, Z. Du, L. S. Li, Z. Zhang, *Nat. Photonics* 2017, 13, 192.

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- [5] L. Wang, J. Lin, Y. Hu, X. Guo, Y. Lv, Z. Tang, J. Zhao, Y. Fan, N. Zhang, Y. Wang, X. Liu, ACS Appl. Mater. Interfaces 2017, 9, 38755.
- [6] Y. Yang, Y. Zheng, W. Cao, A. Titov, J. Hyvonen, J. R. Manders, J. Xue, P. H. Holloway, L. Qian, *Nat. Photonics* 2015, 9, 259.
- [7] C. Pu, X. Dai, Y. Shu, M. Zhu, Y. Deng, Y. Jin, X. Peng, Nat. Commun. 2020, 11, 937.
- [8] Y. Shirasaki, G. J. Supran, M. G. Bawendi, V. Bulović, Nat. Photonics 2013, 7, 13.
- [9] H. Zhang, X. Ma, Q. Lin, Z. Zeng, H. Wang, L. S. Li, H. Shen, Y. Jia, Z. Du, J. Phys. Chem. Lett. 2020, 11, 960.
- [10] E.-P. Jang, C.-Y. Han, S.-W. Lim, J.-H. Jo, D.-Y. Jo, S.-H. Lee, S.-Y. Yoon, H. Yang, ACS Appl. Mater. Interfaces 2019, 11, 46062.
- [11] C.-Y. Han, S.-H. Lee, S.-W. Song, S.-Y. Yoon, J.-H. Jo, D.-Y. Jo, H.-M. Kim, B.-J. Lee, H.-S. Kim, H. Yang, ACS Energy Lett. 2020, 5, 1568.
- [12] T. Kim, K.-H. Kim, S. Kim, S.-M. Choi, H. Jang, H.-K. Seo, H. Lee, D.-Y. Chung, E. Jang, *Nature* **2020**, *586*, 385.
- [13] W. H. Jung, J.-Y. Yoo, H. J. Kim, J.-G. Kim, B. D. Chin, J. S. Kim, Opt. Mater. Express 2020, 10, 3372.
- [14] H. Morkoc, Ü. Özgür, Zinc Oxide, Wiley-VCH Velag GmbH & Co. KGaA, Weinheim 2009.
- [15] E. Furno, F. Bertazzi, M. Goano, G. Ghione, E. Bellotti, Solid-State Electron. 2008, 52, 1796.
- [16] J.-S. Park, J. Kyhm, H. H. Kim, S. Jeong, J. H. Kang, S. Lee, K.-T. Lee, K. Park, N. Barange, J. Han, J. D. Song, W. K. Choi, I. K. Han, *Nano Lett.* **2016**, *16*, 6946.
- [17] V. Ischenko, S. Polarz, D. Grote, V. Stavarache, K. Fink, M. Driess, *Adv. Funct. Mater.* **2005**, *15*, 1945.
- [18] Y. Gong, T. Andelman, G. Neumark, S. O'Brien, I. Kuskovsky, Nanoscale Res. Lett. 2007, 2, 297.
- [19] R. Shimada, B. Urban, M. Sharma, A. Singh, V. Avrutin, H. Morkoç, A. Neogi, Opt. Mater. Express 2012, 2, 526.
- [20] D. I. Son, B. W. Kwon, D. H. Park, W.-S. Seo, Y. Yi, B. Angadi, C.-L. Lee, W. K. Choi, Nat. Nanotechnol. 2012, 7, 465.
- [21] C. V. Pham, S. Repp, R. Thomann, M. Krueger, S. Weberce, E. Erdem, Nanoscale 2016, 8, 9682.
- [22] D. I. Son, B. W. Kwon, J. D. Yang, D. H. Park, W. S. Seo, H. Lee, Y. Yi, C. L. Lee, W. K. Choi, *Nano Res.* 2012, *5*, 747.
- [23] D. I. Son, B. W. Kwon, J. D. Yang, D. H. Park, B. Angadi, W. K. Choi, J. Mater. Chem. 2012, 22, 816.
- [24] S. Vempati, A. Celebiogluab, T. Uyara, Nanoscale 2015, 7, 16110.
- [25] J. Ding, M. Wang, J. Deng, W. Gao, Z. Yang, C. Ran, X. Zhang, J. Alloys Comp. 2014, 582, 29.

[26] F. Han, S. Yang, W. Jing, K. Jiang, Z. Jiang, H. Liu, L. Li, Opt. Express 2014, 22, 11438.

/ANCED

- [27] H. H. Kim, Y. Lee, Y. J. Lee, J. Jeong, Y. Yi, C. Park, S.-Y. Yim, B. Angadi, K.-J. Ko, J.-W. Kang, W. K. Choi, ACS Photonics 2020, 7, 723.
- [28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, et al. *Gaussian 09*, Gaussian Inc., Wallingford CT, **2009**.
- [29] M. Boffito, F. Meglio, P. Mozetic, S. M. Giannitelli, I. Carmagnola, C. Castaldo, D. Nurzynska, A. M. Sacco, R. Miraglia, S. Montagnani, N. Vitale, M. Brancaccio, G. Tarone, F. Basoli, A. Rainer, M. Trombetta, G. Ciardelli, V. Chiono, *PLoS One* **2018**, *13*, e0199896.
- [30] S. Gupta, L. Qiao, S. Zhao, H. Xu, Y. Lin, S. V. Devaguptapu, X. Wang, M. T. Swihart, G. Wu, Adv. Energy Mater. 2016, 6, 1601198.
- [31] Y. Kayanuma, Solid State Commun. 1986, 59, 405.
- [32] L. Brus, J. Phys. Chem. 1986, 90, 2555.
- [33] D. P. Norton, Y. W. Heo, M. P. Ivill, K. Ip, S. J. Pearton, M. F. Chisholm, T. Steiner, *Mater. Today* 2004, *7*, 34.
- [34] H. H. Kim, H. Lee, J. K. Kang, W. K. Choi, Ann. Phys. 2022, 534, 2100382.
- [35] J. Chen, D. Zhao, C. Li, F. Xu, W. Lei, L. Sun, A. Nathan, X. W. Sun, Sci. Rep. 2015, 4, 4085.
- [36] P. S. Xu, Y. M. Sun, C. S. Shi, F. Q. Xu, H. B. Pan, Nucl. Instrum. Methods Phys. Res., Sect. B 2003, 199, 286.
- [37] C. H. Ahn, Y. Y. Kim, D. C. Kim, S. K. Mohanta, H. K. Cho, J. Appl. Phys. 2009, 105, 013502.
- [38] A. Janotti, C. G. Van de Walle, Appl. Phys. Lett. 2005, 87, 122102.
- [39] H. Zeng, G. Duan, Y. Li, S. Yang, X. Xu, W. Cai, Adv. Funct. Mater. 2010, 20, 561.
- [40] S.-H. Jeong, B.-S. Kim, B.-T. Lee, Appl. Phys. Lett. 2003, 82, 2625.
- [41] B. Lin, Z. Fu, Appl. Phys. Lett. 2001, 79, 943.
- [42] S. Do, W. Kwon, Y.-H. Kim, S. R. Kang, T. Lee, T.-W. Lee, S.-W. Rhee, Adv. Opt. Mater. 2016, 4, 276.
- [43] D. Qu, Z. Sun, M. Zheng, J. Li, Y. Zhang, G. Zhang, H. Zhao, X. Liu, Z. Xie, Adv. Opt. Mater. 2015, 3, 360.
- [44] S. Yang, J. Sun, X. Li, W. Zhou, Z. Wang, P. He, G. Ding, X. Xie, Z. Kang, M. Jianga, J. Mater. Chem. A 2014, 2, 8660.
- [45] B. Lin, Z. Fu, J. Phys. Chem. C 2012, 16, 3305.
- [46] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.