Enhanced UV Emission of GaN Nanowires Functionalized by Wider Band Gap Solution-Processed p-MnO Quantum Dots

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ABSTRACT: GaN-based UV light-emitting devices suffer from low efficiency. To mitigate this issue, we hybridized GaN nanowires (NWs) grown on Si substrates by plasma-assisted molecular beam epitaxy with solution-processed p-type MnO quantum dots (QDs) characterized by a wider band gap (~5 eV) than that of GaN. Further investigations reveal that the photoluminescence intensity of the GaN NWs increases up to ~3.9-fold (~290%) after functionalizing them with p-MnO QDs, while the internal quantum efficiency is improved by ~1.7-fold. Electron energy loss spectroscopy (EELS) incorporated into transmission electron microscopy reveals an increase in the density of states in QD-decorated NWs compared to the bare ones. The advanced optical and EELS analyses indicate that the energy transfer from the wider band gap p-MnO QDs to n-GaN NW can lead to substantial emission enhancement and greater radiative recombination contribution because of the good band alignment between MnO QDs and GaN NWs. This work provides valuable insights into an environmentally friendly strategy for improving UV device performance.

KEYWORDS: III-nitrides, semiconductor nanowires, light-emitting devices, p-type MnO quantum dots, electron energy loss spectroscopy

INTRODUCTION

Technologies based on GaN and related III-nitrides are widely used in several applications, such as light-emitting diodes (LEDs), laser diodes, photodetectors, and high-power and high-frequency devices, owing to the unique electrical and optical properties of these materials, such as direct band gap, wide spectral tunability, good conductivity, and durability in harsh environments. In particular, GaN-based UV LEDs have been extensively studied, with the view of utilizing them in curing, medical devices, and diverse industrial domains. However, the UV GaN-based LED performance is significantly lower than that of the devices emitting in the visible spectral range due primarily to low external efficiency (<10%) at the emission wavelengths below 365 nm. The low internal quantum efficiency (IQE) is one of the issues that undermine the external efficiency as a result of high threading dislocation (TD) density caused by the lattice mismatch between GaN and commonly utilized substrates, which introduces high density of nonradiative centers. Therefore, developing a UV LED structure that can yield the required efficiency remains highly challenging.

Recently, GaN nanowires (NWs) have emerged as promising candidates for enhancing the optical efficiency of UV LEDs and reducing the TD effects. Indeed, their large surface-to-volume ratio promotes an elastic strain relaxation mechanism, thus preventing the penetration of TDs to the NW regions. Moreover, NW structures, which are inherently diffusive, permit light extraction efficiency enhancement. However, the GaN NW surface states lead to nonradiative recombination, which can markedly reduce the NW optical efficiency. In this case, Fermi-level pinning effects (because of the presence of the surface defects, which form trapping centers), reduce LED efficiency because of the enhanced Shockley–Read–Hall nonradiative recombination rate. This issue can be partly mitigated by NW surface passivation using complex chemicals. However, this method relies on highly toxic solutions, such as diluted potassium hydroxide (KOH) solution, for the removal of unwanted surface defects from III-nitride NWs. Available evidence indicates that inhalation of vapor produced by such solutions can cause serious damage to the upper respiratory tract and the mucous membranes. When the KOH passivation methods were used, <100% improvement in the UV emission of GaN NWs was attained as this method reduces the trap states only, which can result in insufficient emission enhancement (less than two-
Thus, there is still a need for a method that is environmentally friendly and is capable of producing greater improvements in the GaN-based NW UV emission, while being cost-effective (that can be used for large-scale applications).\textsuperscript{5,13} Thus, as more effective alternatives are still needed, significant efforts were being dedicated to the improvement of GaN emission.\textsuperscript{13,14}

QD-functionalized Si NWs for solar cell applications have been used to enhance light absorption\textsuperscript{15}; however, such designs have not been used to enhance the emission emitted from III-nitride-based emitting devices. Recently, we explored new wide band gap (>4.5 eV) crystalline p-type manganese oxide quantum dots (p-MnO QDs) synthesized by a solution-processed femtosecond laser ablation in liquid (FLAL) technique.\textsuperscript{16,17} However, the effect of GaN NWs hybridized with these p-MnO QDs that are characterized by wider band gap (∼4.8 eV, located in the deep UV spectral region) has not yet been investigated.

These gaps in extant knowledge have prompted this investigation, as a part of which a novel strategy based on hybridizing p-type MnO QDs with GaN by a simple and cost-effective drop-casting method was adopted to improve the optical GaN efficiency through energy transfer (ET) from QDs to GaN. The obtained findings demonstrate that functionalizing GaN NWs by solution-processed p-MnO QDs are effective in enhancing the UV optical efficiency. This study included advanced optical characterizations and analyses, as well as electron energy loss spectroscopy (EELS) measurements, all of which indicated that the ET can occur from the QDs to GaN, resulting in significant UV emission enhancement. Hence, this work provides valuable insights into the UV-emitting device development. The novelty of our work stems from using wider band gap QDs to enhance the III-nitride UV and deep UV emission significantly. In addition, the optical properties of solution-processed p-MnO QD-functionalized III-nitrides have not been investigated.

As a part of our previous work focusing on the properties of solution-processed p-type MnO QDs and their synthesis,\textsuperscript{17} p-MnO QDs were synthesized by cost-effective FLAL at room temperature (RT) and under ambient conditions. The FLAL synthesis of p-MnO QDs was carried out using a Ti:sapphire Coherent Mira 900 laser (pulse width ~150 fs, 800 nm wavelength, operating at 76 MHz frequency) that was focused on a MnO target placed in ethanol solution.\textsuperscript{17}

The GaN NWs were grown along the c-axis by catalyst-free, plasma-assisted molecular beam epitaxy (MBE) in a MECA2000 MBE apparatus. The substrates were 2 in. wide Si(111) oriented wafers, which were deoxidized in hydrofluoric acid prior to their introduction into the MBE chamber. The NWs were grown under nitrogen-rich conditions with a radio frequency power of 300 W for the plasma cell and a N$_2$ flux of 0.6 sccm. The Ga/active N$_2$ flux ratio was typically equal to 0.3. A thin (∼3 nm) AlN buffer layer was deposited on Si prior to the GaN NW growth to prevent the in-plane tilt and twist of the wires and to homogenize the NW density across the entire Si wafer surface.

The NW material morphology was characterized by scanning electron microscopy (SEM, FEI Nova Nano 630). Moreover, high-resolution transmission electron microscopy (HR-TEM) and scanning TEM (STEM), as well as ultrahigh-resolution EELS measurements, were performed to study QD-decorated NW structures and to measure the band gap differences between bare and QD-decorated GaN NWs. STEM imaging or spectrum imaging measurements were performed at 80 kV using Titan Temis Z TEM system (Thermo Fisher, formerly known as FEI Co, USA) operating in the 40–300 kV range, which was equipped with a double Cs (spherical aberration) corrector, a high brightness electron gun (x-PEG), an electron beam monochromator, and a Gatan Quantum 966 imaging filter (GIF). The low-loss spectra were acquired in the so-called microprobe STEM mode with about 1 mrad semiconvergence angle (4 nm probe size). The electron beam monochromator operation was optimized by adopting the method first implemented by Govyadinov and colleagues\textsuperscript{18} and described in detail by Lopatin et al.\textsuperscript{19} A UV–vis Varian Cary 5000 spectrophotometer was employed to evaluate the GaN NW band gap through RT absorption measurements. Material optical properties before and after QD drop-casting on NWs were examined by conducting RT micro-photo-luminescence (μ-PL) measurements using a Horiba LabRAM Aramis Raman spectrometer attached to Kimmon Koga continuous-wave (CW) He–Cd laser (λ = 325 nm) and 40x objective. PL measurements before and after QD drop-casting on NWs were performed at 5 K and RT by a 325 nm CW He–Cd laser and a 244 nm (the double frequency of the 488 nm line) Ar$^+$ LEXEL laser, whereby PL signals were captured by an Andor monochromator connected to a charge-coupled device camera. In addition, to obtain RT PL excitation (PLE) spectra, a Edinburgh Instruments FLS980 spectrometer attached to a 1000 W Xe lamp (Newport) was used. Note that no PL measurements were acquired within the first 30 min after drop-casting the solution-processed MnO QDs on GaN NWs as our prior examinations indicated that this is sufficient for ensuring that ethanol is evaporated completely.

Figure 1. (a) Cross-sectional SEM image of GaN NWs (with the top view shown in the inset). (b) HR-TEM images of MnO QDs in a TEM grid. (c) STEM image of MnO QD-decorated GaN NWs (the image is obtained using a monochromated electron beam with a very small convergence angle to improve the EELS energy resolution).
MnOOH (12.0%) and Mn₂O₃ (6.5%) phases, resulting in the unique characteristics discussed in our previous work.¹⁷,²⁰ As a part of the same study, we demonstrated their p-type conductivity using field effect transistor and Kelvin probe measurements.¹⁷

To determine the band gap of the p-MnO QDs, absorption and PLE measurements were performed at RT. Figure 2b shows the corrected PL emission from the p-MnO QDs. The corrected PLE and absorption spectra of MnO QDs, as shown in Figure 2a, confirm that their band gap (∼5 eV) is wider than that of GaN (3.5 eV), which is in line with our previously reported findings.¹⁷ A slight tail shown in the 4.65–4.3 eV (265–285 nm) range can be related to surface states in QDs, as discussed in our recent reports.¹⁶,¹⁷ It should be noted that both the absorption and the PLE spectra have been corrected by subtracting the ethanol signal (the PL and PLE spectra of ethanol are provided in Figure S1 in the Supporting Information).

To study the effect of MnO QD functionalization on GaN emission, we investigated the PL and µ-PL emission produced by GaN before and after functionalizing NWs with QDs. Figure 2c shows the GaN near band edge emission (NBE) at 363.5 nm (3.41 eV) before and after MnO QD drop-casting at RT, whereby the samples were excited by 244 nm (corresponding to the energy above the MnO band gap), with the µ-PL emission obtained by exciting the samples by 325 nm presented in the inset. Notably, no MnO emission from QD-decorated NWs was observed even when the samples were excited by λ = 244 nm. The PL (and µ-PL) spectra shown in Figure 2c (and its inset) demonstrate that up to 2.8-fold integrated intensity enhancement at RT is achieved in the QD-decorated GaN NW emission compared to that produced by bare GaN NWs (before QD drop-casting), whereas no peak shift is observed. It is worth noting that the presence of a very weak yellow band indicates superior quality of the GaN NWs.

To confirm this emission enhancement, we repeated RT µ-PL measurements on QD-decorated NWs by recording the PL spectrum at different time intervals within the first 3 h after the drop-casting process. The findings reported in Figure S2 in the Supporting Information demonstrate that there is no significant change in the emission intensity of QD-decorated NWs over time, confirming the consistency of our results.

Figure 2d shows typical PL spectra produced by bare and QD-decorated NWs at low temperature (5 K) and at RT. At 5 K, there are two dominant peaks; the most intense peak (peak 1) is located at ∼3.47 eV (357 nm), which was attributed to the common GaN NBE, including free and bound exciton-related emissions.²¹,²² This peak is observed at both 5 K and RT (360 nm). The second peak (peak 2), located at ∼3.42 eV (362 nm) at 5 K, is also a common GaN peak at low temperature and is dissociated at RT, likely due to excitons bound to stacking faults.²¹,²² As can be seen from Figure 2d, the PL emission of QD-decorated NWs is considerably enhanced at both RT and 5 K, which is in line with the RT µ-PL measurements.

The higher-resolution PL spectra provided in the inset of Figure 2d confirm that the PL integrated intensities of peak 1 and peak 2 increase by ∼3.66-fold and ∼3.9-fold at 5 K, respectively, after MnO QD drop-casting compared to bare GaN NWs. We attribute the greater enhancement at 5 K (compared to that at RT) to the fact that the electron–hole recombination process is dominated by radiative recombination at low temperatures. These findings show that PL measurements indicate that, after QD functionalization, the
NW emission increases by 1 order of magnitude compared to bare NWs, which is superior to the enhancement (< 2-fold) reported for NWs surface passivated by KOH solution.5

To rule out any laser or ethanol influence on the PL enhancement, we conducted detailed investigations of their effect on bare GaN NWs as a function of time. As shown in Figure S3a, the PL intensity of bare GaN (recorded at several time intervals) remained unchanged after prolonged laser exposure. Similarly, Figure S3b confirms that no significant change is observed in the GaN emission intensity after drop-casting ethanol only on bare NWs. Thus, these results confirm that QDs are solely responsible for enhancing the GaN emission.

The emission enhancement of QD-decorated NWs was optimized based on the QD density as we observed that the GaN emission intensity decreased after several drop-casting cycles. μ-PL measurements (shown in Figure 3a) reveal that the optimized density yields ~2.8-fold NBE intensity enhancement at RT compared to that of bare NWs, which declines to ~2-fold after several cycles, and remains at this level thereafter.

To further elucidate the QD effect on GaN efficiency, we estimated the IQE for both bare and QD-decorated NWs. In this case, the IQE represents the ratio of the integrated PL intensity of GaN NWs at 5 K to that at RT. We considered that maximum efficiency (100%) is attained at 5 K by assuming that the nonradiative centers are frozen at low temperature (according to the Rashba treatment).25−27 We estimated the IQE for NBE emission (peak 1) as peak 2 was absent from the PL spectra obtained at RT, as shown in Figure 2d. The IQE value increases from ~28% for bare GaN NWs to ~46% when GaN NWs are hybridized with QDs, which confirms that radiative recombination contribution increases after QD functionalization. These results demonstrate that a considerable improvement in the GaN optical efficiency is achieved by functionalizing NWs with QDs.

To investigate the mechanisms underlying the observed emission enhancement, we performed PLE and ultrahigh-resolution EELS measurements on both the bare GaN NWs and the QD-decorated NW samples. Figure 4a shows the PLE spectra in close proximity to the NBE of GaN NWs (at 370 nm) before and after QD drop-casting. It is evident that the GaN PLE spectrum is enhanced in the deep UV range (250−340 nm) after functionalizing the GaN NWs with QDs, while the GaN band gap remains at 354 nm. The greatest PLE signal enhancement (~2-fold) occurs at > 250 nm (4.95 eV, which is close to the QD band gap). This value is similar to the
enhancement ratio of the RT PL integrated peak intensity after functionalizing NWs with QDs.

Ultrahigh-resolution EELS measurements at a very low loss energy (200 meV) were also conducted, and the results are shown in Figure 4b. For this purpose, the spatial variation of the band gap was mapped with the energy resolution of about 45−50 meV, defined as the full width at half maximum of the zero energy loss peak (ZLP).\textsuperscript{21,22} Moreover, the background subtraction was performed by fitting the ZLP measured in a vacuum. Ultrahigh-resolution EELS analysis demonstrates that QDs absorb some energy, as indicated by “glowing” QDs in the EELS map in Figure 4c. The EELS signal in the energy range above the band gap produced by bare GaN differs from that obtained for QD-decorated GaN NWs. Specifically, the signals shown in Figure 4b indicate that, for both bare NWs and QD-decorated NWs, the onset of the conduction band transition (band gap width) starts at about the same energy level (~3.4 eV), corresponding to the NW band gap,\textsuperscript{18} which is in line with the PLE results. However, at 4.95 eV (corresponding to λ = 250 nm, which is close to the QD band gap), the signal grows faster for QD-decorated NWs compared to the bare ones. The EELS findings indicate a significant increase in the density of states of the QD-decorated GaN NWs because of QD functionalization, compared to bare GaN NWs,\textsuperscript{21,22} thus confirming the PL and PLE results. It is worth noting that, as expected, no plasmonic effect has been observed by EELS as the QDs are wide band gap semiconductor material.

The energy band diagram of the QD-decorated GaN sample is shown in Figure S4 in the Supporting Information, confirming a good band gap overlap between GaN and p-MnO QDs. Moreover, based on the PLE and EELS findings, the PL enhancement of QD-decorated NWs can be attributed to the ET from MnO QDs to GaN because of the band gap difference. In this case, for QD-decorated NWs, after exciting QDs and generating electron−hole (e−h) pairs, the energy resulting from the e−h recombination process is transferred to the GaN NW band to excite more electrons from the valence band to the conduction band, thus increasing the e−h pair density (i.e., the ET process occurred from a higher to a lower band gap energy, as shown in Figure 4d). In this case, the GaN carriers are excited directly by laser as well as via the ET process, resulting in enhancement of the radiative recombination processes\textsuperscript{29} compared to bare GaN NWs. The band alignment (shown in Figure S4) facilitates such an ET mechanism. Specially, there is energy resonance between the QD band edge tail (shown below the MnO band edge) and the GaN band edge, as indicated by the PLE and absorption measurements of MnO QDs. The nonradiative ET phenomenon has been observed, but such ET direction was reverse (i.e., from III-nitride material to smaller band gap QDs)\textsuperscript{28−30} facilitating development of visible LED. However, ET from wider band gap QDs to GaN has never been reported.

To elucidate our ET transfer hypothesis, we carried out time-resolved PL (TRPL) measurements before and after functionalizing NWs by QDs. We analyzed the carrier lifetime (τ\textsubscript{PL}) for peak 2 of GaN NWs at 5 K as this peak emerges at low temperature, suggesting that the radiative-recombination process is dominant in this spectral range. In addition, as noted earlier, it was assumed that most nonradiative recombination centers are frozen at low temperature.\textsuperscript{25,26,28,29,31} As shown in Figure S5 in the Supporting Information, τ\textsubscript{PL} of peak 2 decreases from 2.03 ns (for bare GaN NWs) to 1.39 ns (for QD-decorated GaN), resulting in a ~0.68 τ\textsubscript{PL} ratio, from which it can be inferred that the radiative recombination rate increases after QD functionalization, confirming the PL findings and our ET hypothesis\textsuperscript{29,32}.

To further confirm our ET hypothesis, we functionalized ZnO nanotubes (NTs) grown on Si (~3.7 eV band gap) by MnO QDs using the same drop-casting process (the growth process and the properties of these NTs are reported elsewhere\textsuperscript{18} using pulsed laser deposition)\textsuperscript{33,34} As shown in Figure S6, the emission intensity increases by >4-fold, providing evidence in the support of our assertion that depositing wider band gap QDs on the surface of smaller band gap semiconductor nanostructures can lead to semiconductor emission enhancement.

As this is a novel study, additional investigations are needed to elucidate the underlying mechanisms. Nonetheless, this finding has important implications for future efforts aimed at utilizing wide band gap QD materials to obtain high-efficiency devices operating in the deep UV range. We expect that, in QD-decorated NW-based LED structures, the turn-on voltage is reduced due to greater carrier density, which can result in higher EL intensity compared to that from bare NW-based LEDs. In addition, antireflective coating may be needed to further improve the light-extracting efficiency that can leads to high efficiency UV LEDs.\textsuperscript{15,35}

CONCLUSIONS

In this work, we reported on the first study as a part of which the UV emission of NWs was enhanced significantly by functionalizing them by p-MnO QDs characterized by a wider band gap to transfer the energy from the QDs to GaN. Our findings show that when highly crystalline p-MnO QDs are drop-casted on GaN NWs, the NBE emission of GaN is significantly enhanced (~290%), that is, it is ~3.9-fold greater than that produced by bare GaN NWs. A considerable IQE increase obtained after decorating GaN with QDs further demonstrates that the radiative recombination rate increases after decorating NWs with QDs. EELS and PLE measurements showed enhancement in the deep UV range after functionalizing the GaN NWs, while also revealing that above 4.9 eV (equivalent to the QD band gap), the signal grows faster for QD-decorated NWs, indicating an increase in the density of states after functionalizing GaN with QDs. These analyses show that the ET occurs from MnO to GaN NWs, which is the most likely reason behind the GaN emission enhancement. As this process has never been used or studied for enhancing III-nitride emission, we have succeeded in demonstrating that functionalizing QDs (with 5 eV band gap) with III-nitrides (including GaN, InGaN, or AlGaN NWs) can have the potential to enhance the LED efficiency. Thus, this novel environmentally friendly (with zero waste) strategy would be highly beneficial for state-of-the-art technology development aimed at enhancing the performance of LEDs, as well as to be used in wide band gap semiconductor applications, such as transistors, photovoltaic cells, and photodetectors.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c07029. PL and PLE spectra of ethanol; PL emissions of QD-decorated NWs and bare NWs as a function of time to
investigate laser effect and ethanol effect; TRPL measurements; and enhancement of PL emission from MnO QD-decorated ZnO NTs (PDF)

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**Author Contributions**
D.A. and I.S.R. have equal first author contribution. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

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