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# Environmentally Benign, Beyond-InP Quantum Dots for Self-Emissive Display Devices

**Heesun Yang***, **Sun-Hyoung Lee, Dae-Yeon Jo, Suk-Young Yoon, Sun-Kyo Kim, Hyun-Min Kim, Yuri Kim, Seong Min Park**

hyang@hongik.ac.kr
Department of Materials Science and Engineering, Hongik University, Seoul, 04066 Korea
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**ABSTRACT**

*Last decade witnessed great advance in photoluminescent (PL) quality of visible III−V InP quantum dots (QDs) toward bright, sharp emissivity. Nowadays, InP QDs hold an unrivaled position in the field of next-generation display devices. In this work, for an effort to develop non-Cd blue and green QDs as potential alternatives to InP counterparts, viable synthesis of ternary ZnSeTe, InGaP and quaternary Ag-In-Ga-S QDs integrated with elaborate heterostructures for high PL performances is explored and fabrication of their high-efficiency electroluminescence devices is further demonstrated.*

## 1 Introduction

III−V type indium phosphide (InP) quantum dots (QDs) are now firmly positioned as heavy metal-free, environmentally benign visible emitters in next-generation display devices. On the basis of synthetic advances of InP QDs toward bright and sharp emissivity, they have been successfully exploited in the platform of light-emitting diode (LED) based on color conversion or self-emissive electroluminescence (EL). State-of-the-art InP QDs double-shelled with ZnSe/ZnS in a two-step manner exhibited exceptional photoluminescence (PL) figures-of-merit such as 90−100% in PL quantum yield (QY) and 35−36 nm in full-width-at-half-maximum (fwhm) for both green and red colors [1-3].

In contrast to such substantial progress of InP QD-based green and red emitters, synthesis of blue InP QDs with a bright, deep-blue emissivity is not likely viable, which is primarily associated with their intrinsic size limitation [4,5], thus necessitating the development of alternative QDs with non-InP compositions. Meanwhile, although green InP QDs can exhibit comparable PL features in PL QY and fwhm to red InP counterparts, performances of green QD-based devices are inferior in both color conversion and EL to those of red QD-based ones (highly associated with the smaller size of green InP core relative to red one), thus demanding alternative non-InP green emitters. In this contribution, we introduce non-Cd, non-InP QD compositions such as ZnSeTe, InGaP, and Ag-In-Ga-S (AIGS), their viable QD synthesis toward bright-, sharp-emissivity, and their application to EL devices.

## 2 Experiment

ZnSeTe QDs as blue and green emitters were synthesized mainly relying on our earlier publications [4,6]. Blue and green ZnSeTe QDs consisted of their own core/shell heterostructures of ZnSe/ZnS and ZnSe/ZnSeS/ZnS as multi-shells, respectively. In the case of blue-emissive InGaP QDs were prepared via a cation exchange route by reacting pre-grown InP QDs with $GaI_3$ in a given condition, followed by ZnSeS/ZnS double shellings [5]. Green-emissive ternary AIGS QDs were prepared by reacting $AgS_x$ stock solution with cationic ($In^{3+}$, $Ga^{3+}$) oleylamine solution at 200°C for a few hours, followed by shelling with $GaS_x$.

QD-light-emitting diodes (QLEDs) with a multilayered architecture were fabricated through sequential spin-depositions of all functional layers, consisting of ITO/ poly(ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/poly(9-vinylcarbazole) (PVK) hole transport layer (HTL)/QD emitting layer (EML)/ZnMgO nanoparticles electron transport layer (ETL)/Al.

## 3 Results and Discussion

Non-Cd II−VI composition of ZnSe has emerged for synthesis of blue QD emitters. However, PL of most of ZnSe QDs is beyond the desired deep-blue range, typically covering from near UV to violet as a consequence of quantum confinement effects on its relatively high bulk band gap (2.7 eV). One plausible way to obtain the blue emissivity from ZnSe-based QDs is to optimally alloy them with a lower band gap ZnTe. For this, we varied Te/Se ratio of blue-emissive ZnSeTe cores in 0.023−0.047 to tune PL in blue color regime with an identical shelling scheme of ZnSe/ZnS double shells. Increase in Te/Se ratio of ZnSeTe/ZnSe/ZnS core/shell/shell QDs led to systematic red-shifts in PL from 451 to 463 nm (Fig. 1a), while producing exceptional PL QY levels of 89−93%. Based on the device platform of multilayered architecture (Fig. 1b), those blue QDs were individually tested as QD EML. Luminance became markedly brighter with an increasing Te/Se ratio of ZnSeTe QD, showing peak values of 6538, 7841, and 12654 cd/m$^2$ for Te/Se ratios of 0.023, 0.035, and 0.047, respectively (Fig. 1c). Accordingly, the current efficiencies were higher across the entire current density region for the device with a higher Te/Se ratio-based QD, also displaying increasing peak values from 7.2 cd/A for Te/Se=0.023 up to 14.8 cd/A for Te/Se=0.047. Meanwhile, their overall EQEs were not much different, producing similarly exceptional peak EQEs of 13.4−13.7% (Fig. 1d).

Te/Se ratio in ZnSeTe core was further varied to extend the emission tunability beyond the blue region. A set of ZnSeTe cores with Te/Se molar ratios in the range of 0.14−0.38 were synthesized, and then the identical

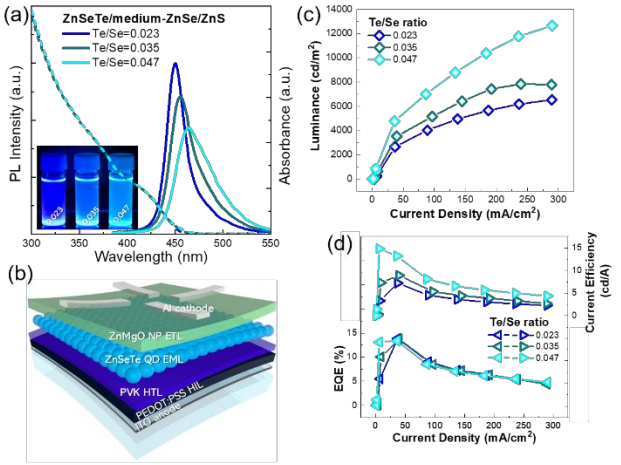


**Fig.1 (a) Absorption/PL spectra of blue ZnSeTe/ZnSe/ZnS QDs with different core Te/Se ratios. (b) Device structure of blue QLED and (c) luminance-current density and (d) current efficiency/EQE-current density of blue devices integrated with QDs as a function of Te/Se ratio.**

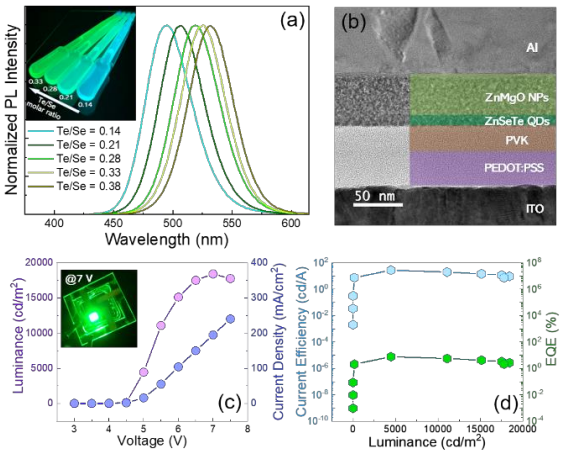


**Fig.2 (a) Normalized PL spectra of green ZnSeTe/ZnSe/ZnSeS/ZnS QDs with different core Te/Se ratios. (b) Cross-sectional TEM image, (c) luminance/current density-voltage and (d) current efficiency/EQE-luminance relations of green QLED.**

multiple shells of ZnSe/ZnSeS/ZnS were applied. As intended, spectral red-shifts of PL (Fig. 2a) were well proportional to the Te/Se ratio. Specifically, PL spanned from 495 nm for Te/Se = 0.14 to 532 nm for Te/Se = 0.38 at the peak wavelength, while an identical fwhm of 45 nm as obtained regardless of Te/Se ratio. PL QY tended to marginally decrease from 83% for Te/Se = 0.14 to 80% for Te/Se = 0.28, followed by appreciable reductions to 74 and 68% for Te/Se ratios of 0.33 and 0.38, respectively. Given PL QY and the green territory-relevant wavelength, Te/Se = 0.28-based, 520 nm-emitting ZnSeTe/ZnSe/ZnSeS/ ZnS QDs were integrated as the representative green emitters for the following first demonstration of solution-processed multilayered green QLED (Fig. 2b). The maximum luminance of 18420 cd/m$^2$ was achieved at a driving voltage of 7 V (Fig. 2c). Device efficiencies were also impressively high, showing maximum values of 27.6 cd/A in current efficiency and 7.6% in EQE obtainable at a high luminance level of 4456 cd/m$^2$ (Fig. 3d).

Then, the first synthesis of blue-emissive ternary InGaP QDs through a unique $In^{3+}$-to-$Ga^{3+}$ cation exchange strategy was implemented (Fig. 3a). As the amount of $GaI_3$ added for cation exchange increased, we observed systematic shifts of absorption spectra to the blue as a consequence of effectively increasing Ga incorporation (Fig. 3b). Upon ZnSeS/ZnS double shelling, the resulting InGaP/ZnSeS/ZnS QDs produced consistent blue-shifts in PL from 475 to 465 nm (Fig. 3c), while maintaining high PL QYs in the range of 80−82%. Among a series of QD samples above, 465 nm-emitting InGaP/ZnSeS/ZnS QDs were further employed as an emitting layer of all-solution-processed QLED. This unprecedented InGaP QD-based blue device yielded maximum values of 1038 cd/m$^2$ in luminance and 2.5% in external quantum efficiency (Fig. 3d,e).

Lastly, I-III-VI type AIGS QDs as another alternatives to InP ones were synthesized. In that quaternary composition, their band gap and resulting PL wavelength were widely tunable by adjusting In/Ga ratio, as seen from Fig. 4a, while we focus on green-emissive AIGS QDs with a given In/Ga ratio. After growth of AIGS core, higher-band gap $GaS_x$ shell was deposited, resulting in a size increment from 6.3 to 7.3 nm (Fig. 4b). Fig. 4c presents PL spectra of AIGS core versus AIGS/$GaS_x$ core/shell QDs, where PL markedly increased from 20 to 75% in PL QY.

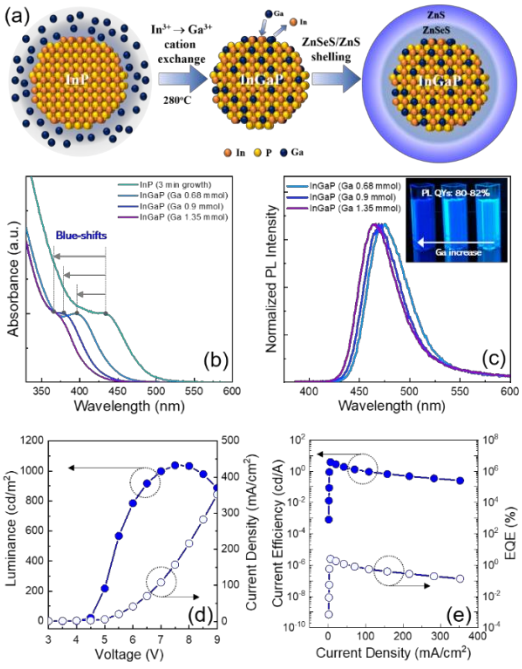


**Fig.3 (a) Schematic of In-to-Ga cation exchange-based InGaP core and subsequent ZnSeS/ZnS double shelling. (b) Absorption spectra of InP and a series of cation-exchanged InGaP and (c) normalized PL spectra of a series of InGaP/ZnSeS/ZnS QDs. (d) Luminance/current density-voltage and (d) current efficiency/EQE-current density relations of blue InGaP QLED.**

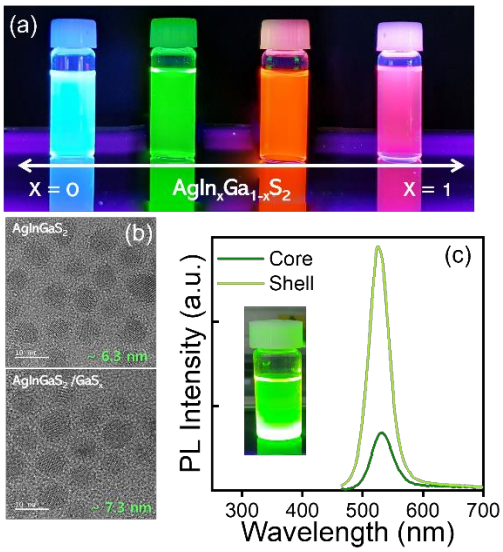


**Fig.4 (a) Photo of a series of AIGS/GaS$_x$ QDs with varying In/Ga ratio. (b) TEM images of AIGS core versus AIGS/GaS$_x$ core/shell QDs. (c) PL spectral comparison of AIGS and AIGS/GaS$_x$ QDs.**

The fwhm of AIGS/GaS$_x$ QDs was as narrow as 38 nm, which is comparable to that of state-of-the-art green InP QDs. Further synthetic tuning toward sharper and brighter PL is under way, followed by the fabrication of high-performance EL device.

## 4 Summary

In this contribution, we introduced environmentally benign, beyond-InP QDs primarily as efficient blue and green emitters. First, relying on ZnSeTe composition, high-PL QY blue and green emissions were realized simply by adjusting Se/Te ratio. Based on such high-quality ZnSeTe QDs, high-efficiency blue and green EL devices were further demonstrated, showing maximum EQEs of ca. 13 and 7%, respectively. Then, ternary InGaP QDs derived from effective cation exchange were addressed as potential efficient blue emitters. Lastly, highly fluorescent, color-pure I-III-VI AIGS QDs with 75% in PL QY and 38 nm in fwhm was further presented as strong candidates that will compete with InP green emitters.

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