Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Composition-Tailored ZnMgO Nanoparticles for Electron Transport Layers of Highly Efficient and Bright InP-based Quantum Dot Light Emitting Diodes

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EXPERIMENTAL

Chemicals

Zinc acetate dihydrate (reagent grade), magnesium acetate tetrahydrate (ACS reagent, 98%), tetramethylammonium hydroxide pentahydrate (TMAH, 97%), copper thiocyanate (CuSCN, 99 %), chlorobenzene (anhydrous, 99.8%), poly-n-vinylcarbazole (PVK, average Mw ~1,100,000, powder) were purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO, HPLC grade, 99.9%), octane (98+%) and ethanol (alcohol reagent, anhydrous, denatured, ACS, 94-96%) were purchased from Thermo Fisher Scientific Chemicals. Isopropy alcohol (IPA, HPLC, 99.5%), Methanol (EP, 99.5%) and Acetone (EP, 99.5%) was purchased from Daejung. Poly(ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS, AI4083) was purchased from Clevious. Poly(N,N'-bis-4-butylphenyl-N,N'-bisphenyl)benzidine (poly-TPD) was purchased from SolarisChem. InP-based QDs with diameter between 5.45 nm to 7.74 nm were dispersed in octane as shown in Figure S4. Energy levels of InP-based QDs were provided by supplier.

Synthesis of ZnMgO ETL NPs

ZnMgO ETL NPs were synthesized at ambient condition using a solution based hydrolysis reaction.[1] For ZnO, 30mL of 0.1 M Zn acetate solution in DMSO were stirred for 1 h at ambient condition. 10 mL of 0.5 M TMAH solution in ethanol were added dropwise into the Zn acetate solution at 0.5 mL/min and the mixture was vigorously stirred for 1 h. The mixture was then washed with acetone and centrifuged at 10,000 rpm for 10 min. The resulting white precipitation was dispersed in ethanol at a concentration of 30 mg/mL. For ZnMgO, Mg acetate was added to

the Zn acetate solution at 10.0, 12.5, or 15.0 mol% of the total metal precursor, then the same procedure was followed as for the ZnO.

Fabrication of electron only devices

ITO substrates were cleaned successively with acetone, IPA, methanol for 15 min and stored in a natural convection oven at 100 °C for 10 min. After drying, an Al layer (50 nm) was evaporated onto the ITO substrate at 1.4 x 10^{-5} hPa. The synthesized ETL NPs in ethanol at a concentration of 65 mg/mL were spin coated (3000 rpm, 30 sec, 100 nm) and annealed at 180 °C for 20 min. Then, an Al layer (150 nm) was evaporated at the 1.4 x 10^{-5} hPa condition.

Fabrication of InP-based QLEDs

ITO substrates were successively by acetone, IPA, methanol for 15 minutes consecutively and stored at natural convection oven of 100 °C for 10 min. After drying, the ITO substrates were treated by UV/ozone for 15 min. A layer of PEDOT:PSS was spin coated (3000 rpm, 30 s, 40 nm) onto the ITO glass under ambient conditions and annealed at 150 °C for 15 min. The ITO substrates were transferred to a N_2-filled glovebox. For the HTL, the poly-TPD and PVK mixture in chlorobenzene at a concentration of 10 mg/mL was spin coated (3000 rpm, 30 s, 50 nm) on the PEDOT:PSS layer and annealed at 170 °C for 30 min. A QD solution in octane with an absorbance of 1.8 at 500 nm was spin coated (3000 rpm, 30 s, 12 nm) on the HTL and annealed at 95 °C for 5 min. ETL NPs in ethanol at a concentration of 30 mg/mL was spin coated (3000 rpm, 60 s, 50 nm) on the QD layer without annealing. An Al cathode (150 nm) was evaporated at 1.4 x 10^{-5} hPa.

Fabrication of a hole only device with InP-based QDs

A hole only device (HOD) with QDs was fabricated based on the structure of ITO/PEDOT:PSS/poly-TPD:PVK/QD/Copper thiocyanate (CuSCN)/Al. Fabrication methods from ITO to QD layers are identical to the fabrication of QLEDs. CuSCN was selected as electron blocking layer due to high conduction band (1.8 eV).[2] CuSCN in diethyl sulfide at a concentration of 20 mg/mL was spin coated (2000 rpm, 60 s, 45 nm) on the QD layer without annealing. An Al cathode (150 nm) was evaporated at 1.4 x 10^{-5} hPa.

Fabrication of electron only devices with InP-based QDs

EODs with QDs were fabricated based on the structure of ITO/ZnO/QD/ETL/Al. Cleaning of ITO substrates is identical to the fabrication of QLEDs. ZnO NPs in ethanol at a concentration of 30 mg/mL was spin coated (3000 rpm, 60 s, 50 nm) on the QD layer without annealing. A QD solution in octane with an absorbance of 1.8 at 500 nm was spin coated (3000 rpm, 30 s, 12 nm) on the HTL and annealed at 95 °C for 5 min. ETL NPs in ethanol at a concentration of 30 mg/mL was spin coated (3000 rpm, 60 s, 50 nm) on the QD layer without annealing. An Al cathode (150 nm) was evaporated at 1.4 x 10^{-5} hPa.

Characterization

The chemical composition and binding information of ETL NPs were analyzed by X-ray photoelectron spectroscopy (ESCALAB250Xi, Thermo-Scientific) (XPS). The shape of the ETL NPs and QDs was analyzed by transmittance electron microscopy (TEM, JEM-2100F, Cold Field Emission Type, JEOL). The absorbance of ETL NPs and QDs was measured by UV-vis-spectrometer (JASCO V-650 spectrophotometer, Easton). Crystallinity of the ETL NPs was measured by X-ray diffraction spectroscopy (D8 Advance, Bruker Corporation). The valence bands of the ETL NPs were measured by ultraviolet photoelectron spectroscopy (k-alpha,

Thermo Scientific). The emission wavelength and absolute quantum yield of QDs were measured by spectro-photometer with an integration hemi-sphere (QE-2100, PHOTAL Otsuka Electronics Company, Ltd., Osaka). The current density–voltage–luminance of QLEDs was characterized using a spectroradiometer with a source measure unit (CS-2000, Konica Minolta, Inc.).

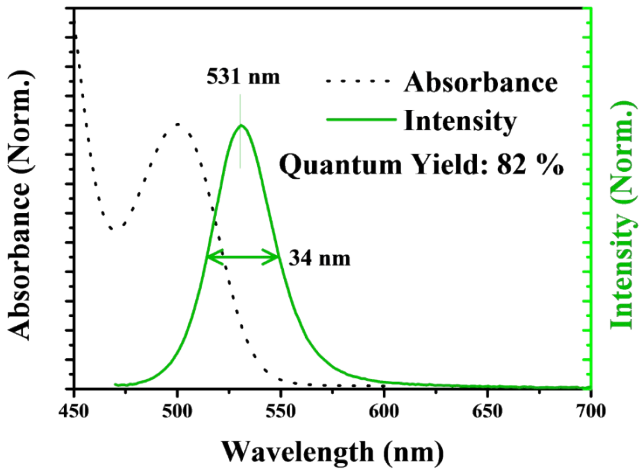

Figure S1. Absorption and emission spectra of InP-based QDs. Inset values are emission wavelength, FWHM, and quantum yield. Quantum yield of InP-based QDs in solution phase is measured by spectro-photometer with integration hemi-sphere.

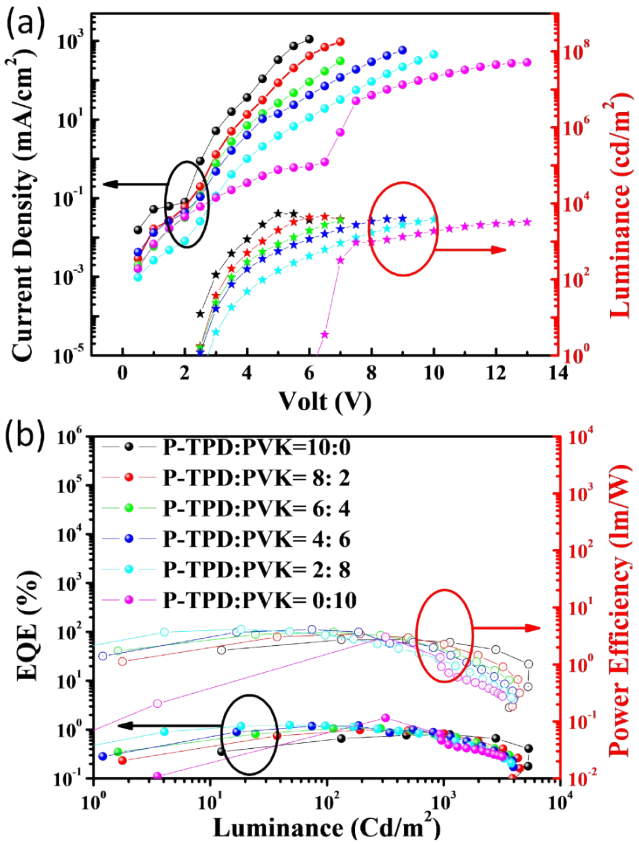

Figure S2. (a) J-V-L characteristics of QLEDs with ZnO ETL according to different P-TPD:PVK ratio and (b) EQE and power efficiency of QLEDs as a function of luminance.

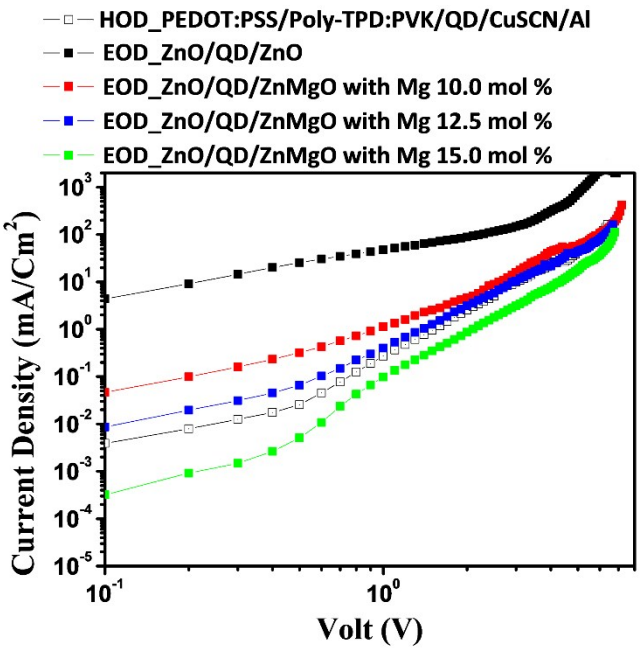

Figure S3. Current density-voltage curves of a HOD and EODs. ZnMgO with Mg 12.5 mol% demonstrated current density of the EOD that is closest to that of the HOD. ZnMgO with Mg 15.0 mol% demonstrated lowest current density.

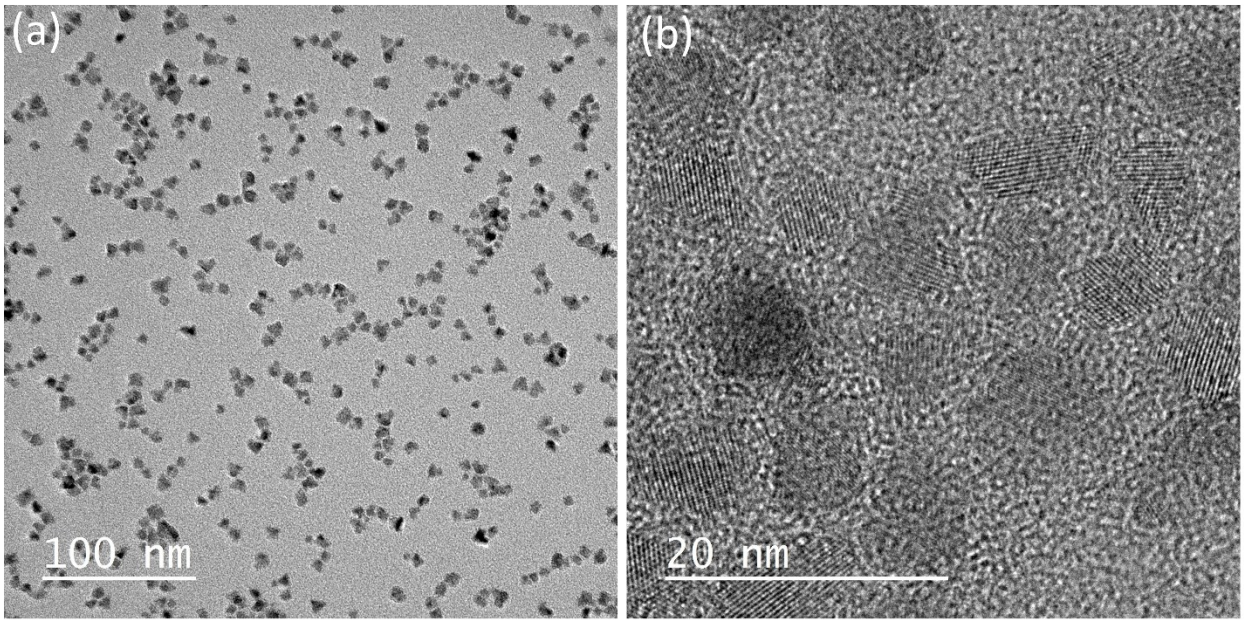

Figure S4. TEM images of InP-based non-Cd QDs with magnification of (a) x50000 and (b) x300000.

Table S1. Key characteristics of QLEDs with ZnO ETL according to different P-TPD:PVK ratio.

P-TPD:PVK ratio	Maximum Luminance [cd/m^2]	Voltage for Maximum Luminance [V]	Power Efficiency [lm/W]	EQE [%]
10 : 0	5352	5.0	2.73	0.77
8 : 2	4494	6.5	3.43	0.97
6 : 4	3657	7.0	3.69	1.04
4 : 6	3976	9.0	4.11	1.20
2 : 8	3803	10.0	4.13	1.22
0 : 10	3193	13.0	3.01	1.72

References

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2. A. Perumal, H. Faber, N. Yaacobi-Gross, P. Pattanasattayavong, C. Burgess, S. Jha, M. A. McLachlan, P. N. Stavrinou, T. D. Anthopoulos and D. D. C. Bradley, *Adv. Mater.*, 2015, **27**, 93.