High-efficiency quantum dot light-emitting diodes based on Li-doped TiO_2 nanoparticles as an alternative electron transport layer

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Synthesis of pristine and Li-doped TiO_2 nanoparticles

In a typical reaction of colloidal TiO_2 nanoparticles (NPs), 3 ml (10 mmol) of titanium iso-propoxide, 5 ml of oleylamine and 0.5 mmol of lithium hydroxide monohydrate (only for Li-doping) were dissolved in 15 ml isopropyl alcohol (IPA) solvent. The solution was stirred a few minutes and then mixed with 100 ml of IPA and distilled water solution. After stirred for 1 h at 100 ^{o}C, the TiO_2 NPs were collected via centrifugation of the solution at 13000 rpm. Finally, the collected TiO_2 NPs were redispersed in ethanol solvent and filtered to remove of impurity.

Synthesis of green, red, and blue quantum dots (QDs)

For a typical synthesis of green CdZnSeS/ZnS QDs, 0.14 mmol of Cd oxide and 3.41 mmol of Zn oxide were placed with 7 mL of oleic acid (OA) in a three-neck flask and heated to 150°C with N_2 flowing. Then, 15 mL of 1-octadecene (ODE) was added and heated to 310°C. Subsequently, a Se+S stock solution (2.2 mmol of Se and 2.2 mmol of S dissolved in 2.2 mL of trioctylphosphine (TOP)) was swiftly injected to the mixture, and the reaction of composition-gradient CdZnSeS core was carried out at 310°C for 10 min. 1.6 mmol of S dissolved in 2.4 mL of ODE was introduced into the reactor and the reaction was maintained for 12 min. For a successive ZnS shelling, 2.86 mmol of Zn acetate dihydrate dissolved in 1 mL of OA and 4 mL of ODE was rapidly put to the above reactor and the reaction was held at 270 °C for 10 min. Then, 9.65 mmol of S dissolved in 5 mL was dropwisely added, followed by the ZnS reaction at that temperature for 20 min. For a synthesis of red CdZnSe/ZnS QDs, 0.6 mmol of Cd oxide and 1.2 mmol of Zn acetate were mixed with 3 mL of OA and 15 mL of ODE in a three-neck flask. The temperature of the mixture was elevated to 300°C with N_2 pursing. At that temperature, CdZnSe cores were synthesized by injecting a Se stock solution containing 1.2 mmol of Se in 0.1 mL of TOP, followed by the core growth for 2 min 30 s. Then, for consecutively forming ZnS shell on the CdZnSe cores, 0.18 mL of 1-dodecanethiol was slowly added and the reaction was held for 20 min. A S stock solution including 1 mmol of S dissolved in 0.83 mL of TOP was additionally injected to the mixture and the reaction was maintained for 10 min, followed by an addition of 0.12 mL of 1-octanethiol. For a typical synthesis of blue CdZnS/ZnS QDs, 1 mmol of Cd oxide and 10 mmol of Zn oxide with 7 mL of OA was prepared in a reactor and heated to 150 °C with N_2 flowing. 15 mL of ODE was introduced to the reactor and heated to 310 °C. The nucleation and growth of CdZnS cores were held by injecting a S-ODE solution including 1.6 mmol of S dissolved in 2.4 mL of ODE at

that temperature and maintaining the reaction for 12 min. A successive ZnS shelling was carried out by dropwisely adding a S-OA solution prepared by dissolving 8 mmol of S in 5 mL of OA to the above mixture. The shelling reaction was maintained at 310 ^{o}C for 8 h. The resulting green CdZnSeS/ZnS, red CdZnSe/ZnS, and blue CdZnS/ZnS QDs were repeatedly purified by centrifugation with a solvent/nonsolvent combination. Then, the purified QDs were redispersed in hexane for characterizations and formation of the emitting layer (EML).

Fabrication of quantum dot light-emitting diodes (QLEDs)

The inverted QLEDs were fabricated on indium-tin-oxide (ITO) coated glass substrates. The substrates were sequentially cleaned with isopropyl alcohol and then rinsed with deionized water. After the patterned ITO substrates were treated in ultraviolet-ozone for 15 minutes. Pristine or Li-doped TiO_2 NPs were deposited on ITO substrates by spin-casting at a spin-rate of 1000 rpm for 60 seconds. For the fabrication of EML, QDs dispersion was spin-cast on top of ITO/pristine or Li-doped TiO_2 NPs substrates at a spin-rate of 2000 rpm for 25 seconds. The organic materials and metals were deposited in continuance by thermal evaporation without breaking vacuum. 4,4'-bis (carbazol-9-yl) biphenyl (CBP) for hole transport layer, MoO_3, and Al were thermally evaporated with a deposition rate of ~ 1 Å /s for CBP, ~ 0.5 Å /s for MoO_3, and, ~ 3 Å /s for Al electrode.

Characterization

The current density-voltage-luminance (J-V-L) characteristics of the devices were measured by using a spectroradiometer (CS2000, Konica Minolta) with Keithley 2400 source meter under ambient conditions. From these J-V-L measurements, the changes in the

luminance and current efficiency of the devices as a function of the applied voltage were studied systematically. The average diameter of TiO_2 NPs was measured by the dynamic light scattering method (Zetasizer Nano ZS, Malvin). The high-resolution transmission electron microscopy was used to measure the particle size of TiO_2 NPs (JEM-2100F, JEOL). The crystal phase of pristine and Li-doped TiO_2 NPs was analyzed using X-ray diffractometer (MiniFlex2, Rigaku). X-ray photoelectron spectroscopy (XPS) (Thermo VG) with Al Kα x-ray (E=1486.6 eV) was used to analyze the actual chemical composition of Li-doped TiO_2 NPs. The surface roughness was measured by atomic force microscopy (XE-100, PSIA). The electronic structures of pristine and Li-doped TiO_2 NPs were investigated by ultraviolet photoelectron spectroscopy (ESCALAB 250, Thermo Scientific). The lifetime result of the QLEDs was obtained using a multi-channel lifetime test system with an embedded photodiode. (M6000 Plus, McScience).

Table S1 Performance of QLEDs with various TiO_2 NPs.

ETL	Max. luminance (cd/m^2)	Max. current efficiency (cd/A)	Max. EQE (%)
TiO_2	149,479 (@9.5 V)	32.07 (@8 V)	7.93 (@8 V)
Li-doped TiO_2 (3%)	159,840 (@9.5 V)	36.45 (@8 V)	9.12 (@8 V)
Li-doped TiO_2 (5%)	169,790 (@9.5 V)	40.97 (@8 V)	10.27 (@8 V)
Li-doped TiO_2 (7%)	143,703 (@9.5 V)	31.79 (@8 V)	7.98 (@8 V)
Li-doped TiO_2 (10%)	157,103 (@10.5 V)	34.97 (@8 V)	8.86 (@8 V)

Table S2 Energy levels of ETL with different Li doping concentrations.

ETL	Valence band onset (eV)	VBM (eV)	Bandgap (eV)	CBM (eV)
TiO_2	4.01	7.95	4.08	3.87
Li-doped TiO_2 (5%)	4.08	7.70	4.17	3.53
Li-doped TiO_2 (10%)	4.13	7.47	4.25	3.22

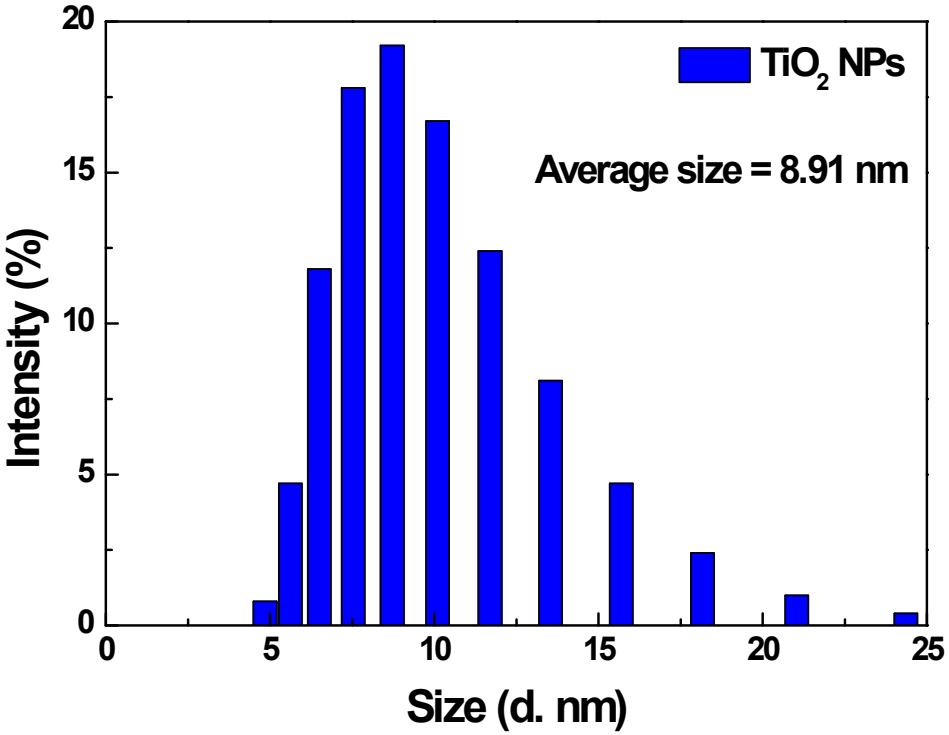
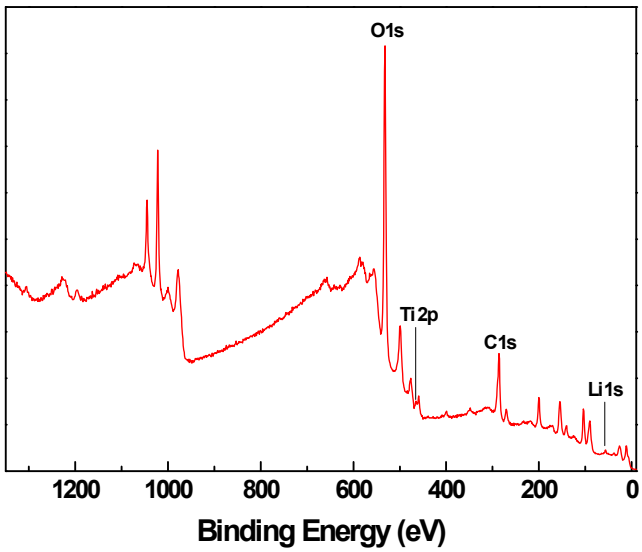


Fig. S1 Particle size distribution of TiO_2 nanoparticles by dynamic light scattering method.

(a)



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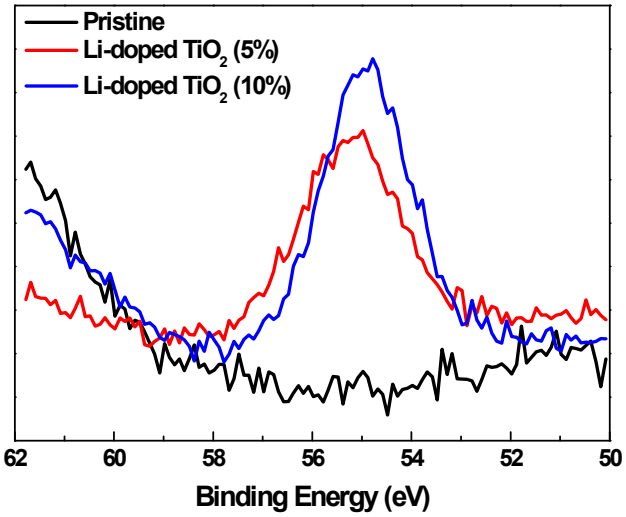


(c)

	TiO_2	5% Li-doped TiO_2	10% Li-doped TiO_2
Ti	15.26	17.13	17.26
O	42.45	41.95	43.15
Li	-	4.51	7.48
C	42.29	36.41	32.11

Fig. S2 (a) Survey scan, (b) Li 1s spectra and (c) chemical composition of Li-doped TiO_2 NPs.

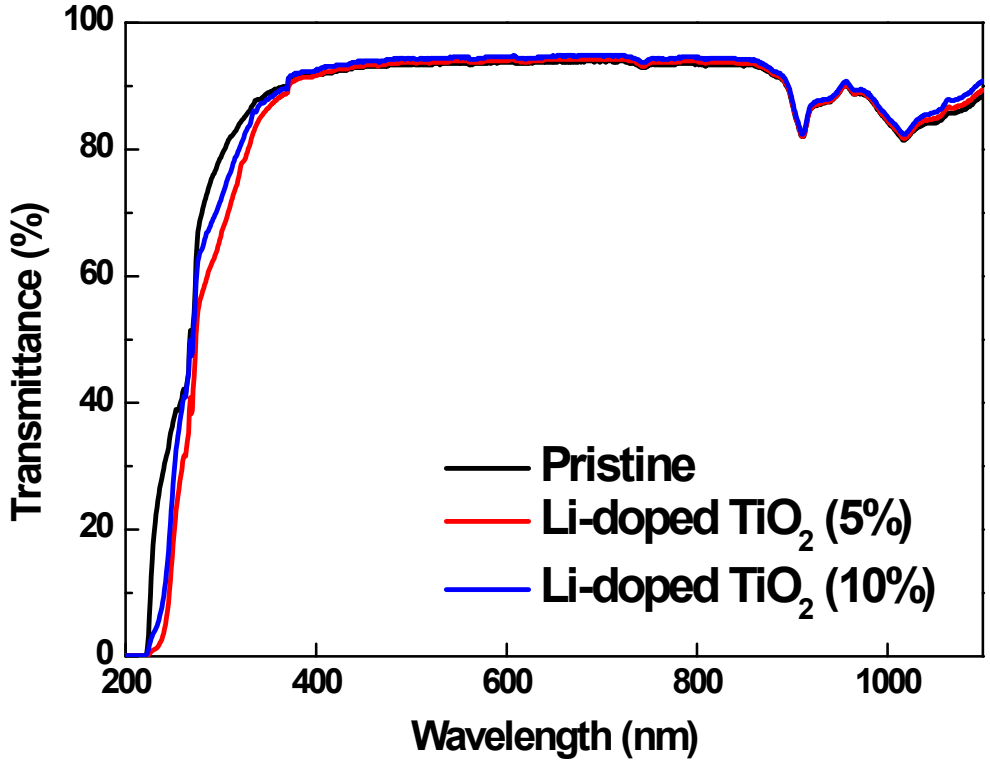


Fig. S3 Optical transmittance from pristine, 5% and 10% Li-doped TiO_2 NPs.

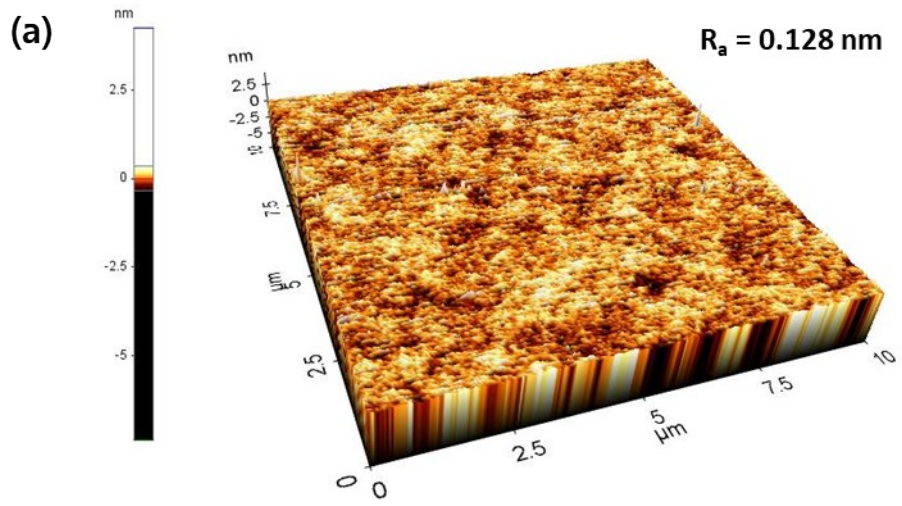
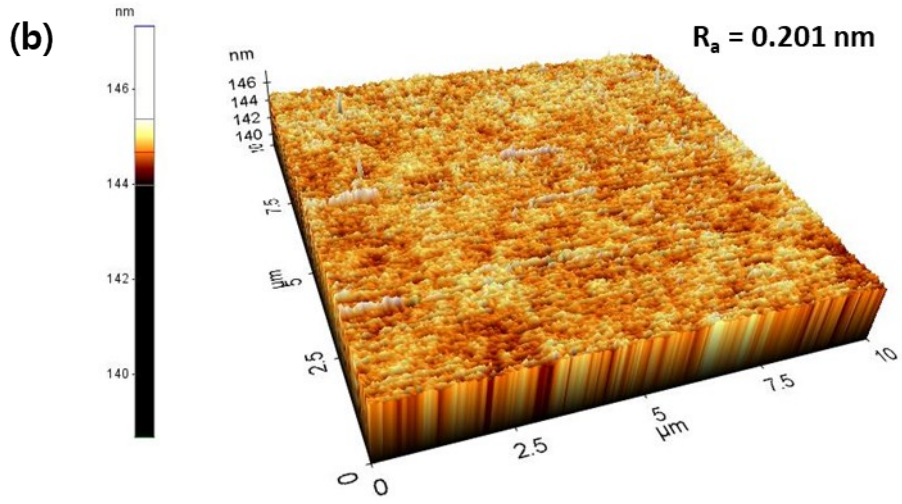


Fig. S4 AFM images of (a) pristine and (b) 5% Li-doped TiO_2 NPs on ITO glass.



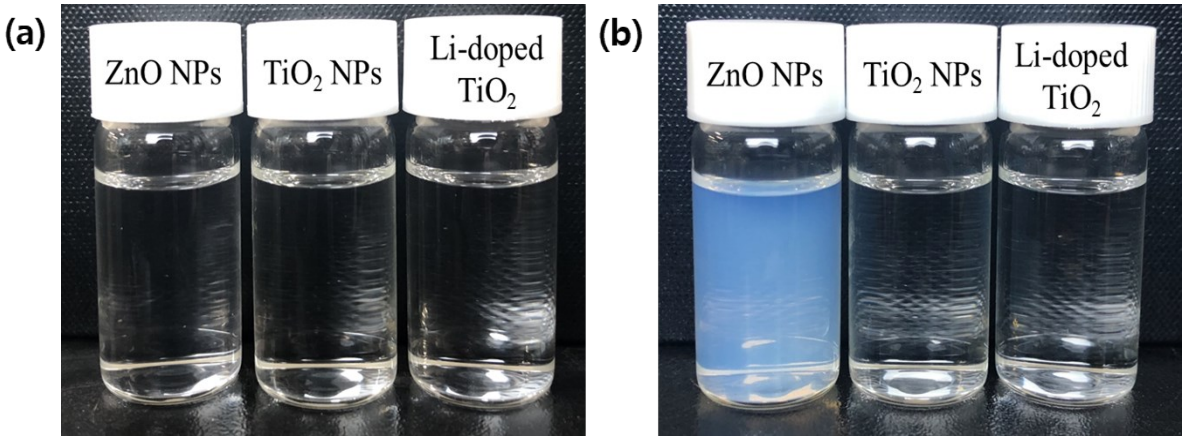


Fig. S5 Observation of the aggregate formation from ZnO, TiO_2 and 5% Li-doped TiO_2 NPs in ethanol at room temperature: (a) As-redispered and (b) after 2 days.

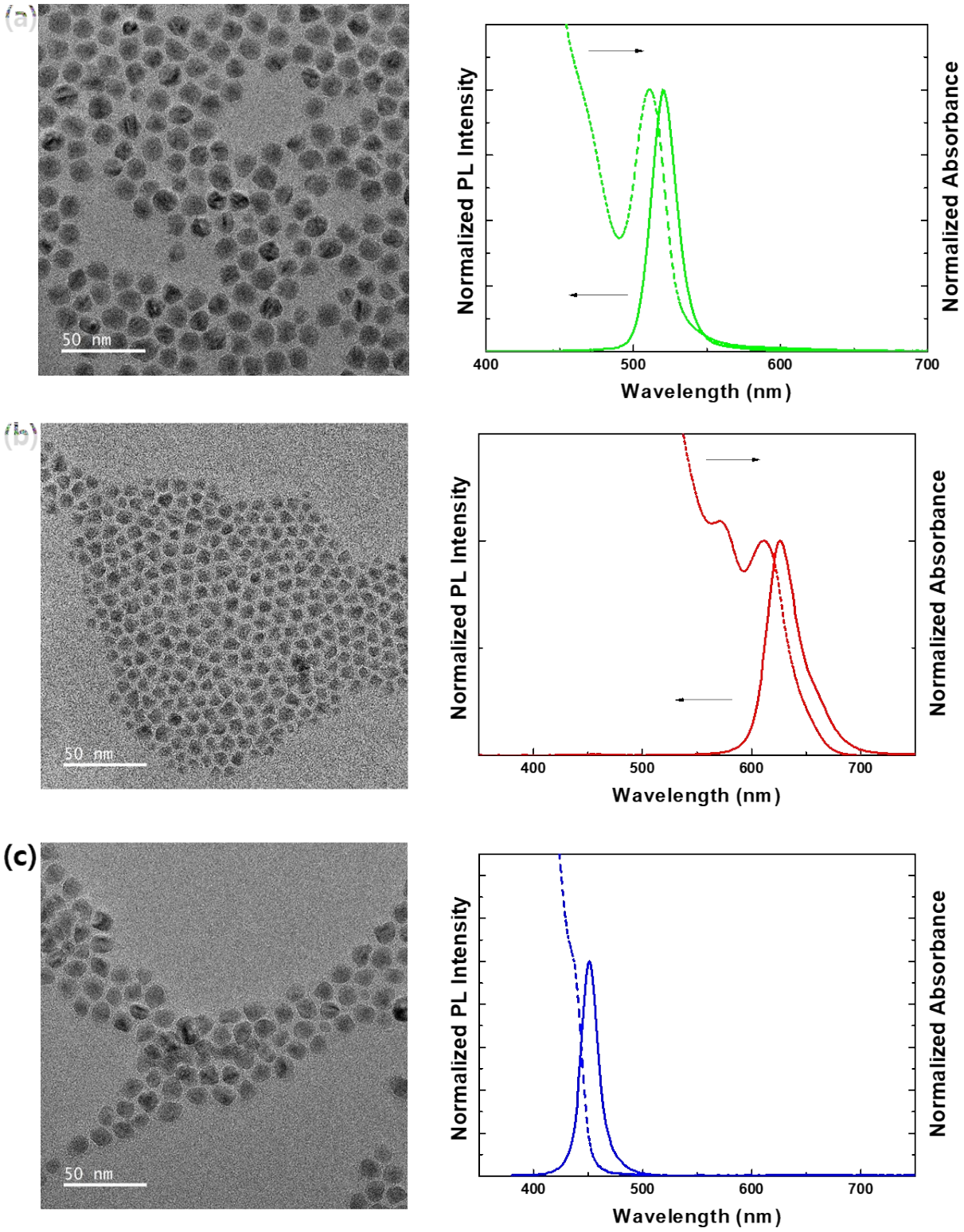


Fig. S6 TEM images and absorption/PL spectra of (a) green, (b) red, and (c) blue QDs.

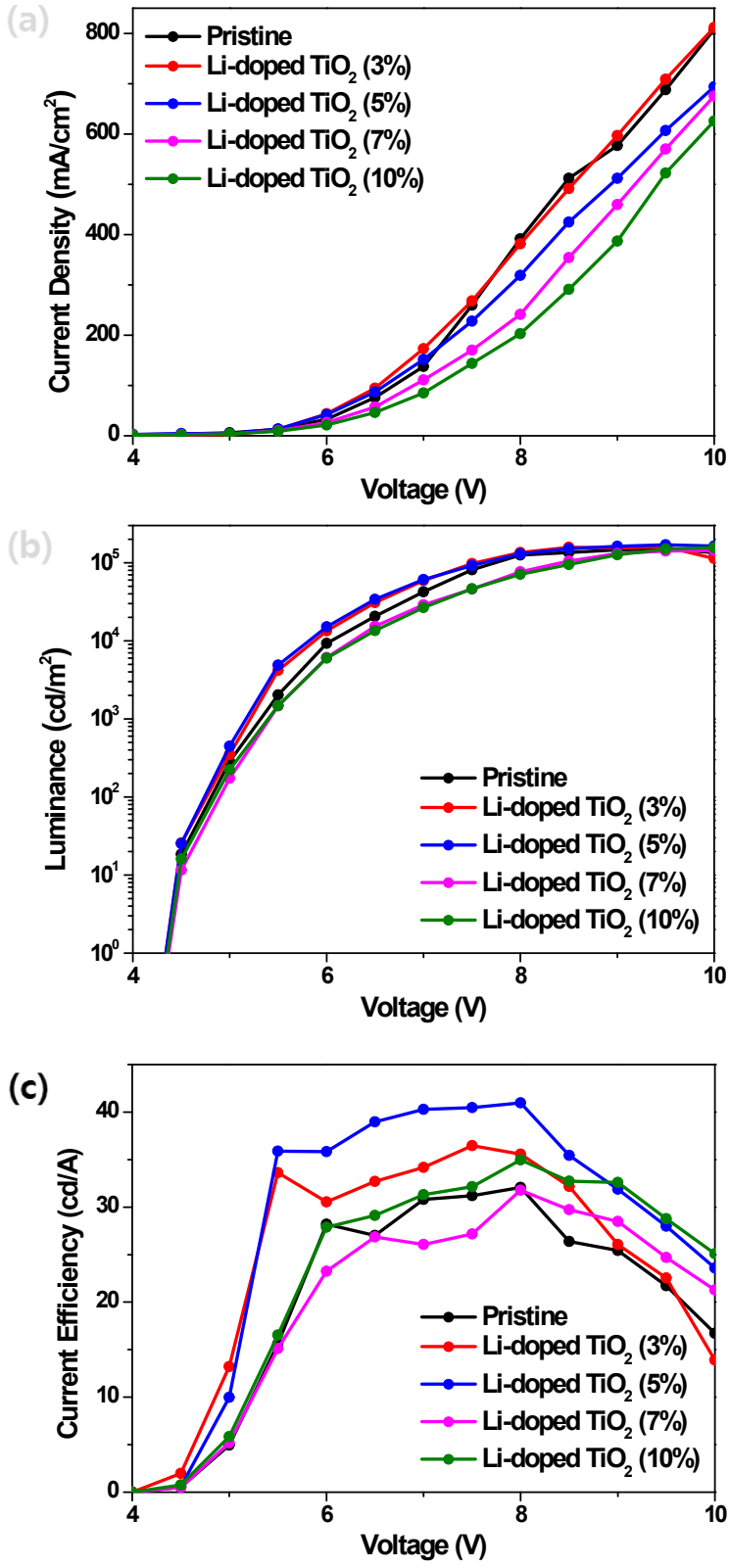


Fig. S7 Voltage-dependent variations of (a) current density, (b) luminance, and (c) current efficiency of QLEDs with pristine or Li-doped TiO_2 NPs as the ETL.

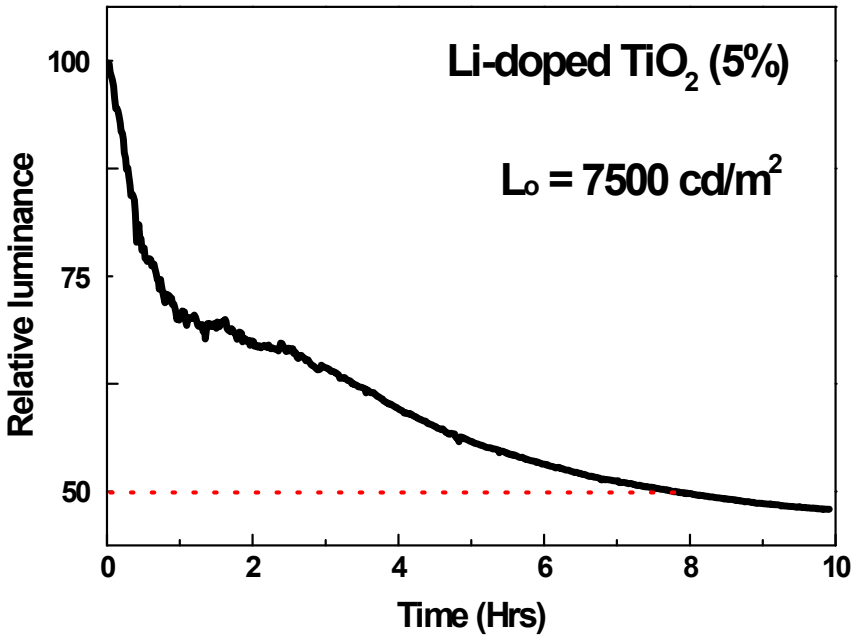


Fig. S8 Lifetime measurement of QLEDs with 5% Li-doped TiO_2 NPs as the ETL.

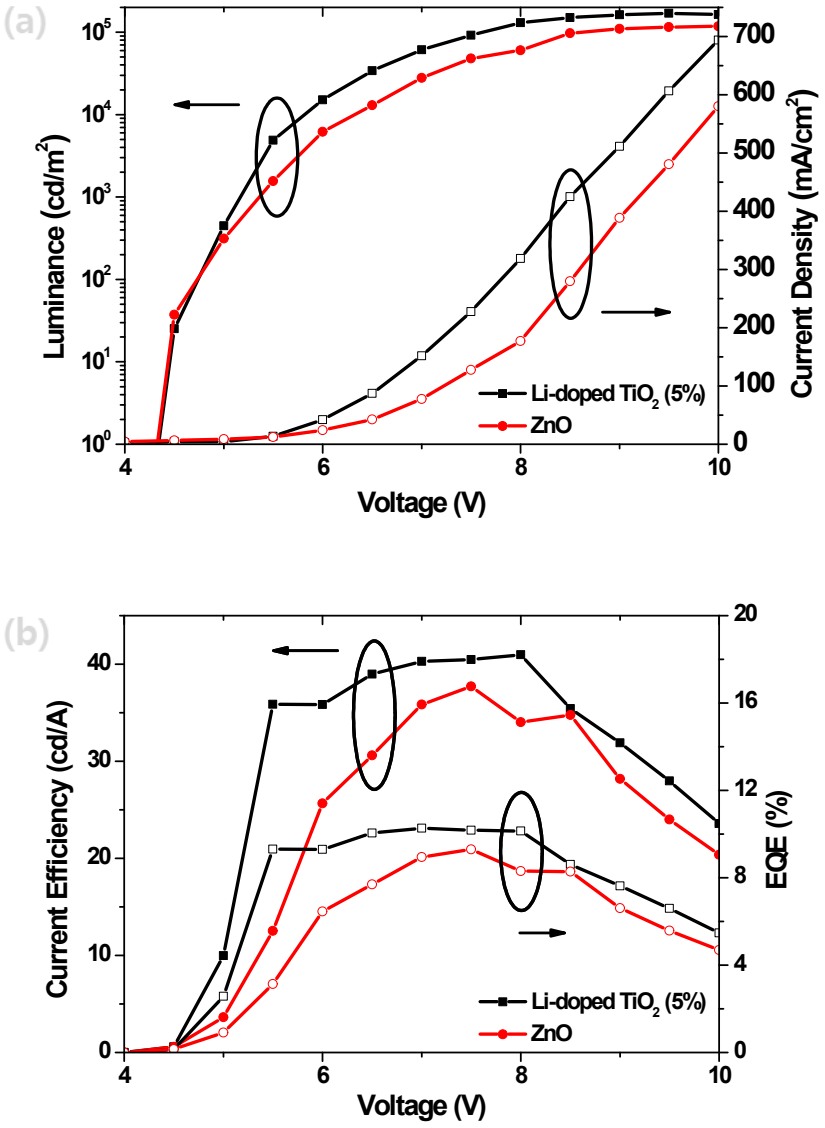


Fig. S9 Voltage-dependent variations of (a) current density and luminance and (b) current efficiency and EQE of QLEDs with 5% Li-doped TiO_2 NPs or ZnO NPs as the ETL.

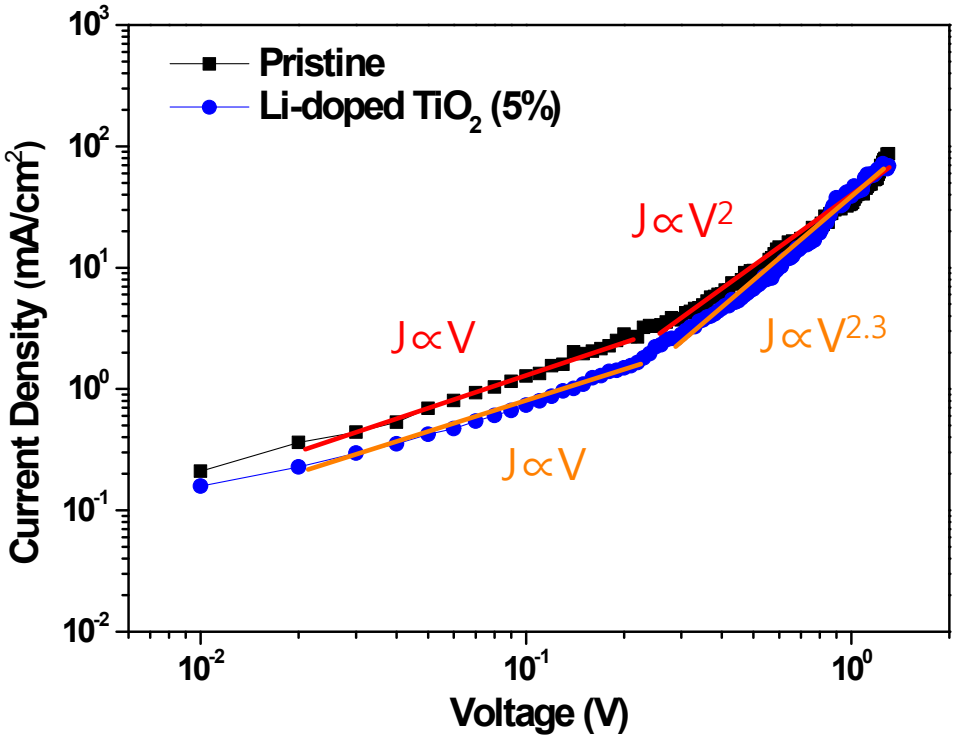


Fig. S10 Current density-voltage curves of two comparative EODs based on pristine and 5% Li-doped TiO_2 NPs. EOD structure consists of ITO/Al/200 nm-thick pristine or 5% Li-doped TiO_2 NPs/Al. Electron mobilities were calculated by Child's law (inset) to be 3.3×10^{-6} and 2.8×10^{-6} cm^2/Vs for pristine or 5% Li-doped TiO_2 NPs, respectively. Relative permittivity of TiO_2 was taken as 85 for this calculation.

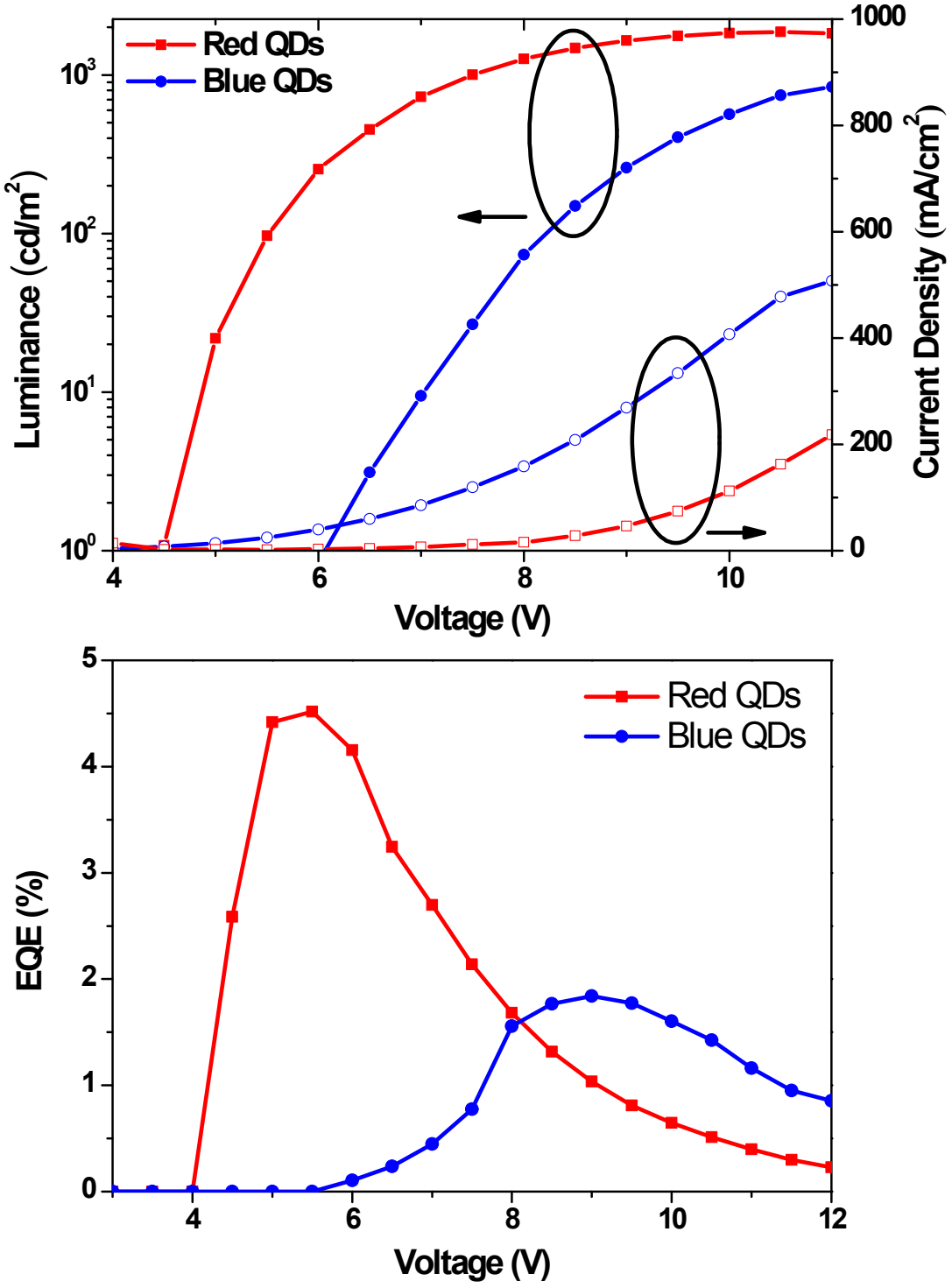


Fig. S11 (a) Luminance-voltage-current density curves and (b) EQE-voltage curves of red and blue QLEDs with 5% Li-doped TiO_2 NPs.