Supporting Information

Inverted Device Architecture for Enhanced Performance of Flexible Silicon Quantum Dot Light-Emitting Diode

Batu Ghosh,[*,†,‡] Hiroyuki Yamada,[§] Shanmugavel Chinnathambi,[⊥] İrem Nur Gamze Özbilgin,[†,#] and Naoto Shirahata,[*,†,§,#]

[†]International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, 305-0044, Japan

[‡]Department of Physics, Triveni Devi Bhalotia College, Raniganj, West Bengal, India

[⊥]International Center for Young Scientists (ICYS), NIMS, 1-2-1 Sengen, Tsukuba 305-0047, Japan

[§]Department of Physics, Chuo University, 1-13-27 Kasuga, Bunkyo, Tokyo 112-8551, Japan

[#]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0814, Japan

Corresponding Author

*E-mail: ghosh.batu@gmail.com.

*E-mail: SHIRAHATA.Naoto@nims.go.jp.

Experimental Methods:

Reagents and Materials: Triethoxysilane (TES) was purchased from TCI chemicals. 1-Decene was purchased from Sigma-Aldrich, and used as received. 1,3,5-tris (Nphenylbenzimidazole-2yl) (TPBi) was purchased from Luminescence Technology Corp. and used as received. Electronic grade hydrofluoric acid (49% aqueous solution, Kanto Chemical), HPLC grade toluene, dicholrobenzene, ethanol, and methanol were purchased from Wako chemical. Poly-TPD, (LumTech), zinc acetate dehydrate, PEDOT:PSS solution (Sigma-Aldrich) were used as received. Water was purified and deionized using a Sartorius (arium 611 UV) water purification system.

Preparation of SiQD: Preparation was performed in a two-step process we reported in our previous papers.[29,44] Triethoxysilane (TES) following our previous papers. In a typical, TES was employed as a starting precursor. The hydrolysis product, i.e., $(HSiO_{1.5})_n$, of TES was disproportionated at 1100°C for 1h in 5%/95% H_2/Ar atmosphere to produce SiQD dispersed in SiO_2 matrix. After cooling to room temperature, the dark-brown solid (i.e., Si/SiO_2 composite) as powder was mechanically ground in an agate mortar with a pestle. The fine powder thus obtained was stirred in a mixture of ethanol and 48% HF (aq) to liberate SiQD from the oxide. The resultant QD

was terminated with hydrogen atoms. Thermal hydrosilylation was carried out in 1-decene at 200°C to yield decane-capped SiQD (i.e., SiQD-De).

Preparation of ZnO nanocrystals: ZnO was prepared from Zn acetate di-hydrate. In a typical synthesis, 312 mg $Zn(OAc)_2$ was dissolved in 15ml of methanol and stirred. 30 mL methanol of 0.1N KOH was added slowly with continuous stirring. After refluxing 2 hrs at 60^{O}C ZnO nanocrystals was collected and washed with methanol.

Device Fabrication: Devices were fabricated ITO-coated polyethylene terephthalate (PET) substrates. A 150 nm thin film indium tin oxide (ITO) uniformly sputtered on a sheet of PET gives a resistivity of 10-14 Ω/sq which is good value for EL device fabrication.

Conventional device structure: The ITO-coated substrates were first etched using HCl and Zn dust in a narrow strip. Then, they were cleaned by ultrasonic agitation with a nonionic detergent, followed by washing with ethanol, acetone, and isopropanol and finally rinsed with distilled water (resistivity= 18.2 MΩ/cm). After drying, the substrates were subjected to VUV lamp (Ushio Corp.) for oxidation for 30 min under a pressure of 10 Pa air. Then PEDOT:PSS solution was first spin-coated onto plasma-treated substrates at a speed of 5000 rpm for 45 s. Afterward, the

PEDOT:PSS-coated substrates were loaded into an Ar-filled homemade chamber and baked at 140 °C for 30 min to eradicate any remaining solvent before the deposition of subsequent organic and ncSi layers. Poly-TPD was spun from chlorobenzene solution 10 mg/mL at a speed of 1800 rpm. The films were dried at 110 °C for 1 h in Ar environment. A ~20 nm of the ncSi-De layer was coated on the PEDOT:PSS surface by spin-coating the ncSi-De solution (10 mg/mL) for 1 min at 800 rpm. The films were dried in an Ar atmosphere at 100 °C for 1.5 h. TPBi and aluminum (Al) were deposited as an electron transportation layer (ETL) and a top electrode cathode from vacuum evaporation.

Inverted device structure: ITO coated PET substrates were prepared in a manner similar to the conventional device fabrication. Next, the colloidal ZnO nanocrystals were spin-coated from a solution of concentration 20 mg/mL in isopropanol with rotation speed 2000 rpm. After baking the film at 120^{o}C in air, the emission layer of SiQD-De have been spin-coated with a concentration 10 mg/mL in cholorobenzene with a speed of 1500 rpm. Then an organic layer CBP has been thermally evaporated with thickness 40 nm. 30 nm MoO_3 layer has been deposited with vacuum level 10^{-4} Pa by thermal evaporation. As the top electrode Al of thickness 150 nm was deposited with musk over the film.

Characterization: The morphology of the SiQD-De was analyzed using high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100) operated at 200 kV. Major crystalline phase of the product was evaluated with X-ray powder diffraction (HT-XRD, RINT-TTR II and Reactor X, Rigaku, Japan). Surface roughness and morphology were observed at ambient conditions by atomic force microscope (AFM; Seiko Instruments Inc., SPA-400, SPI-3800N) in dynamic force mode (DFM) using a Si probe (Seiko Instruments Inc., cantilever; force constant = 0.12 N/m). Optical absorbance spectra were recorded by UV–VIS spectrophotometer (JASCO V-650, Japan) with integrated sphere. PL measurements at room temperature were carried out with a spectrofluorometer (NanoLog, Horiba Jovin Yvon, Japan). Absolute PL QYs were measured by with an absolute PL QY measurement system (C9920-02, Hamamatsu Photonics, Japan). Time-resolved fluorescence decay profiles were recorded at room temperature on a TTL trigger from the DeltaHub time-correlated single photon counting (TCSPC) electronic module, operating in the MCS mode lifetime spectroscopy system in phosphorous mode with pulse laser diodes of λ_{em} = 370 nm (NanoLog, Horiba Jovin Ybon, Japan). The quality of the fi t has been judged by the fitting parameters such as χ^2 (<1.2) as well as the visual inspection of the residuals.

Calculation of EQE: EQE was calculated as the ratio, per unit time, of the number of forward-emitted photons to the number of injected electrons, $I_d/|e|$, where I_d is the current passing through the QLED device at an applied bias, V. We can express this as,

$$\text{EQE } [\%] = N_{phot*}|e|I_d*g*100$$

where N_{phot} is the number of forward-emitted photons actually collected by the photodiode, and the geometric factor, g, accounts for the solid angle of the EL profile (assumed to be Lambertian) subtended by the photodiode, $\Omega = \pi/g$:

$$g = (a^2+L^2)/a^2$$

where 'a' is the diameter of the active area of the photodiode and L is the distance between the emitting QLED pixel and the photodiode.N_{phot} was calculated from the photocurrent output of the photodiode in response to detected EL. The Photodiode current, divided by the responsivity value of the photodiode at the peak wavelength of the EL curve gives the light output power from the LED device. Then number of photon is calculated by just dividing with hc/λ. So the simplified formula we used for EQE is:[1]

$$\text{EQE}(\%) = \frac{I\,(Photodiode) * \lambda(peak) * electron\ charge * g * 100}{R(\lambda) * hc * I\,(device)}$$

Brightness also calculated from the EQE value and the EL spectrum. EL*CIE gives the typical human response. Total luminance intensity has been calculated by integrating the EL spectra over the all wavelength range. Brightness is then calculated by dividing active device area and 2π. So the formula becomes[2]

Brightness or Luminance (Cd/m^2)=

$$\frac{683.002 \ * \ EL\ area\ under\ the\ curve\ Normlaized \ * \ CIE \ * \ I\ (device) * \ EQE}{2\pi * Device\ Area}$$

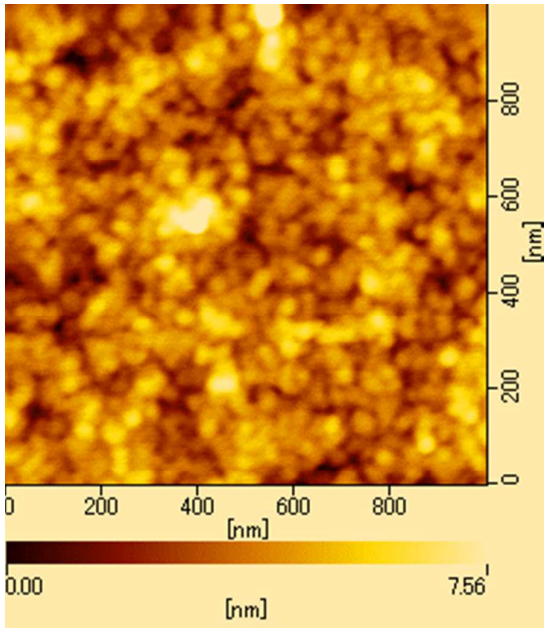

Figure S1. AFM image taken by DFM operation mode for SiQD-De film

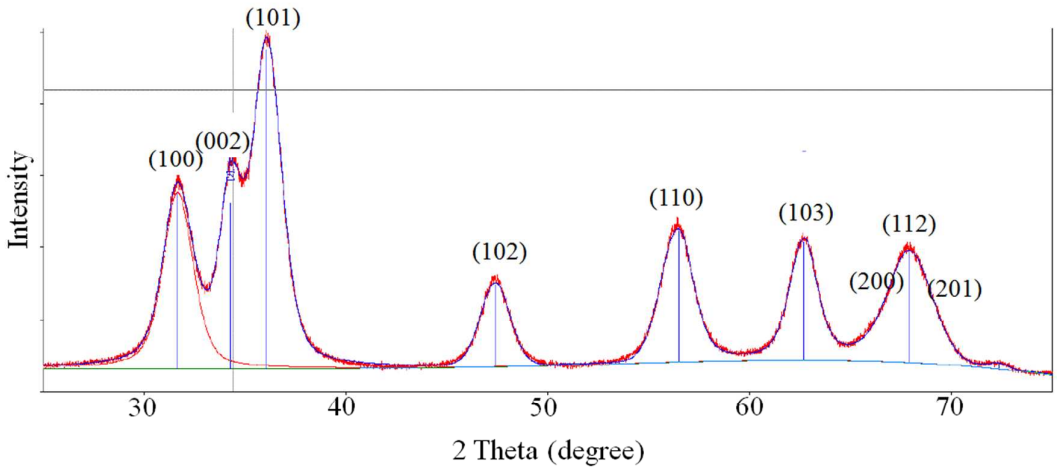

Figure S2. XRD pattern of ZnO nanocrystals. The pattern (red) experimentally measured is fitted with calculated curve for analysis. Clearly, the product was composed of high crystalline and single phase of ZnO. An average diameter of the ZnO nanocrystals were calculated from Scherrer equation to be 5.4±0.7 nm.

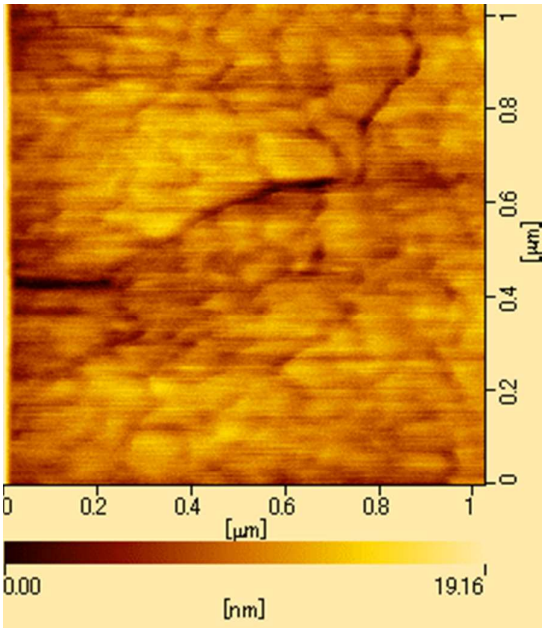

Figure S3. AFM image taken by DFM operation mode for the MoO_3 film.

REFERENCES

(1) Supran, G. J. S. Enhancing quantum-dot luminescence in visible and infrared light emitting devices. **2016**, Massachusetts Institute of Technology.

(2) Wood, V. C. All inorganic colloidal quantum dot LEDs. **2007**, Massachusetts Institute of Technology.