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Supporting Information

Inverse µ-Photonic Crystals Enhanced Mini-sized Quantum Dot LEDs

Shih-Jung Ho and Hsueh-Shin Chen*

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan (ROC). E-mail: chenhs@mx.nthu.edu.tw

Experimental

Synthesis of monodisperse microspheres. The 306 nm monodisperse PMMA microsphere was prepared by an soap-free polymerization method.^[1] Briefly, 9 ml methyl methacrylate (MMA), 1.35 ml divinylbenzene (DVB), 1 ml methacrylic acid (MAA) and 100 ml deionized water were poured into a 250 ml 3-neck round flask with magnetic stirring. The solution was purged with N₂ for 30 min and then heated to 70 °C. Until the reaction temperature was stable for 30 min, 50 mg potassium persulfate (KPS) was added to the solution as an initiator to start polymerization under N₂. After reacting for 16 hours, the solution was cooled naturally and centrifuged thrice with deionized water and ethanol to remove unreacted residue. Different sizes of monodisperse PMMA (160 to 500 nm) could be prepared with the same method by adjusting the amount of MMA (2 to 10 ml), DVB (0.6 to 1.5 ml), MAA (0.5 to 1 ml) and KPS (50 to 200 mg), and reaction temperature (70 to 90 °C).

Preparation of inverse photonic crystal TiO₂ powder. The PC template was prepared by the centrifuge assembly method.^[2,3] Monodisperse microsphere solution was added into the centrifuge tube and was centrifuged at 500 rpm for 48 hours. After centrifugation, the precipitate was dried in atmosphere and a pellet possessing a PC structure with a structural color was obtained after about 3 days. The polymer PCs was then used as a template for preparing TiO₂-based inverse PCs by the forced impregnation method.^[2,3] Aft first, the polymer PC template were soaked in methanol for 30 min, followed by immersing the template in titanium butoxide immediately. The sample was then placed in a vacuum condition to remove methanol, which could lead to penetration of titanium butoxide into the polymer PC template. The sample was kept in atmosphere for 24 hours to allow titanium butoxide to hydrolyze to titanium oxide. After that, inverse TiO₂ PCs with the rutile phase without the polymer PC template could be obtained by heating at 100 °C/2 h, followed by 575 °C/6 h with a heating rate of 1 °C/min. Finally, the product was milled and downsized to around 5 to 15 µm. The inverse photonic crystal µ-iPC-452 was prepared from 306 nm PMMA microsphere, and the µ-iPC-X was prepared from mixing 186, 210, and 240 nm different PMMA microsphere.

Preparation of photonic crystal quantum dot light-emitting diode (PC QD-LED). Quantum dots (QDs) were obtained from Hsinlight Inc. The optical propeties (wavelength / FWHM / QY) of green and red QDs are 525 nm / 32 nm / 85.3% and 631 nm / 32 nm / 88.9%. PDMS-based QD resins were prepared by mixing 0.25 to 7 wt% red and green QDs, 1 wt% inversed PC powders, and polydimethylsiloxane (PDMS). QD-LEDs were prepared by dispensing the QD resin to a surface mount device (SMD, ~ 3 mm × 0.6 mm) containing a 450 nm blue LED chip (~ 0.9 mm × 0.2 mm), followed by curing at 120 °C for 30 min in atmosphere.

Characterization. Microstructure of samples was analyzed by field emission gun scanning electron microscopy (SEM). Photonic bandgap (PBG) or stopband of samples was measured by a UV-Vis spectrometer (HITACHI U-3900) equipped with a fixed-angled detector. The device performance and photoluminescence (PL) spectra were directly obtained from QD-LEDs operated at 20 mA by a spectrometer with the integration sphere.



Figure S1. Photograph of PC template with vivid structure color by the large area periodic structure. PC template prepared by (a) 238 nm and (b) 306 nm monodisperse microspheres. (c) Template of the nonperiodic structure prepared by mixing 186, 210, and 240 nm monodisperse microspheres.



Figure S2. Photoluminsecne spectra of red and green QDs (from Hsinlight Inc.) under 450 nm excitaion in this research. The PL QY of both QDs are apparoximately 90% in toluene.



Figure S3. (a) Light transmittance spectra of photonic crystal template prepared by microspheres with different sizes. Black numbers are marked as PBG of photonic crystal templates, and red numbers are marked as PBG of inverse photonic crystal (iPC) in PDMS after calcination. (b) SEM images of photonic crystal template prepared by different monodisperse microspheres and corresponding inverse photonic crystal after a calcination process. (i) 186 nm template and 98 nm pore size, (ii) 306 nm template and 162 nm pore size, marked as μ -iPC-452, (iii) 325 nm template and 176 nm pore size, (iv) nonperiodic template and pore size prepared by mixing 186, 210, and 240 nm monodisperse microspheres, marked as μ -iPC-X.

		Polymer PC template			TiO2 iPC (after calcination)	
Sample No.	Ave. center-to- center distance (nm)	PBG in air (nm) (Experimental)	PBG in air (nm) (Calculated)	Ave. center-to- center distance (nm)	PBG in air (nm) (Experimental)	PBG in air (nm) (Calculated)
#1	186	416	414	98	227	274
#2	210	465	467	119	275	333
#3	238	533	530	136	303	380
#4	251	553	558	142	316	397
#5	288	642	636	155	345	433
#6 (µ-iPC-452)	306	683	681	162	375	452
#7 (μ-iPC-X, control)	Mixed 186/210/240	-	-	-	-	-

Table S1. Summary of properties of polymer PC template and $TiO_2 \mu$ -iPCs.



Figure S4. Schematic diagram of conventional PC application and the optimized PC structure in this work. (a) Because of the excitation light, LED is not at a single incident angle, and the excitation light beyond PBG will not be able to resonate and limit the intensity improvement effect. (b) The optimized PC QD-LED structure in this work. PC powders are employed as scatters in LED, which have a scattering effect and a resonate enhancement effect. To increase the probability of exciting QDs by the scattering effect and increase the probability of hitting the desired incident angle of PBG to further improve the intensity by resonate enhancement.



Figure S5. (a) μ -iPC-452 improves the luminescence EQE of QD-LEDs loaded with difference QD concentrations. μ -iPC-452based QD-LEDs have higher EQEs than either μ -iPC-X particles or conventional TiO₂ scatters. (b) Connventional scatters can scatter more blue light to increase the probability of QD ecitation, which can emit more green light, but the green light may be scattered or absorb by the scatters again. On the other hand, μ -iPC-452 can selectively reflect the blue light with limited scattering and absorption in the QD emission range, so it produces similar QD emission intenisty in a lower comsumation of blue light. Noted the intenisty is more related to QD excitation probability and reabsorption. The QYs of QDs are similar for all samples. (c) Illustration of luminescent and scattering processes of conventional particle and μ -iPC-452.



Figure S6. Normalized transmittance spectra of μ -iPC-452 and μ -iPC-X in PDMS. The μ -iPC-452 sample increases the transmittance in the 500-700 nm region, which increases the EQE of QD-LEDs.



Figure S7. Digital photos showing the assembly processes of current μ -iPC-enhanced QD-LED displays. (a) μ -iPC-enhanced QD-LEDs were prepared after dispensing μ -iPC QD-glue in 3006 SMT LEDs. (b) PC QD-LEDs were loaded to a circuit board to prepare light bars. (c) A light bar was integrated into a backlight module containing a light guide plate, diffuser and prism films. (d) A 6-inch μ -iPC-enhanced QD-LED display.

Sample No.	NTSC	Reference
YAG-LED LCD	70-80	[4]
QD film LCD	98-130	[4, 5]
QD-LED LCD	100	[6]
PC QD-LED LCD (in this work)	113	-
OLED	75-106	[7]
QLED (EL)	140-170	[8]

Table S2. Comparision of color gamut for displays.

¹ S. Zhang, X. W. Zhao, H. Xu, R. Zhu and Z. Z. Gu, J. Colloid Interface Sci., 2007, 316, 168-174.

² X. Chen, Z. Li, J. Ye and Z. Zou, Chem. Mater., 2010, 22, 3583-3585.

³ X. Chen, J. Ye, S. Ouyang, T. Kako, Z. Li and Z. Zou, ACS Nano, 2011, 5, 4310-4318.

⁴ J. S. Steckel, J. Ho, C. Hamilton, J. Xi, C. Breen, W. Liu, P. Allen and S. Coe-Sullivan, J. Soc. Inf. Display, 2015, 23, 294-305.

⁵ Y. Kang, Z. Song, X. Jiang, X. Yin, L., Fang, J. Gao, Y. Su and F. Zhao, Nanoscale Res. Lett., 2017, 12, 154.

⁶ Jang, E., Jun, S., Jang, H., Lim, J., Kim, B., & Kim, Y. (2010). Adv. Mater., 2010, 22, 3076-3080.

⁷ B. W. Lee, Y. G. Ju, Y. I., Hwang, H. Y., Lee, C. W., Kim, J. S., Lee and J. H. Souk, J. Soc. Inf. Disp., 2009, 17(2), 151-157.

⁸ J. R. Manders, L. Qian, A. Titov, J. Hyvonen, J., Tokarz-Scott, K. P. Acharya, Y. Yang, W. Cao, Y. Zheng, J. Xue and P. H. Holloway, *J. Soc. Inf. Disp.*, 2015, 23, 523-528.