Ultra Stable Quantum Dot Composite Film in Severe Environment

Zunxian Yang¹*, Yuxiang Zhang¹, Jiahui Liu¹, Jingwei Ai¹, Shouqiang Lai¹, Zhiwei Zhao¹, Bingqing Ye¹, Yushuai Ruan¹, Tailiang Guo¹*, Xuebin Yu², Gengxu Chen¹, Yuanyuan Lin¹, Sheng Xu¹

¹National & Local United Engineering Laboratory of Flat Panel Display Technology, Fuzhou University, Fuzhou 350116, P. R. China

²Department of Materials Science, Fudan University, Shanghai 200433, P. R. China

Corresponding Authors

*E-mail: yangzunxian@hotmail.com	(Z. Yang)		
*E-mail:gtlfzu@hotmail.com	(T. Guo)		



Fig. S1 the photographs of quantum dot composite films fabricated with different solvents.

 Table S1 the composition of precursor solution for fabricating composite film

 samples

Soundas	The composition of precursor solution for fabricating							
Samples	composite film samples							
$S_{0.25ml\ chloroform}$	0.25ml QDs chloroform solution and 1.75ml DMF							
$S_{0.5ml\ chloroform}$	0.5ml QDs chloroform solution and 1.5ml DMF							
$S_{0.75ml\ chloroform}$	0.75ml QDs chloroform solution and 1.25ml DMF							
$S_{1ml\ chloroform}$	1 ml QDs chloroform solution and 1 ml DMF							
$\mathbf{S}_{\text{QDs solution}}$	chloroform diluted quantum dot solution							

Table S2 the PL lifetime τ and the quantum yields of the quantum dot composite films fabricated with different solvent under the same batch with the middle evaporated speed. For comparison, the PL lifetime τ and the fit goodness of the chloroform diluted quantum dot solution were also obtained.

Sample	f ₁ (%)	$\tau_1(ns)$	f ₂ (%)	$\tau_2(ns)$	$\tau_{avg}(ns)$	χ^2	
$\mathbf{S}_{\text{QDs solution}}$	96.03	21.96	3.97	83.1	24.03	1.50857	
$S_{0.25ml}$ chloroform	96.15	16.4	3.85 68.5 18.41		18.41	1.458742	
$S_{0.5ml}$ chloroform	97.29	21.3	2.71	98.7	23.4	1.332799	
$S_{0.75ml}$ chloroform	97.25	22.9	2.75	106.4	25.18	1.257296	
$S_{1ml\ chloroform}$	97.5	18.4	2.5	90.1	20.21	1.401323	

Note: The QY of quantum dots (QY₀) were obtained by the slope method. where the $\tau_{avg(f)}$ referred to decay lifetime of films and the $\tau_{avg(0)}$ referred to the decay lifetime of the chloroform diluted quantum dot solution, the χ^2 referred to the fit goodness. The PL decay lifetime were fitted by bi-exponential function with $\tau_{avg}=f_1\tau_1+f_2\tau_2$.



Fig. S2 The QY of quantum dots obtained by the slope method.

Here, the QYs were determined by slope method using the reference of rhodamine B. Quantum dots were dissolved in hexane to form several kinds of different concentrations dilute solutions, the absorbance and the fluorescence spectra of the same solution were measured, then the integrated photoluminescence intensity and the absorbance value were plotted to give the curve of the samples with that of the The QY references. values were calculated using the following equation: $\Phi_x = \Phi_s(K_x/K_s)(\eta_x/\eta_s)^2$. Where Φ was the QY, K was the slope determined by the curves and η was the refractive index. The subscript "s" refers to rhodamine and "x" referred to the quantum dots.



Fig. S3 the PL decay lifetime of the quantum dot composite films fabricated under relatively low temperature and high pressure environment by the quantum dot solution with the different optical density (OD) value, and that of the original quantum dot solution. The PL decay lifetimes of quantum dot composite films decreased sharply as compared with that of original quantum dot solution and the quantum dot concentration of quantum dot solution to some extent influenced the PL decay lifetime of the quantum dot composite films. (Note: "OD@510nm0.1" represented the quantum dot composite films fabricated by the quantum dot solution with the optical density (OD) value of 0.1 at testing light with optical wavelength of 510nm. The names of other samples could also be obtained by similar method).

Actually, the optical density (OD) value of quantum dot solution showed positive correlation with or, to some extent, was proportional to the quantum dot

concentration of the quantum dot solution. For quantum dot solutions, higher optical density (OD) value meant higher concentration of quantum dots in solution. For convenience, here, the optical density (OD) value of quantum dot solution was used as the quantum dot concentration of solution. All the quantum dot composite films were fabricated under relatively low temperature and high pressure to reduce the evaporation rate of solvent in the composite films.



Fig. S4 the photo image of the film with and without the shelter under UV radiation. (a) The uniform color distribution under uniform UV irradiation.
(b) Sheltering a part of composite film for several minutes under UV irradiation. (c) Just removing the shelter showing that there is an obvious chromatic aberration. (d) Removing the shelter for several minutes showing that the chromatic aberration disappears.



Fig. S5 the time-dependent PL spectra of sample under the constant 465nm excitation for different time

S-9



Fig. S6 The SEM images and the fluorescence optical microscopy images of the composite film: (a) the cross-sectional SEM image of the composite film;
(b) the surface SEM image of the composite film; (c) the fluorescence optical microscopy image of the composite film (the scale bar is 20um); (d) the higher magnification fluorescence optical microscopy image of the composite film (the scale bar is 5um).



Fig. S7 the PL spectra of the precursor $Cd_xZn_{1-x}Se_yS_{1-y}$ quantum dots for fabricating the quantum dot composite film.



Fig. S8 the step profile of the film, which cut by blade for test the thickness.



Fig. S9 the photos of PMMA/QDs film and PVDF/QDs film before/after being immersed in boiling water: **(a)** the photos of PMMA/QDs film before being immerserd into boiling water; **(b)** the photos of PVDF/QDs film before being immerserd into boiling water; **(c)** the photos of PMMA/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for just ten seconds; **(d)** the photos of PVDF/QDs film after being immerserd into boiling water for four hours.

Video S1 vivid reliability test of quantum dots-PVDF composites film in boiling water. The composite film was put into boiling water for about 240minutes. In the whole process, the quantum dot composite film was being exposed to UV irradiation and then Photos were taken once in a certain time to get its brightness qualitative data under UV irradiation.



Fig. S10 The PL stability of composite film frabricated with middle evaporation speed under continue UV lamp(6w) irradiated versus irradiation time.



Fig. S11 the excitation photo luminescence spectra of red emissive phosphor: $K_2SiF_6:Mn^{4+}$ under different excitation wavelength. When the excitation wavelength is up to 465nm, it exhibits the maximum PL intensity.



Fig. S12 the EL stability of white LED at the high initial brightness is 1.9387×10^4 cd/m² and the current are set at constant of 50 mA. On basis of the monitored brightness and EL spectrum, the WLED maintained 91% initial brightness even after the 3 hours optical radiation at the initial brightness is 1.9387×10^4 cd/m² and there were little variation according to the monitored EL spectrum.

Current(A)	Luminance(cd/m ²)	CCT(K)	CIE		
0.02	8752	5568	(0.3318,0.3389)		
0.03	11290	5533	(0.3327,0.3423)		
0.04	14850	5498	(0.3336,0.3422)		
0.05	20030	5463	(0.3344,0.3444)		
0.05	25210	5544	(0.3324,0.3410)		

 Table S3 the luminance, CCT, and CIE color coordinates for a prototype of white
 lighting emitting diode under different drive currents.

Table S4 the typical processes for synthesizing the red fluorescence quantum dots, the green fluorescence quantum dots and the blue fluorescence quantum dots, respectively.

sample	The processes at low temperature					The processes at high temperature								
	chemicals and corresponding processes					chemicals and corresponding processes				chemicals and corresponding processes				
Red Samples	CdO: 1mmol	ZnAc ₂ .2H ₂ O: 2mmol	OA 5ml	ODE:25ml	150□, 15min, degassing in Ar environment	TOP: 0.2ml	Se: 0.2mmol	300□ 2.5min		0.3ml DDT	V: 1ml/min; 20min	TOP:1ml	S:2mmol	300□,10min
Green Samples	CdO: 0.4mmol	ZnAc ₂ .2H ₂ O: 4mmol	OA 6.5ml	ODE:20ml	150□, 20min, degassing in Nitrogen environment	TOP:3ml	Se:0.1mmol	S:4mmol	300□, 10min					
Blue Samples	CdO: 1mmol	ZnAc ₂ .2H ₂ O: 10mmol	OA 7ml	ODE:15ml	150□, 20min, degassing in Ar environment	S:1.6mmol	ODE:2.4ml	310□,12min		S:4mmol	OA:5ml	310□, injection speed:0.5ml/min., 60min		