Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Quench-resistant and stable nanocarbon dot/sheet emitters with tunable solid-state fluorescence via aggregation-induced color switching

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Experimental Section

Materials

All reagents are used as received without further purification. Anhydrous citric acid (CA, ≥97%), 1-Octadedecylamine (ODA, ≥90%), and Octadecene (ODE, ≥90%) are purchased from Aladdin industrial corporation. Chloroform (≥99.0%) and acetone (≥99.5%) are purchased from Shanghai Lingfeng Chemical Reagent corporation. Ethanol (≥99.7%) is purchased from Wuxi City Yasheng Chemical corporation. Polydimethylsiloxane (PDMS, SYLGARD 184 SILICONE ELASTOMER) is purchased from Shanghai Deji Trading corporation. Dialysis bag (1000 Da) is purchased from MYM Biological Technology company. UV LED chips are purchased from Shenzhen Boya Science and Technology company.

Synthesis of nanocarbon dot/sheet emitters (carbon phosphors, CP)

Critic acid (CA) (0.50 g) and 1-Octadedecylamine (ODA) (0.75 g) are dissolved in octadecene (ODE) (10 mL) and sonicated for 10 min to obtain a homogeneous solution. Then the solution is transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (25 mL) and heated at 180 °C for 0.5-15 h. After the reaction, the autoclave is cooled to room temperature naturally. Then a certain amount of acetone and alcohol are separately added to remove the ODE solvent and excess raw materials. The supernatant is removed by centrifugation (8000 rpm, 10 min) and the precipitation is rotary evaporated at 50 °C to obtain emitter powders (CP-0.5, CP-1, CP-2, CP-3, CP-6, CP-9 and CP-15). Dissolve the emitter powders in chloroform and then load into dialysis membrane (the molecular weight cut off is 1000 Da) for dialysis against chloroform for 10 days and replace dialysate every day to obtain the corresponding CDs.

Synthesis of pristine CDs without ODA

Critic acid (CA) (0.5 g) are dissolved in octadecene (ODE) (10 mL) and sonicated for 10 min to obtain a homogeneous solution. Then the solution is transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (25 mL) and heated at 180 °C for 0.5, 3 and 15 h, respectively. When the autoclave is cooling down, the pristine CD solution is achieved for further characterization.

Multistep washing procedure

Critic acid (CA) (0.50 g) and 1-Octadedecylamine (ODA) (0.75 g) are dissolved in octadecene (ODE) (10 mL) and sonicated for 10 min to obtain a homogeneous solution. Then the solution is transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (25 mL) and heated at 180 °C for 15 h. After the reaction, the autoclave is cooled to room temperature naturally. Acetone is added to wash the product for two times and alcohol is then added to continuously wash the precipitation for one, three, five and seven times, respectively. Finally, yellow, light yellow, green and white light emitters are obtained for further characterization.

Fabrication of nanocarbon-coated LEDs

The emitter powders are dissolved in chloroform (5 mg mL-1) and then drop-coated onto 375 nm UV LED chips, subsequently followed by a heat-solidification process at 50 °C for 10 minutes. The above steps are repeated for 3 times.

Fabrication of CD@PDMS-coated LEDs

The CD solution obtained by dialysis in chloroform is mixed with PDMS uniformly. Then, hardening agent is added into the solution and heated at 50 °C for 30 min. Finally, the CD@PDMS is drop-coated on the 375 nm UV LED chips and heated at 50 °C for 2 h.

Characterization

Transmission electron microscopy (TEM) images are taken on a HITACHI 7605 microscope and the high resolution transmission electron microscopy (HRTEM) images are taken on a JEOL 2100F microscope. The morphology of the nanocarbon phosphors are measured by scanning electron microscope (SEM, JSM 7800F). The Photoluminescence (PL) spectra are recorded by a Fluorescence Spectrometer (F-4600) and UV-Vis absorption spectra are measured with a Shimadzu UV-1750 spectrophotometer. X-ray photoelectron spectroscopy (XPS, Thermo escalab 250Xi) is used to confirm elements and chemical composition of CDs. Transform Infrared Spectroscopy (FTIR, DT-40) is used to conform the functional groups of CDs with the same concentration of samples and the same test condition. TGA data are recorded by METTLER TOLEDO TGA2. The quantum yields (QYs) of CDs are measured by fluorescent life test system (American PTI). The related photoelectric parameters of LEDs are measured by a spectrophotometer (PR-745). The fluorescence decay curves are measured with Transient State Fluorescence Spectrometer (Edinburgh Instruments FLS 980) to study the PL mechanism of dot/sheet nanocarbon emitters.

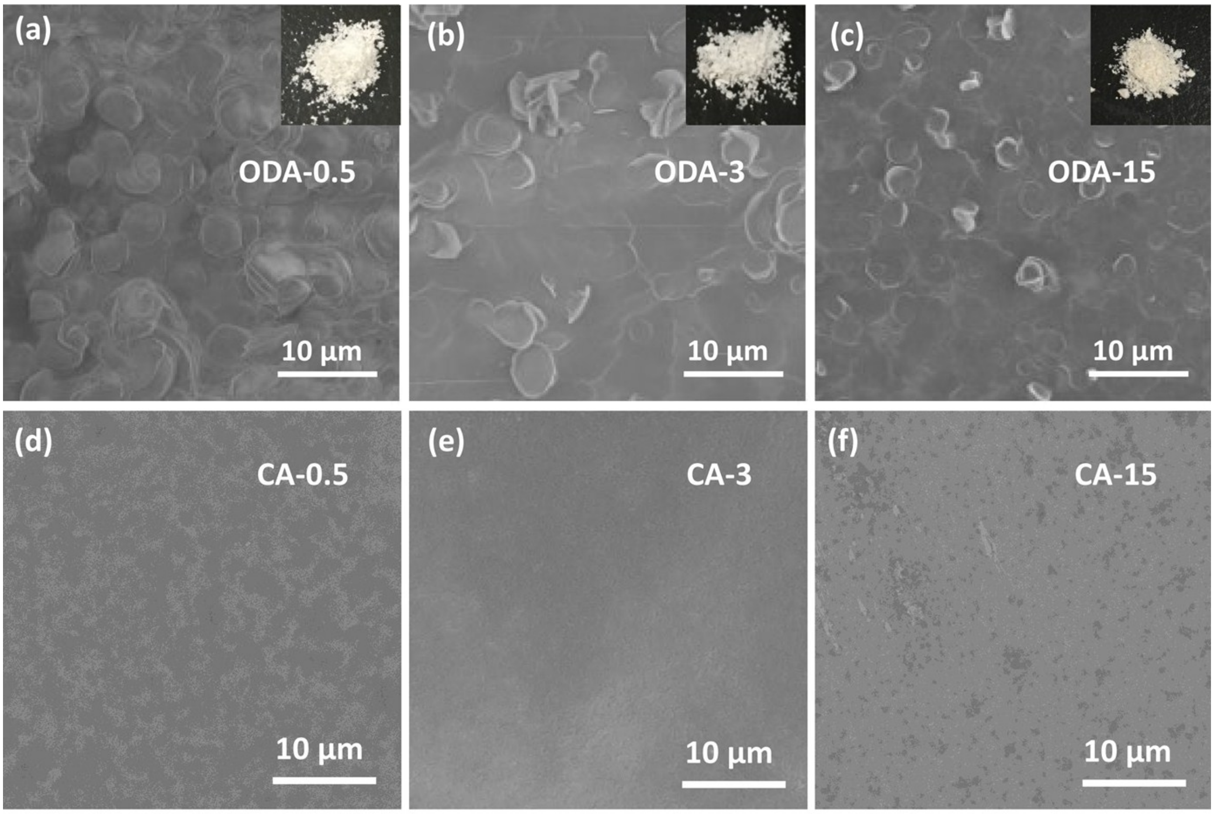

Fig. S1 SEM images of products prepared from ODA with the reaction time of 0.5 h (a), 3 h (b) and 15 h (c) (insets are corresponding photographs in day light). SEM images of products prepared from CA with the reaction time of 0.5 h (d), 3 h (e) and 15 h (f). Without the participation of CA, the obtained powders with extremely low production yields of ~1% exhibit two-dimensional carbon sheet structure. Without the participation of ODA, there is no obvious self-assembly of products from CA, together with the carbon sheets observed from SEM images of ODA, confirming that carbon sheets originate from the self-assembly of ODA.

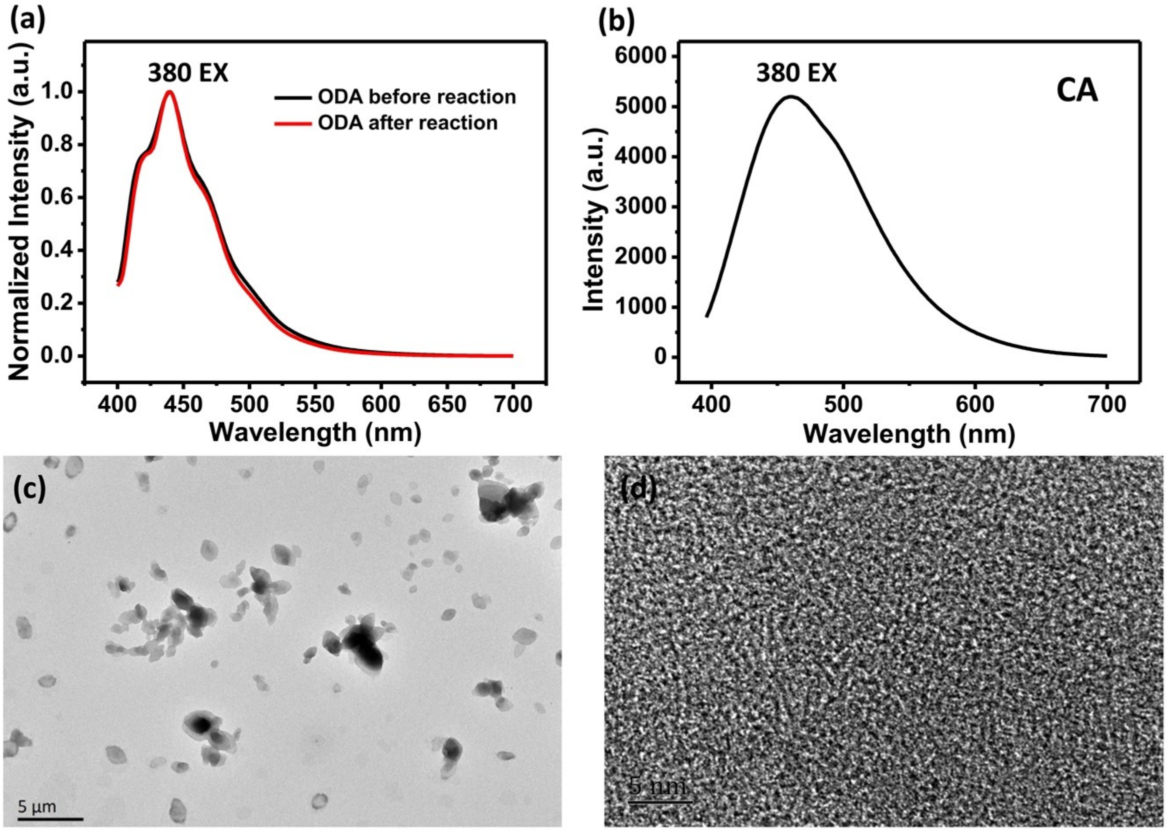

Fig. S2 (a) PL spectrum of ODA before and after the reaction. (b) PL spectrum of the reaction product obtained from CA. (c) TEM and (d) HRTEM of the reaction product obtained from ODA. Shoulder peak appears in the PL spectrum of ODA at 420 nm, but no shoulder peak appears in PL of CA products. Carbon sheets are observed in TEM images of the product obtained from ODA and no obvious crystal lattice of CDs can be observed in the HRTEM image. Combining with the negligible weight loss of independent ODA molecules in the hybrid emitters observed from the TG result in Fig. 3h, it is considered that the shoulder peak at 420 nm originates from ODA molecules adhering on the surface of CDs.

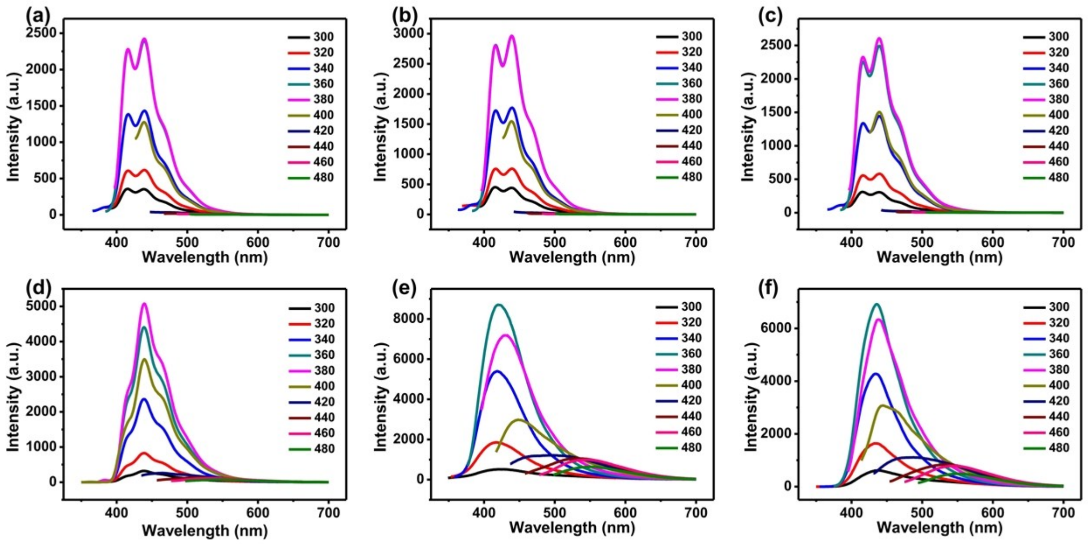

Fig. S3 PL spectra of CD solutions (top) and nanocarbon emitter solutions (down) with different reaction time, (a, d) 0.5 h, (b, e) 3 h, (c, f) 15 h, respectively. The solvent is chloroform.

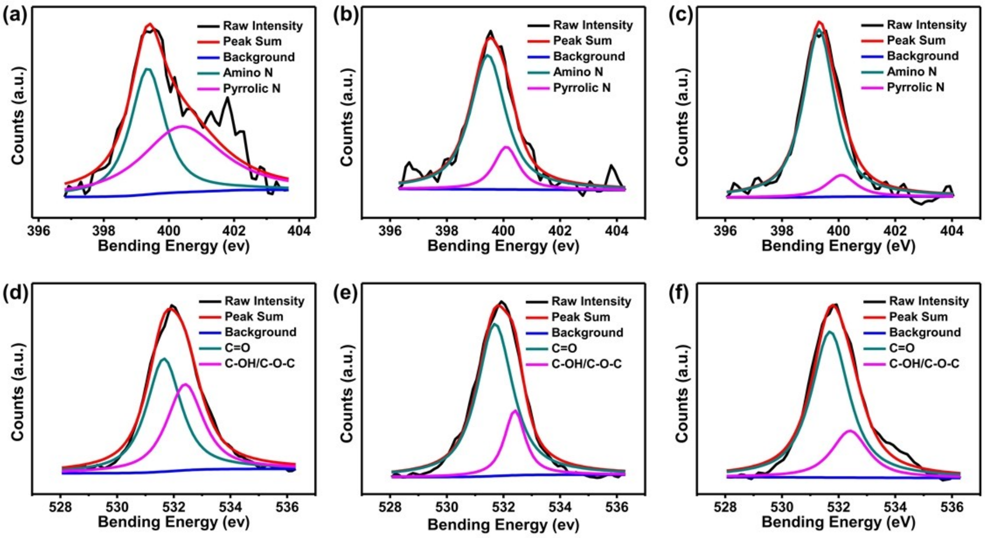

Fig. S4 High-resolution XPS spectra of N 1s (a-c) and O 1s (d-f) of CDs with different reaction time, (a, d) 0.5 h, (b, e) 3 h, (c, f) 15 h, respectively. N 1s band is splitted into two peaks at 399.4 and 400.1 eV, corresponding to amino N and pyrrolic N. Two peaks in O 1s spectra at 531.7 and 532.4 eV are assigned to C=O and C-OH/C-O-C, respectively.

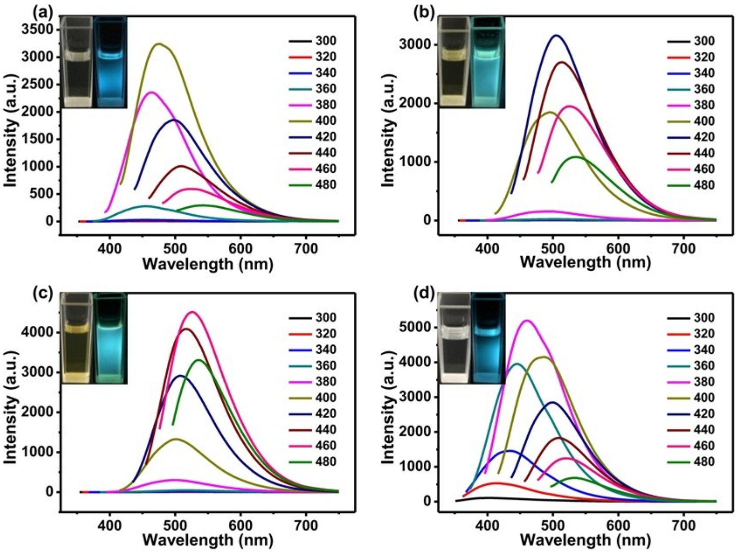

Fig. S5 PL spectra of pristine CDs with different reaction time. CA-0.5 (a), CA-3 (b), CA-15 (c) and CA-15-D (d).

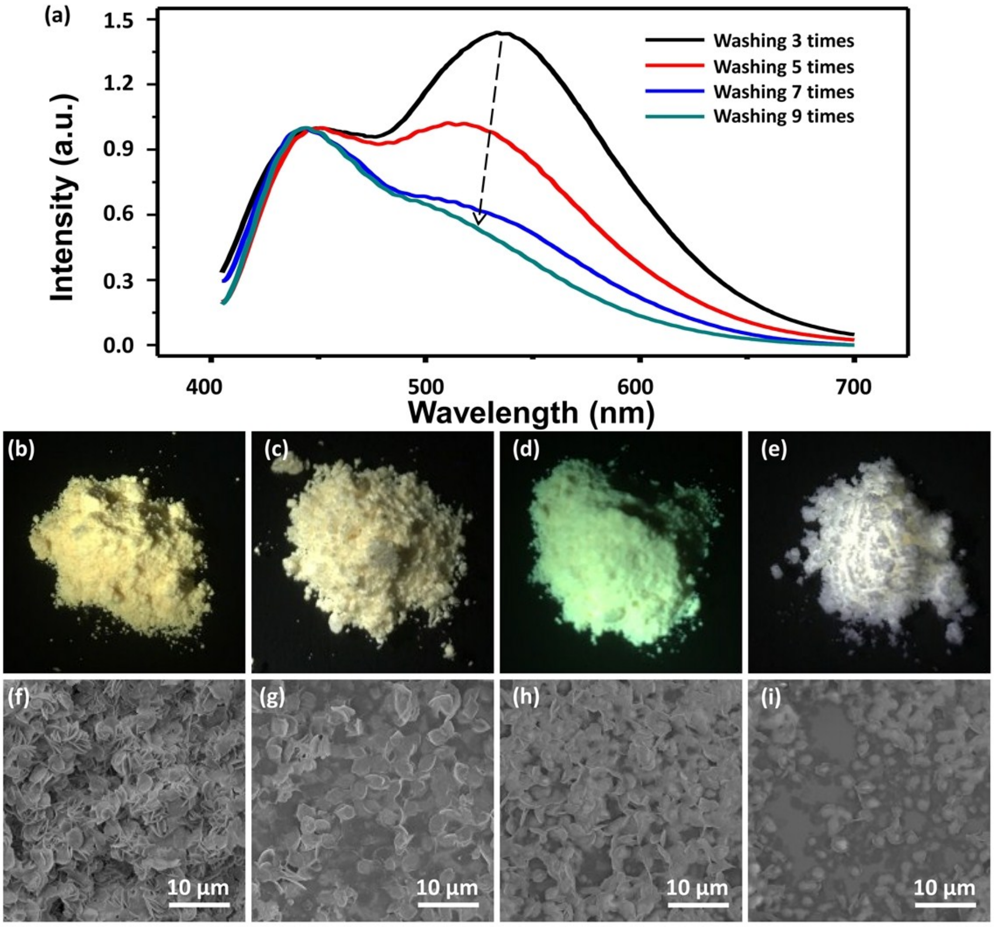

Fig. S6 (a) PL spectra, (b-e) photographs and (f-i) SEM images of CP-15 with different washing times, (b, f) 3 times, (c, g) 5 times, (d, h) 7 times and (e, i) 9 times, respectively.

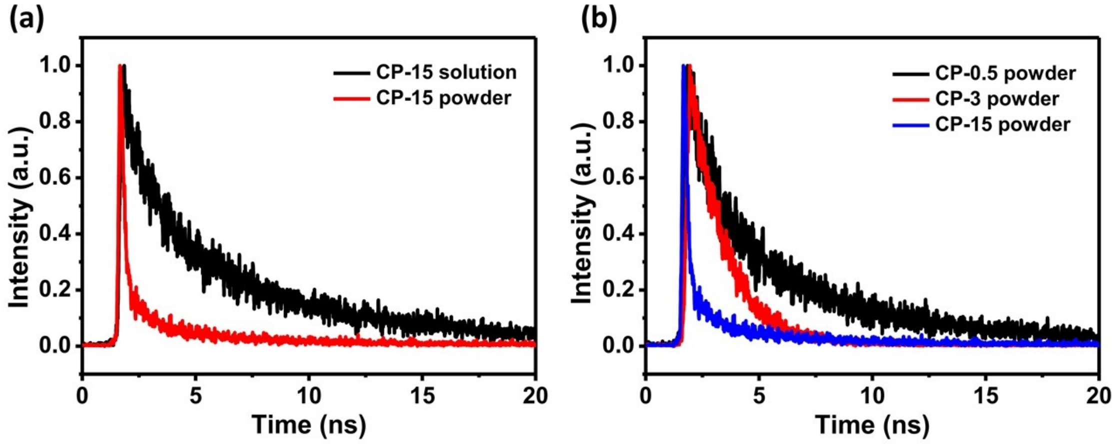

Fig. S7 Fluorescence decay curves of nanocarbon emitter powders and solution.

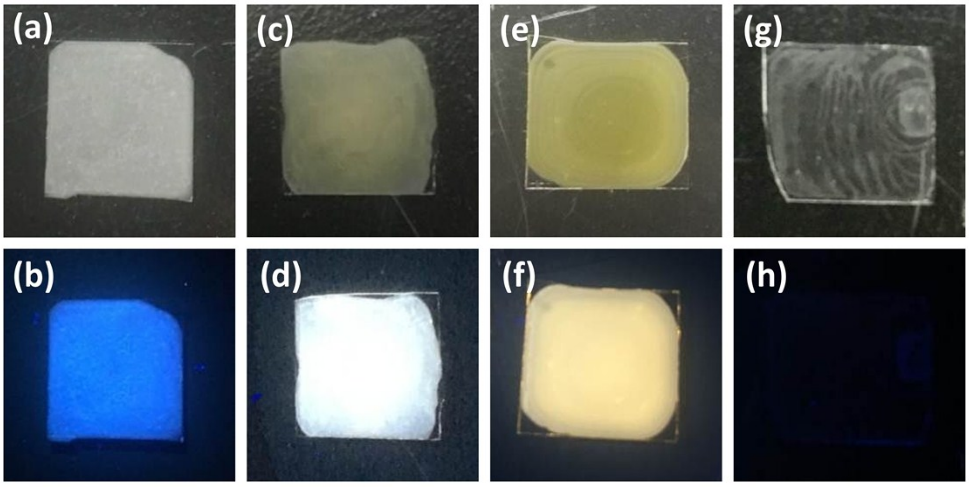

Fig. S8 Photographs of films under daylight (top) and UV light (bottom) by drop-coating CP-0.5, CP-3, CP-15 and the dialyzed CDs on the glass substrates, respectively. The dialyzed CD film exhibits relative poor film-forming ability and weak emission due to AIQ effect.

Table S1 Photoelectric parameters of the phosphor-coated LEDs

Sample	CIE		CCT (K)	CRI
1	0.18	0.16	/	/
2	0.21	0.18	10893	/
3	0.23	0.24	9013	/
4	0.32	0.31	6848	80
5	0.32	0.40	6462	68
6	0.41	0.47	3949	67
7	0.47	0.49	3130	62

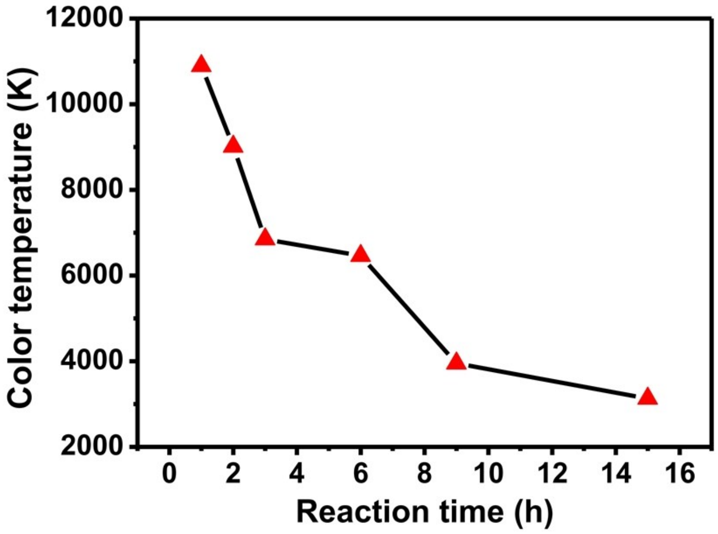

Fig. S9 Graph of the color temperature of the LEDs coated with different emitters.

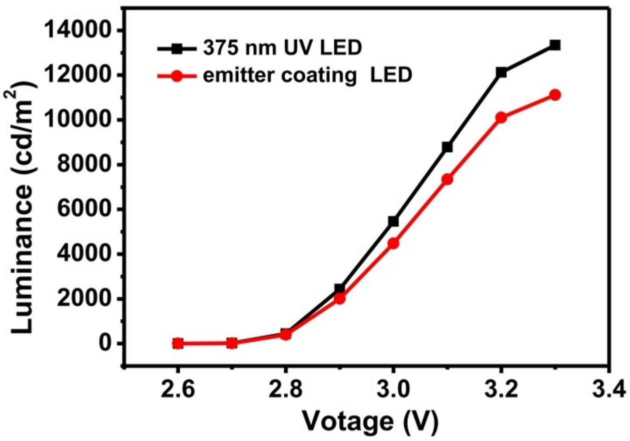

Fig. S10 Graph of luminance of 375 nm UV LED and nanocarbon emitter coating LED.

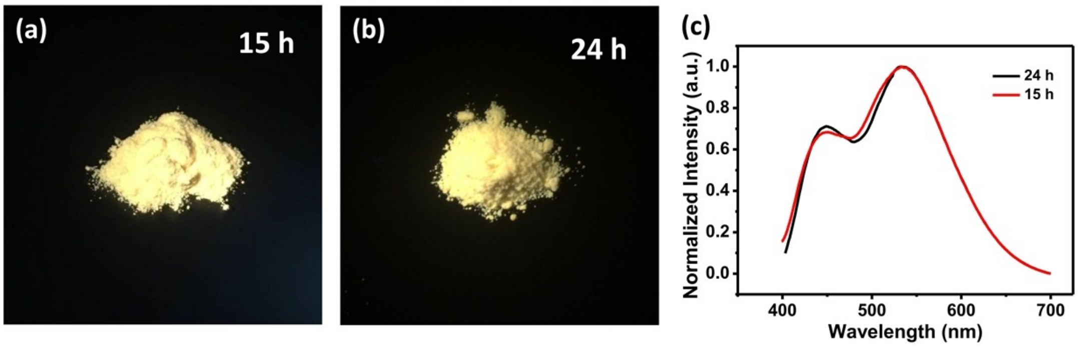

Fig. S11 Photographs of nanocarbon emitters under 380 nm irradiation with different reaction times (a) 15 h and (b) 24 h, respectively. Normalized PL spectra of these two emitters under 380 nm excitation. No obvious change of optical properties can be observed when the reaction time is extended to 24 h.