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## COMMUNICATION

## Down-conversion monochrome light-emitting diodes with the color determined by the active layer thickness and concentration of carbon dots†

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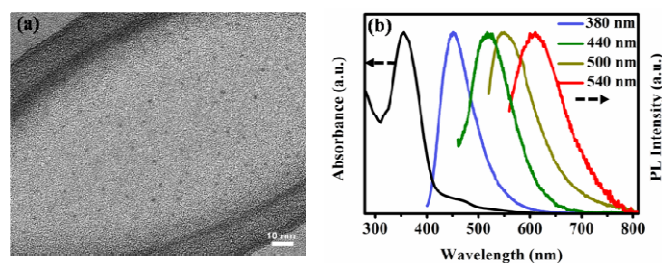
Chun Sun<sup>a,e</sup>, Yu Zhang<sup>a,b,c,\*</sup>, Sergii Kalytchuk<sup>d</sup>, Yu Wang<sup>d</sup>, Xiaoyu Zhang<sup>a</sup>, Wenzhu Gao<sup>c</sup>, Jun Zhao<sup>e</sup>, Klara Cepe<sup>d</sup>, Radek Zboril<sup>d</sup>, William W. Yu<sup>a,e</sup>, and Andrey L. Rogach<sup>b,\*</sup>

**We report a series of monochrome light-emitting diodes based on monodisperse carbon dots with an emission color ranging from blue to red, which is determined by the thickness of the down-conversion layers and the carbon dot doping concentration in the polymer matrix. We further demonstrate the potential of CDs for fabrication of relief graphical pattern with anti-counterfeiting security.**

Multicolor luminescent materials with tunable emission are attractive components of light-emitting displays and energy-saving light sources.<sup>1–5</sup> In virtue of their excitation wavelength dependent photoluminescence (PL),<sup>6,7</sup> carbon dots (CDs) are promising candidates for multicolor luminescent materials.<sup>8,9</sup> These low-toxic nanoparticles possess broadband optical absorption, good chemical stability, and can be easily functionalized.<sup>6,10–15</sup> Recently, pixelated color structures utilizing different kinds of CDs emitting over the broad spectral range in the visible have been reported.<sup>16</sup> Contrary to that concept, we have made use of the excitation wavelength dependent emission of CDs by employing one and the same nanoparticles to fabricate a series of monochrome light-emitting diodes (LEDs), where the emission color is determined by the down-conversion layer thickness and the CD concentration in the polymer matrix. The physical origin of this effect is ascribed to the reabsorption/reemission of light in the down-conversion CD layer. We realized a transparent pattern of different colors from CDs embedded in a PMMA matrix of varying thickness, which can be promising for fabrication of color converters for light-emitting devices and full color displays, where primary three-color pattern of RGB (red, green and blue) subpixels are formed by CD layers with varying thickness. We further demonstrate the potential of CDs for fabrication of relief graphical pattern with anti-counterfeiting security features.

CDs were synthesized by a previously reported method with minor modifications.<sup>17</sup> 10 mL of N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane (AEAPMS) was placed in a 100 mL three-neck round-bottom flask, degassed by applying vacuum for 30 min, and heated up under nitrogen atmosphere. When the temperature reached 240 °C, 0.5 g of anhydrous citric acid was added under vigorous stirring, the reaction mixture solution was kept

at this temperature for 1 min, and cooled down to room temperature naturally. CDs were purified by precipitation with petroleum ether for 3 times, and redispersed in chloroform with a desired concentration of 366 mg/mL. The as-synthesized CDs were monodisperse nanoparticles with an average size of 1.54 nm (Fig 1a), whose emission spectra showed a well documented<sup>18,19</sup> excitation wavelength dependence of the emission maximum (Fig. 1b). Furthermore, as shown in Fig S1, the PL quantum yield (QY) of CDs was as high as 47% at 360 nm excitation. From the Fourier transform infrared (FTIR) analysis of CDs, a characteristic peak at 1654  $\text{cm}^{-1}$  assigned to the stretching vibration of C=O groups and two signals at 1005 and 1126  $\text{cm}^{-1}$  from Si–O–C and Si–O–Si vibrations were observed, which confirmed the capping of CDs by AEAPMS.

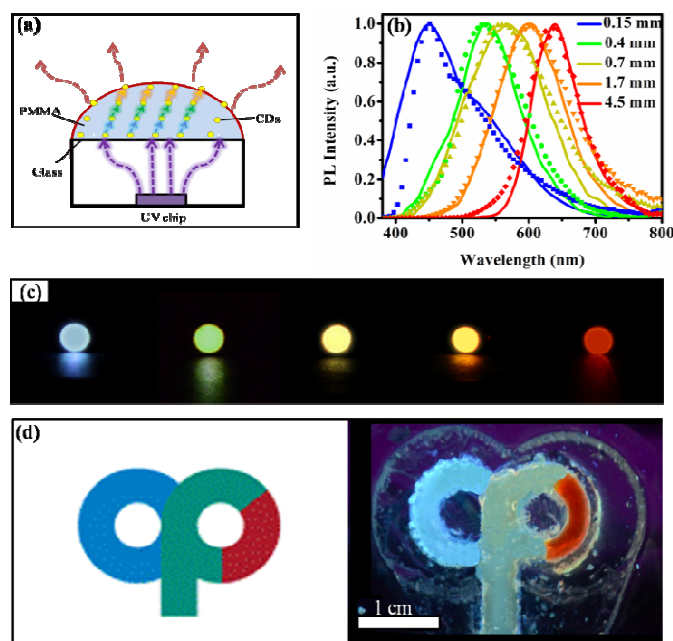


**Fig. 1**(a) TEM image of CDs. (b) Absorption and normalized PL spectra of CDs excited by light of various wavelengths as indicated on the frame.

The emission in the blue peaked at 460 nm is obtained when CDs are excited at 380 nm; the excitation at that wavelength results in a green emission from the same particles with the peak of 540 nm; and, consequently, excitation at 540 nm results in the appearance of the red emission peaked at 620 nm. This effect has been used in our previous work<sup>9</sup> to realize free-standing, transparent CD-based ionogel films with the emission color tunable over the whole visible range from blue to red by adjusting the distance from the excitation beam position to the emitting surface. We made use of this concept to produce the down-conversion layer thickness controlled monochrome LEDs utilizing 385 nm UV chips as an excitation light

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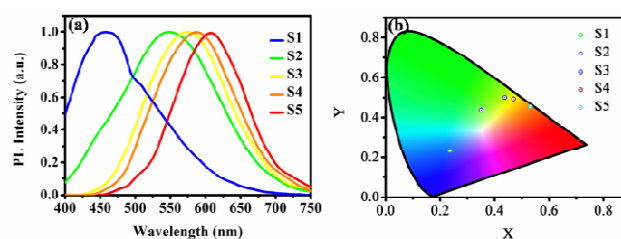
source (Fig. 2a). 0.5 mL of CD solution in chloroform were mixed with 3 mL of a transparent polymethylmethacrylate (PMMA)/chloroform solution (15% by weight), and deposited dropwise in a layer-by-layer fashion onto the UV-LED chips to achieve the desired thickness of the active layer, with curing at room temperature for 30 min to solidify the layers. As Fig. 2b shows, the emission color of LEDs can be smoothly tuned from the blue to the red with down-conversion CD/PMMA layer thickness increasing from 0.15 to 4.5 mm. Thin layers generate blue light; upon the deposition of more CDs, the outer layer absorbed the blue light from the inner layer and reemitted green light. Upon the further increase of the CD layer thickness from 0.7 mm to 4.5 mm, the color of the CD-LED changed from yellow to orange, and finally to red (Fig. 2c). The corresponding Commission Internationale de l'Éclairage (CIE) color coordinates could be thus finely tuned from (0.405, 0.482) to (0.649, 0.343). Fig S3 shows the luminance of the CD-LEDs with increasing applied voltage. The blue and red emitting LEDs show relatively low brightness due to the low eye sensitivity. Thicker layers cause strong reabsorption, which may also decrease the brightness of red emitting LED. The luminous efficiency of LEDs was measured, as shown in Fig S4. The highest luminance and luminous efficiency reached  $11890 \text{ cd/m}^2$  and  $1.21 \text{ cd/A}$ , respectively. The luminous efficiency of red LEDs is relatively low, because of the low PL QY of CDs in this region, strong reabsorption due to the large layer thickness, and low eye sensitivity to red light. Although the luminous efficiency of red LEDs is not high, it is higher than reported in our previous work for electroluminescent CDs-based LED.<sup>8</sup> In order to analyze the stability of these LEDs, the emission intensities were measured at different working time intervals. The emission intensities of all devices decreased only slightly upon continuous operation of LEDs for 6 h (Fig S5).



**Fig. 2**(a) Schematic diagram of the monochrome CD-LED with CDs embedded in a PMMA matrix of a variable layer thickness, which was deposited on top of a UV-LED chip. (b) Experimental PL spectra (solid lines) compared with the modeled spectra (symbols; see main text for details). (c) True-color photographs of monochrome CD-LEDs of five different colors determined by the thickness of the CD active layer. (d) The left picture is the color logo of the Center for Functional Photonics at City University of Hong Kong (<http://www6.cityu.edu.hk/cfp/>), and the right is the pattern of the same logo made of CD/PMMA layers of different thickness taken under 365nm UV light.

To gain a better understanding of the mechanisms behind the marked emission color change within the CD-LED realized by varying the thickness of the CD down-conversion layer, we have modeled the emission of layers with different thickness from the excitation-dependent PL and the absorption spectra by calculating the transmitted and emission spectra for an incremental sample thickness and taking the sum of these spectra as the excitation for the next thickness increment. Approximating the emitted spectrum from each sub-layer section as a single wavelength source for the next section, a very reasonable agreement in the position of emission peaks with the measured PL maximum has been obtained over several millimeter path thicknesses, as demonstrated in Fig. 2b. To illustrate the feasibility of fabrication of thickness-controlled patterns with CD-based down-conversion layers which can be used as anti-counterfeiting elements, we created a logo of the Centre for Functional Photonics (CFP) of City University of Hong Kong from CD/PMMA layers of different thickness, as shown in Fig. 2d. Illuminated with UV light, such prototype exhibits color pattern specified by its relief, so that the documents tagged with such security elements can be easily authenticated by visualization under UV light.

As the full-color monochrome CD-based LEDs can be realized by controlling the thickness of the down-converting layer, we assumed that the same effect could also be achieved by varying the CD concentration in the polymer matrix while maintaining the same layer thickness. Indeed, it was possible to fabricate five monochrome LEDs with the same thickness of 4.5 mm for CD down-conversion layer but different concentration of the CD (Fig. 3) by deposition of 1 mL of the chloroform solution of CDs mixed with the PMMA/chloroform solution (15% by weight) of different volumes (S1: 15 mL, S2: 5 mL, S3: 2.5 mL, S4: 1 mL, S5: 0.3 mL). The increased CD concentration resulted in the higher probability of the re-absorption/reemission of light propagating through the layer, and thus to the red-shifted resulting emission.



**Fig. 3**(a) PL spectra and (b) the corresponding CIE color coordinates of monochrome CD-LEDs of five different colors realised by varying the CD concentration in the down-conversion layer.

In conclusion, monochrome LEDs with full-color emission tunability were realised by variation of the thickness and the concentration of CDs in their down-conversion layers. The physical origin of this effect is ascribed to the excitation wavelength dependent emission of CDs, so that the reabsorption and reemission of light with progressively increased light propagation distance and/or particle concentration results in a continuous red-shift of the emission color. A luminescent logo pattern with anti-counterfeiting security features was fabricated to show their potential in full-color displays, whose primary three-color pattern of RGB (red, green and blue) subpixels could be formed by varying the thickness of CD layers.

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### Notes and references

<sup>a</sup>State Key Laboratory on Integrated Optoelectronics, and College of Electronic Science and Engineering, Jilin University, Changchun 130012, China. E-mail: yuzhang@jlu.edu.cn (Y. Zhang)

<sup>b</sup>Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Hong Kong SAR. E-mail: andrey.rogach@cityu.edu.hk (A. L. Rogach)

<sup>c</sup>State Key Laboratory of Superhard Materials, and College of Physics, Jilin University, Changchun 130012, China

<sup>d</sup>Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacký University in Olomouc, Šlechtitelů 11, 783 71 Olomouc, Czech Republic.

<sup>e</sup>College of Material Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

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