

Supporting Information

Multicolor Tunable Highly Luminescent Carbon Dots for Remote Force Measurement and White Light Emitting Diode

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Electronic supplementary information (ESI) available: the description of various testing methodologies, characterizations, and explanations of these materials can be seen in Table S1-S3, Fig. S1-S16

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Experimental

Materials. Tobias acid, o-phenylenediamine, dimethylformamide, formamide and concentrated sulfuric acid (98 wt%) were obtained from Tianjin Fuchen chemical reagent factory and Energy Chemical Reagent Co., Ltd.. PVA (degree of polymerization: 2699) was purchased from Anhui Wanwei Group Co. Hydroxyethyl cellulose (Analytical Grade) was purchased from Life Technologies Corporation. Chitosan was purchased from Beijing Bellingway Technology Co. Ltd. NaOH, HCl, CuSO₄, HgCl₂, NaCl, FeCl₃, AgNO₃ and sodium tetraborate (Analytical Grade: Na₂B₄O₇·10H₂O) were purchased from Tianjin Guangfu Technology Development Co. Ltd. Glycerol was purchased from Beijing Solarbio Science Technology Co. Ltd (Analytical Grade). Deionized water was used for all experiments. THP-1 monocytes were obtained from ATCC, Manassas, VA, USA. NucleoCounter NC-3000 were

obtained from ChemoMetec A/S, Allerød, Denmark. All chemical reagents are analytical grade and used without further purification.

Synthesis of B/Y/R-CDs. In this study, multiple color emissive CDs were obtained from tobias acid and o-phenylenediamine by solvothermal method. For R-CDs, 0.01 g tobias acid and 0.35 g o-phenylenediamine were dissolved in 10 mL diluted sulfuric acid (3.4 mol/L) and heated at 210 °C for 10 h. For Y-CDs, 0.01 g tobias acid and 0.20 g o-phenylenediamine were dissolved in 10 mL ethanol followed by heating at 180 °C for 10 h. For B-CDs, 0.01 g tobias acid and 0.3 g o-phenylenediamine were dissolved in 10 mL formamide and kept at 210 °C for 10 h. After that, each as-prepared solution was filtered through a membrane filter (0.22 μm), and then precipitated with a KOH aqueous solution. Finally, the precipitation was collected by centrifugation at 10,000 rpm for 10 mins, and dried in vacuum overnight at 60°C to obtain solid powder. 20 μL purified samples were dispersed in 2 mL dilute aqueous solutions for further characterizations.

Preparation of fluorescent hydrogels. In this experiment, PVA (10 g), hydroxyethyl cellulose (0.5 g), chitosan(0.5 g) and glycerin (3 mL) were dissolved in deionized water to prepare 50 mL solution. The solution was manually stirred for 2 minutes and subsequently oil-bathed at 98 °C for 2 hours to form a solution at a 20 wt % PVA mass fraction. Then 50 mL of the solution was mixed with 50 mL borax solution (0.04 mol/L), which was added to B/Y/R-CDs and heated in a 90 °C oil bath for 1 h with stirring. The fluorescent hydrogels were obtained. Next, the hydrogels were pressed for 2 h to remove air bubbles from the gel and shape the material into a desired geometry.

Cytotoxicity assays. The cytotoxicity of CD to THP-1 monocytes was measured by cell counting kit-8 (CCK-8) assay, which could indicate the activities of mitochondria in living cells. Briefly, 6×10⁶ per well THP-1 monocytes were seeded in 24-well plates and exposed to various concentrations of CDs. After 24 h exposure, the cells were rinsed once, and CCK-8 assay was completed with the commercial kits following manufacturer's instructions (Beyotime, Nantong, China). Data were expressed as mean±SD with n=3. Meanwhile, the cytotoxicity of R-CDs to THP-1 monocytes was also confirmed with acridine orange (AO)/DAPI counterstaining. By this assay, living cells were stained with green fluorescence by AO, whereas dead cells were stained with blue fluorescence by DAPI. Briefly, 6×10⁶ per well THP-1 monocytes were seeded in 24-well plates and exposed to 100 μg/mL R-CDs for 24 h. After exposure, the cellular viability was measured with a commercial kit (solution 13) following manufacturer's instruction (ChemoMetec A/S, Allerød, Denmark). The samples were imaged and analyzed by NucleoCounter NC-3000 (ChemoMetec A/S, Allerød, Denmark).

Flow cytometry analysis. Here, THP-1 monocytes were seeded at a density of 6×10⁵ per well in 12-well plates and exposed to 100 μg/mL CD for 24 h. Cells incubated with medium were used as control. After exposure, the cells were rinsed once and then collected by centrifuge. The samples were analysed by NC-3000.

Characterizations. The morphology of the prepared B/Y/R-CDs was investigated by transmission electron microscopy (TEM; Model JEM-2100). Scanning electron microscopy (SEM) images were taken with a SU8010 scanning electron microscope. The atomic force microscopy (AFM) images were obtained with a Bruker Scan-Dimension-Icon System. A fluorescent spectrophotometer (FS5 from Techcomp (China) Ltd.) was used to

characterize the time-resolved fluorescence and ultraviolet-visible (UV-vis) absorption spectra. A Bruker Vertex 70 v was employed for the measurement of Fourier transform infrared (FTIR) spectrum. X-ray photoelectron spectroscopy (XPS) analysis was performed by an ESCALAB 250 spectrometer with a monochromatic X-ray source Al K α excitation (1,486.6 eV). Raman spectroscopy was implemented with a Horiba Jobin Yvon Xplora confocal Raman microscope with 532 nm laser irradiation at room temperature. Zeta potential was measured on a nano Z zeta potential analyzer. Thermogravimetric analysis (TGA) measurements were carried out on a TA Instruments Q500 TGA analyzer.

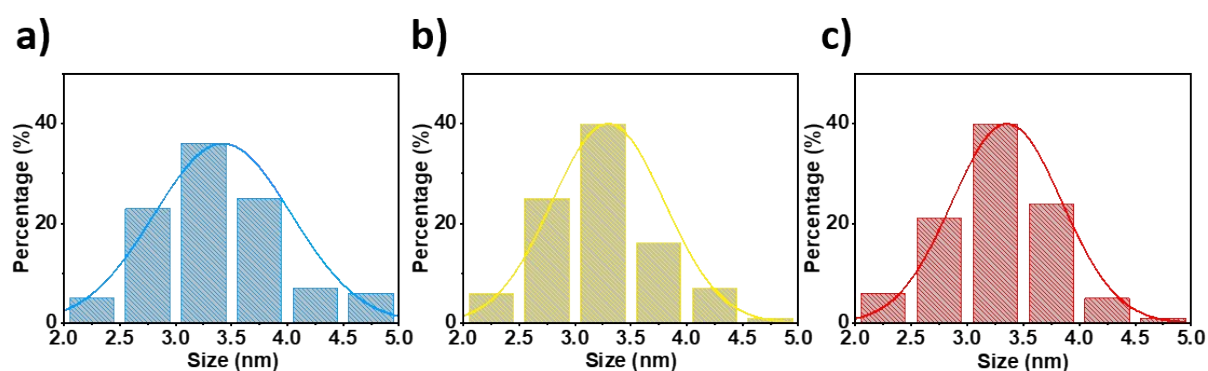


Figure S1 Particle size distribution diagrams of (a) B-CDs, (b) Y-CDs and (c) R-CDs from TEM.

Supplementary explanation

Select a plurality of grains from the Figure 2 (a-c) TEM image as the target, and then perform particle size analysis to obtain particle size distribution diagrams.

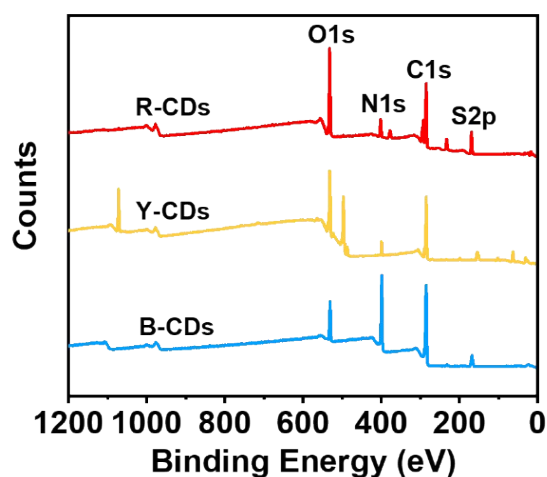


Figure S2 XPS spectra of the B/Y/R-CDs.

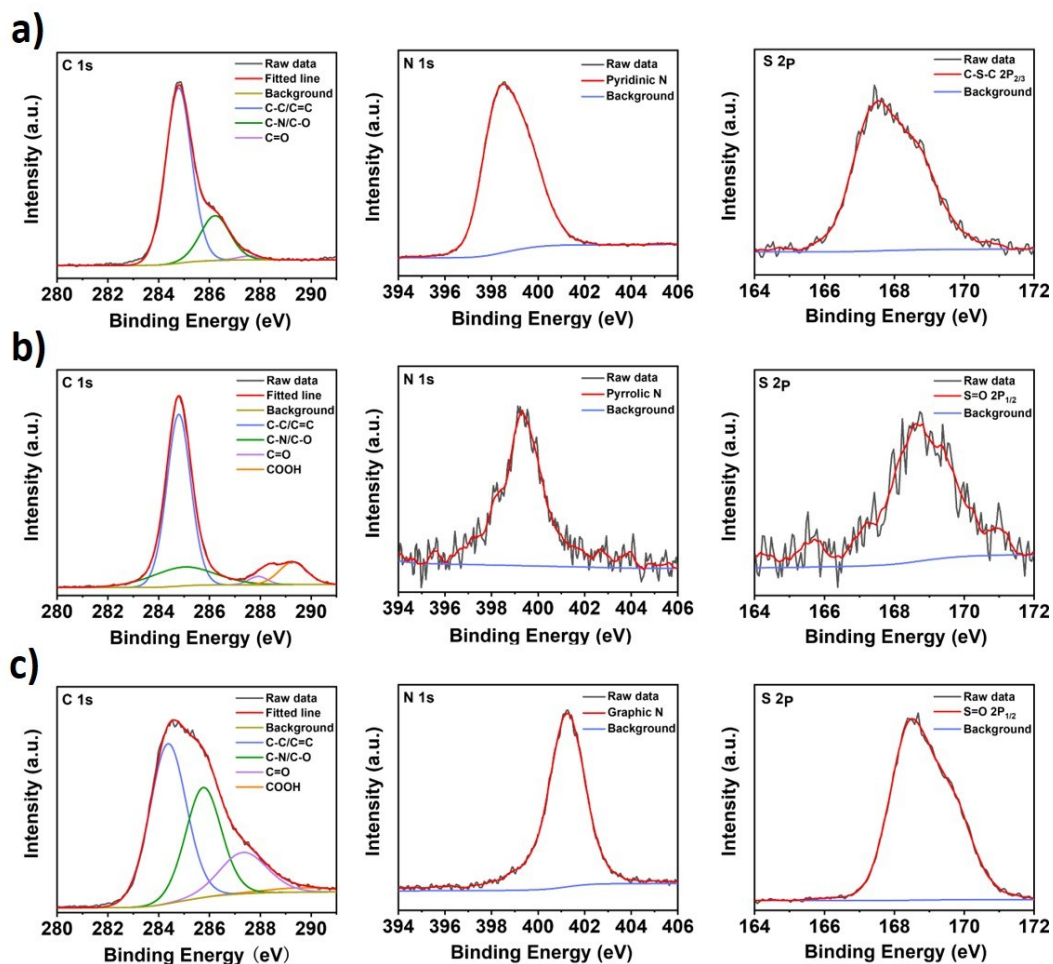


Figure S3 High-resolution XPS C 1s, N 1s, and S 2p spectra of (a) B-CDs, (b) Y-CDs and (c) R-CDs.

Supplementary explanation

The N peak of the three samples shifts from 398.5 to 401.2 eV, as a result of the change in nitrogen bonding configuration from pyridinic N (B-CDs) to graphitic N (R-CDs). The S 2p XPS spectra of the B/Y/R-CDs show one similar peak. The S peak at 167.5 eV observed in B-CDs is assigned to S 2p_{2/3} C–S–C structure, while the S peak of Y-CDs and R-CDs show one main band at slightly higher energy (168.6 eV), corresponding to -C-SO_x-C- sulfone bridges in thiophene-type structure.

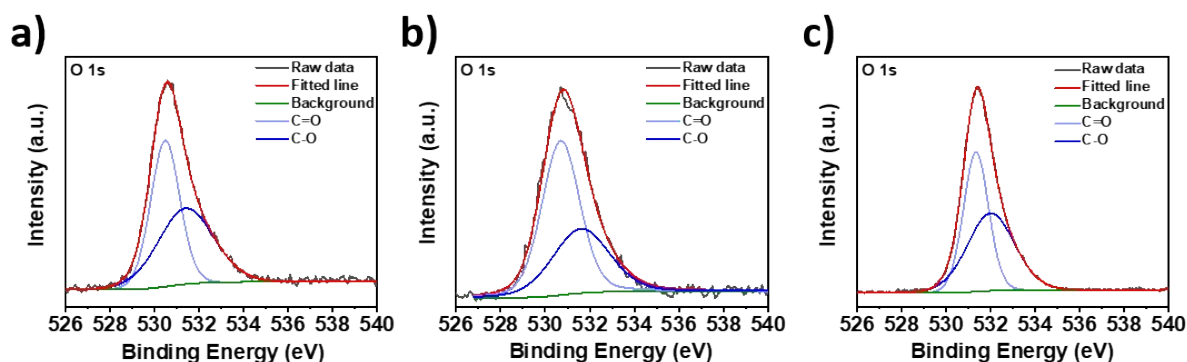


Figure S4 High-resolution XPS O 1s spectra of (a) B-CDs, (b) Y-CDs and (c) R-CDs.

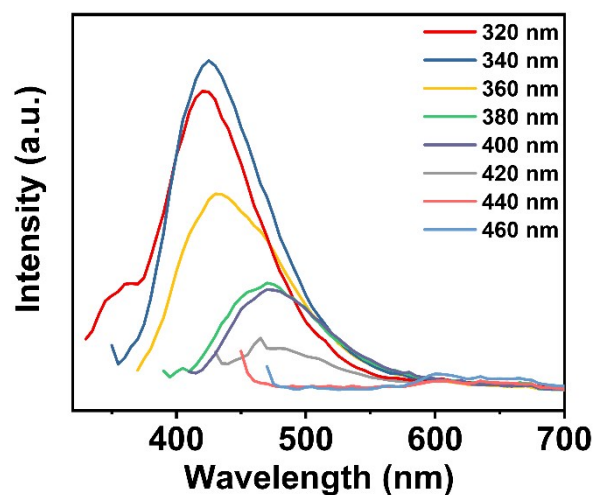


Figure S5 Photoluminescence spectrum of R-CDs in the presence of NaBH₄ with concentration of 10 g/L.

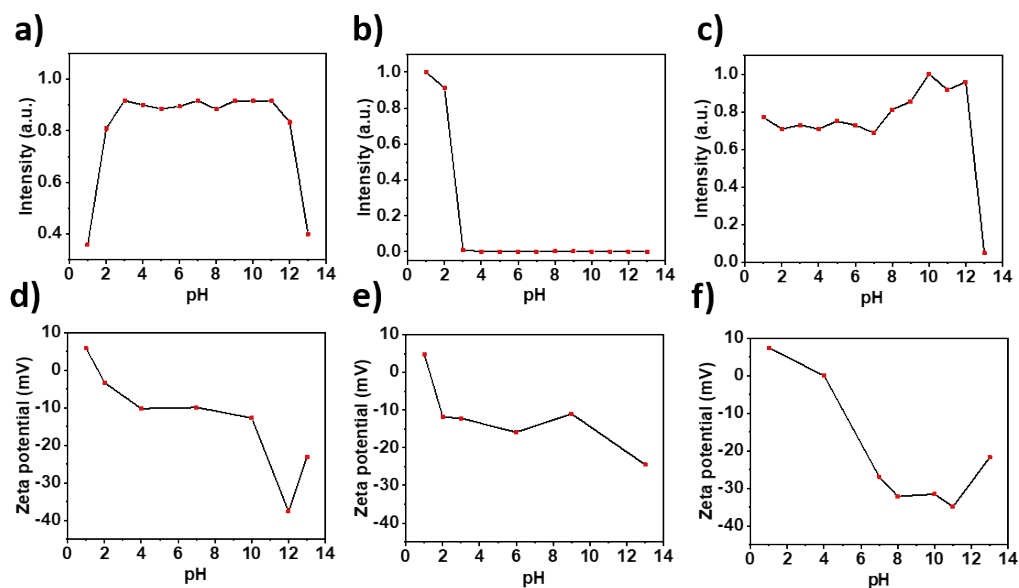


Figure S6 (a-c) Effect of pH on the fluorescence intensity of (a) B-CDs, (b) Y-CDs and (c) R-CDs. (d-f) Zeta potential of (d) B-CDs, (e) Y-CDs and (f) R-CDs as a function of pH.

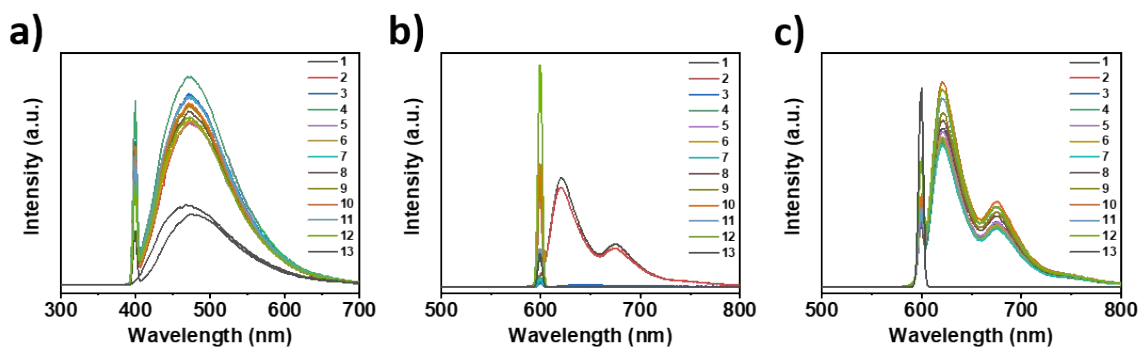


Figure S7 Fluorescence spectra of (a) B-CDs, (b) Y-CDs and (c) R-CDs at different pH values.

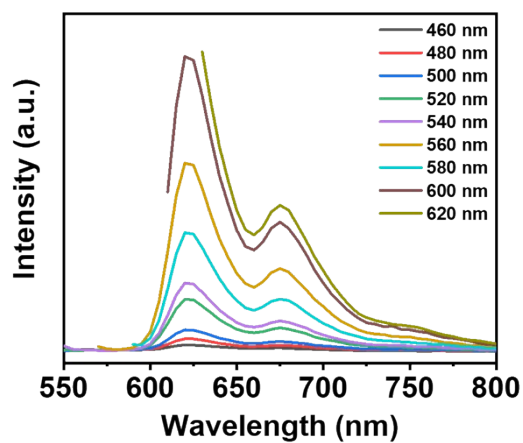


Figure S8 Photoluminescence spectra of the Y-CDs in acidic solutions (pH=1).

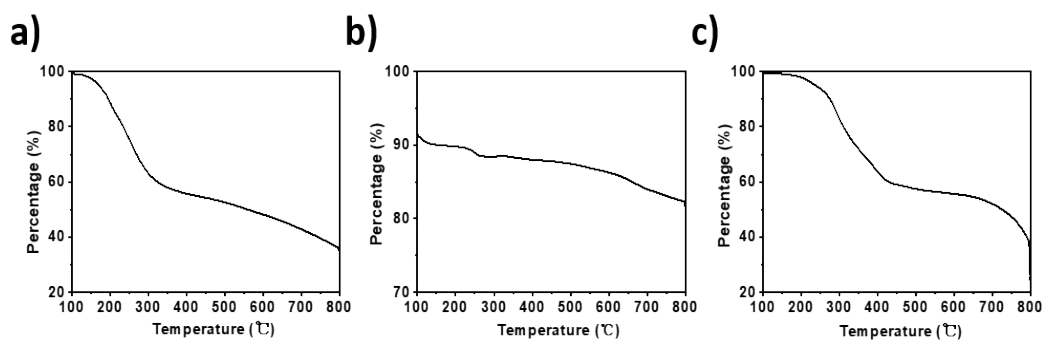


Figure S9 TGA spectrum of (a) B-CDs, (b) Y-CDs and (c) R-CDs.

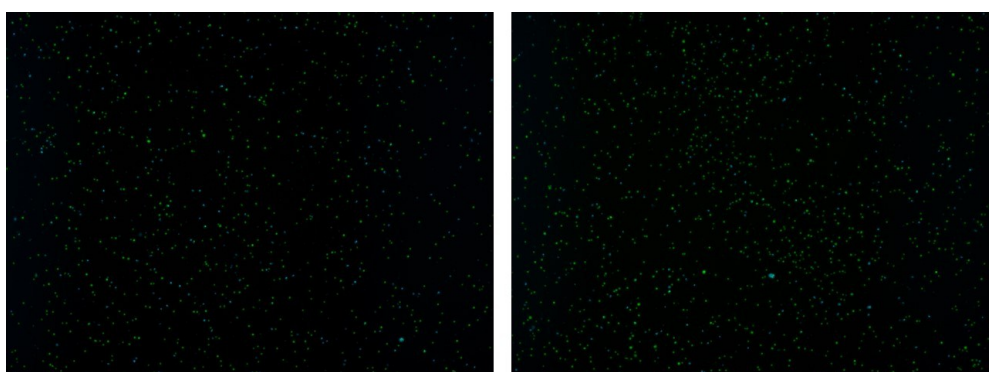


Figure S10 Cytotoxicity assay by AO/DAPI staining of R-CDs (Left control; right R-CDs treated cells).

Supplementary explanation

Fig. S10 confirms that treatment with 100 $\mu\text{g/mL}$ R-CDs did not induce cytotoxicity; the green color indicates viable cells labelled by AO, and blue color indicates dead cells labelled by DAPI.

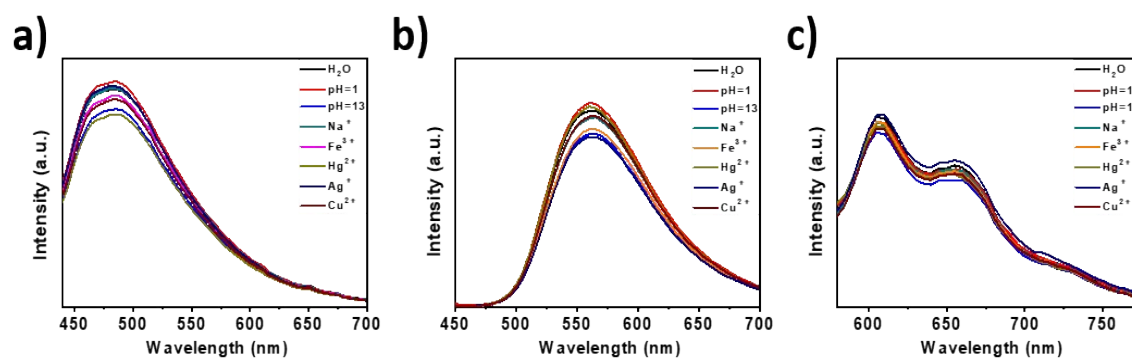


Figure S11 Relationship between fluorescence intensity and emission wavelength of (a) B-CDs, (b) Y-CDs and (c) R-CDs doped hydrogel in different solutions.

Supplementary explanation

Fig. S11 shows the fluorescence properties of the fluorescent hydrogels were tested in different environments.

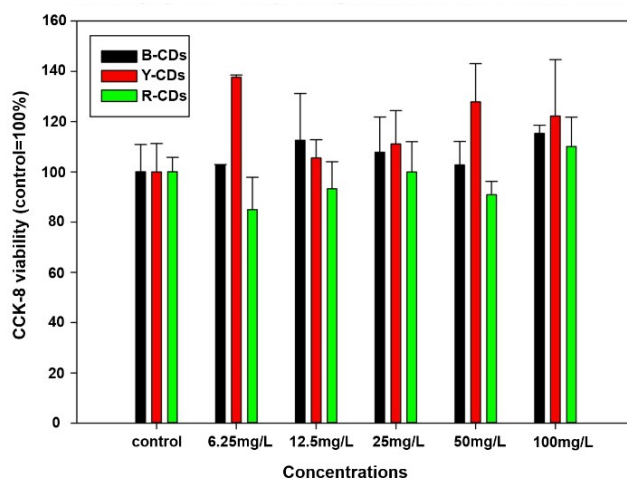


Figure S12 Cell viability of THP-1 monocytes with different concentrations of the B/Y/R-CDs.

Supplementary explanation

Fig. S12 indicates no significant loss of cellular viability after exposure to up to 100 $\mu\text{g/mL}$ CDs.

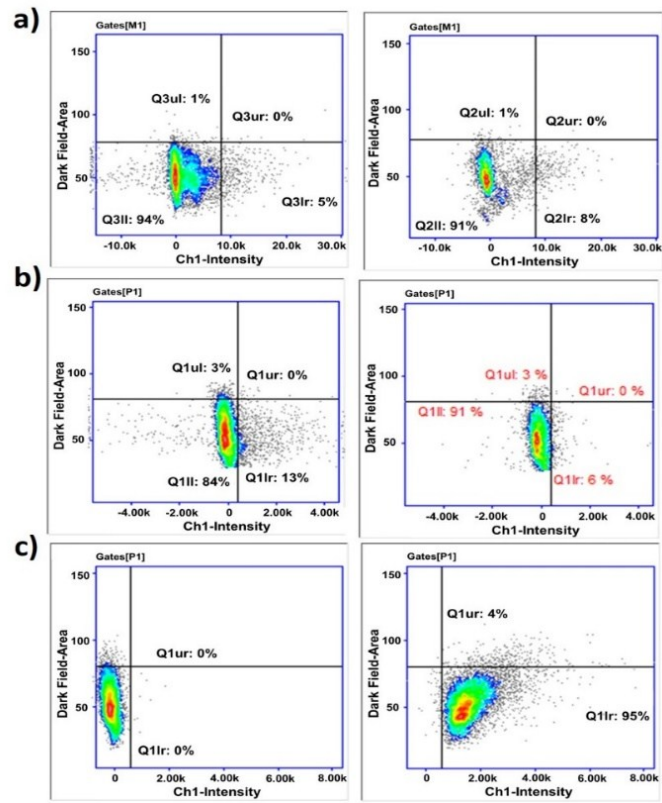


Figure S13 Flow cytometry with (a) B-CDs, (b) Y-CDs and (c) R-CDs (left control, right stained).

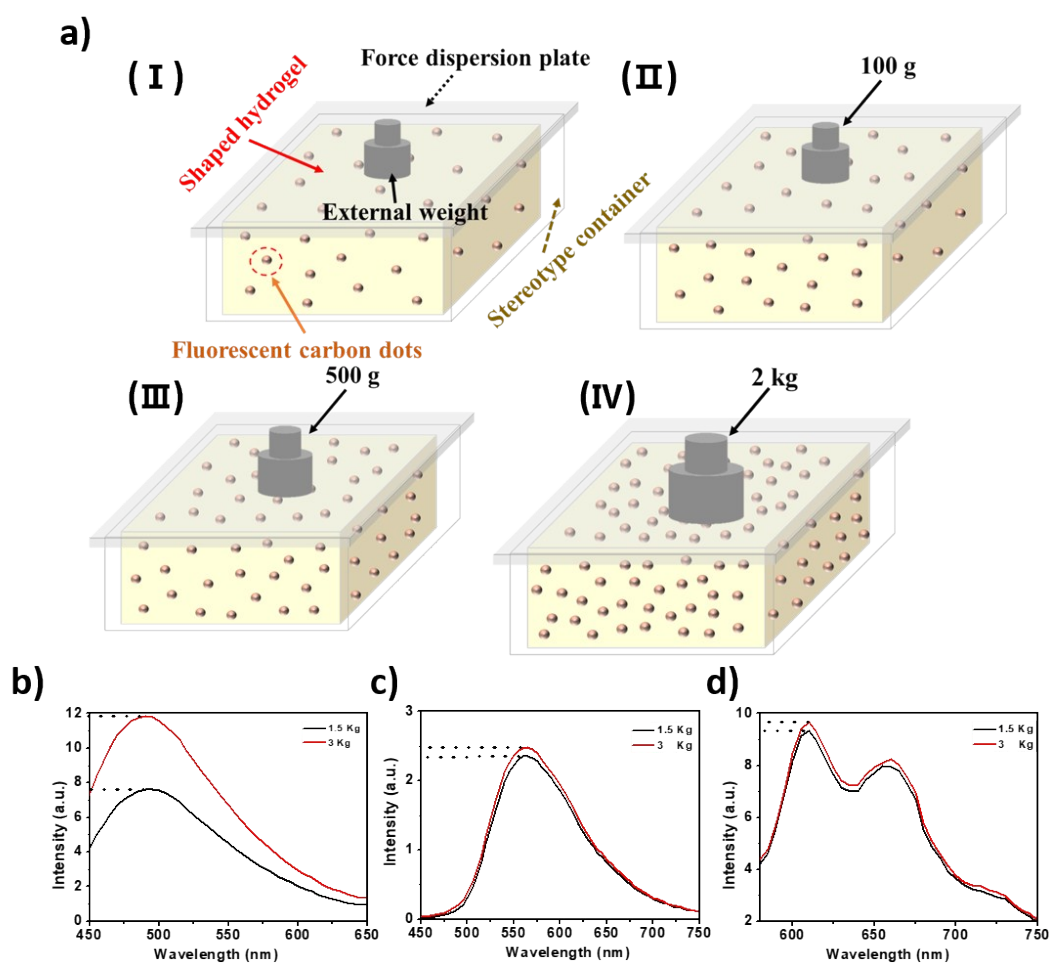


Figure S14 (a) Mechanism of a hydrogel fluorescence emission intensity test. (b-d) The relationship between the fluorescence intensity of (b) B-CDs, (c) Y-CDs and (d) R-CDs doped hydrogel and the external force (3 kg; 1.5 kg) to which hydrogel was subjected.

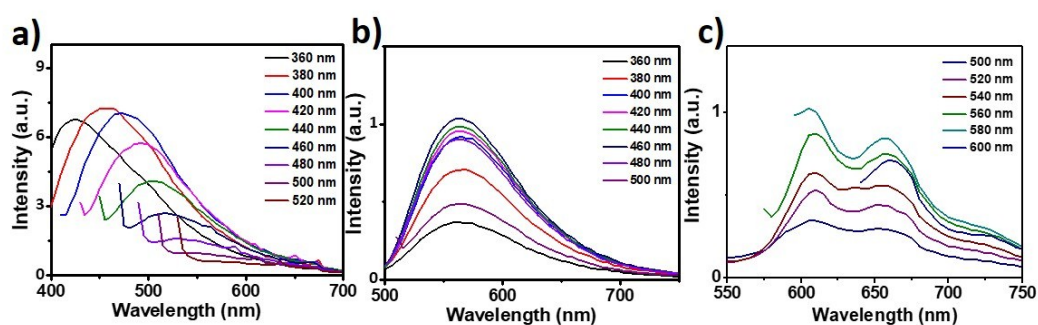


Figure S15 Photoluminescent spectra of multicolor CDs / hydrogel on excited at different wavelengths. (a)B-CDs; (b)Y-CDs; (c) R-CDs.

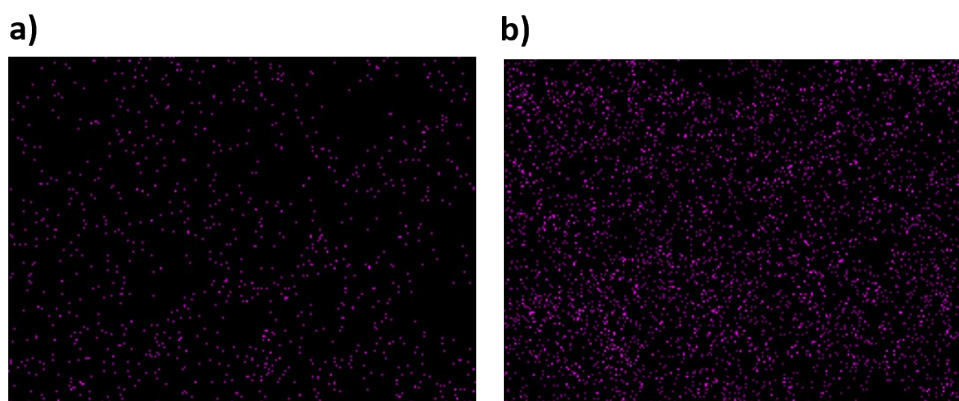


Figure S16 (a) SEM image of hydrogel (1 kg external force). (b) SEM image of hydrogel (5 kg external force).

Table S1 The C, N, O and S element contents of the B/Y/R-CDs determined by XPS results.

Sample	C (%)	N (%)	O (%)	S (%)
B-CDs	58.7	29.69	10.61	1.01
Y-CDs	61.48	1.88	36.14	0.51
R-CDs	50.12	10.72	30.56	8.61

Table S2 XPS data analyses of the C1s spectra of the R/Y/B-CDs determined.

Sample	C-C/C=C (%)	C-N/C-O (%)	C=O (%)	COOH (%)
B-CDs	76.10	22.40	1.50	—
Y-CDs	67.56	19.44	4.12	9.88
R-CDs	48.44	32.62	16.30	2.64

Table S3 The shift of emission wavelength in CDs in solution and their corresponding hydrogels.

Sample	In solution (nm)			In hydrogel (nm)	
	Ex.	Em.		Ex.	Em.
B-CDs	420	495	B-CDs / hydrogel	400	475
Y-CDs	420	575	Y-CDs / hydrogel	420	560
R-CDs	560	625/675	R-CDs / hydrogel	560	610/660