Supplementary Information

Unlocking Metal-free Multicolor Thermoluminescence in Carbon-Dot Composites via Traps Engineering

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Experimental Section

Reagents: Reagent grade of m-phenylenediamine (mPD), resorcinol and tartaric acid (TA) were bought from Aladdin Chemicals Co. Ltd (Shanghai, China). Methylene chloride, methanol, ethanol and urea were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All chemicals were used as received without further purification unless otherwise specified. Deionized (DI) water was used throughout this study.

Preparation of b-CDs: The b-CDs were synthesized in accordance with our previous report.[1] Typically, 0.90 g of mPD was dissolved in 90 mL of ethanol. The resulting solution was transferred into poly(tetrafluoroethylene)-lined autoclaves and heated to 180 °C for 12 hours. After cooling down to room temperature, the crude product was purified via silica column chromatography using a mixture of methylene chloride and methanol as the eluent. Following solvent removal, the products were dried under vacuum. Ultimately, the b-CDs were obtained with a yield of 15–20 wt%.

Preparation of g-CDs: The g-CDs were synthesized in accordance with our previous report.[2] Typically, mPD (0.90 g) and TA (1.2 g) were separately dissolved in 45 mL of ethanol, and the resulting solutions were mixed and transferred into poly(tetrafluoroethylene)-lined autoclaves. The mixture was heated at 180 °C for 12 hours. After cooling to room temperature, the crude product was purified via silica column chromatography using a mixture of methylene chloride and methanol as the eluent. Following solvent removal, the products were dried under vacuum. Ultimately, the g-CDs were obtained with a yield of 30–40 wt%.

Preparation of y-CDs: The *y*-CDs were prepared according to a previous report.[3] Typically, resorcinol (0.10 g) and mPD (0.10 g) were dissolved in 10 mL of ethanol and sonicated for 15 minutes. After being completely dissolved, the mixture was transferred into a poly(tetrafluoroethylene)-lined autoclave and heated at 180 °C for 6 hours. After cooling to room temperature naturally, the brown solution was first purified by filtration through polycarbonate membrane filters (from Filter-Lab) with a pore size of 0.22 μm. The supernatant was collected and further purified via silica column chromatography using a mixture of methylene chloride and methanol as the eluent. After the solvents were removed, the products were dried under vacuum. Finally, the y-CDs were obtained with yields of 20–30 wt%.

Preparation of pure CNs: The CNs were prepared according to our previous report.[4] Typically, 10 g of urea was dissolved in 20 mL of DI water to form a transparent solution. The solution was then transferred into a beaker and heated in a domestic microwave oven at 750 W for 8–10 minutes. The resulting crude product was crushed and purified by washing with 100 mL of boiling water, followed by centrifugation at 5000 rpm for 5 minutes. This process was repeated three times to ensure complete removal of impurities dissolved in the supernatant. Finally, the purified product was dried in a vacuum oven at 60 °C for 24 hours for subsequent use.

Preparation of b-, g- and y-CDs@CN: The CDs@CNs were prepared according to our previous report.[5] Typically, 1 mL of CDs (i.e., b-CDs, g-CDs, and y-CDs, 5 mg/mL in ethanol) was added to 20 mL of urea solution (0.5 g/mL in DI water) to form a transparent solution. The resulting solution was then transferred into a beaker and heated in a domestic microwave oven at 750 W for 8–10 minutes. The crude products obtained were crushed and purified by washing with 100 mL of boiling water, followed by centrifugation at 5000 rpm for 5 minutes. This process was repeated three times to ensure complete removal of impurities dissolved in the supernatant. Finally, the purified products were dried in a vacuum oven at 60 °C for 24 hours for subsequent use.

Preparation of the CDs@CNs-based silicone rubber films: Briefly, 0.20 g of grinded CDs@CNs phosphors and 1.0 g of PDMS were evenly mixed by mechanical stirring for 5 minutes. Subsequently, 0.10 g of silicone curing crosslinker was added to the mixture, and stirring was continued for an additional 5 minutes. The thoroughly mixed solution was transferred into a glass mold and cured in an oven at 50 °C for 4 hours. After cooling to room temperature naturally, the CDs@CNs-based LPL films were carefully removed from the molds.

Equipment and characterization: Afterglow decay profiles were measured using FS5 Spectrofluorometer (Edinburgh Instruments, England). The thermoluminescence (TL) glow curves were measured on SL08 luminescence measuring instrument (Guangzhou Radiation Science and Technology Co., Ltd, China). The PL, afterglow, and TL emission spectra were measured on F-7000 Spectrofluorometer (Hitachi, Japan). Photographs of photoluminescence (PL), afterglow and TL were taken using a EOS 550 camera (Canon, Japan) under excitation by a hand-hold UV (365 nm) lamp.

Supporting Figures and Tables

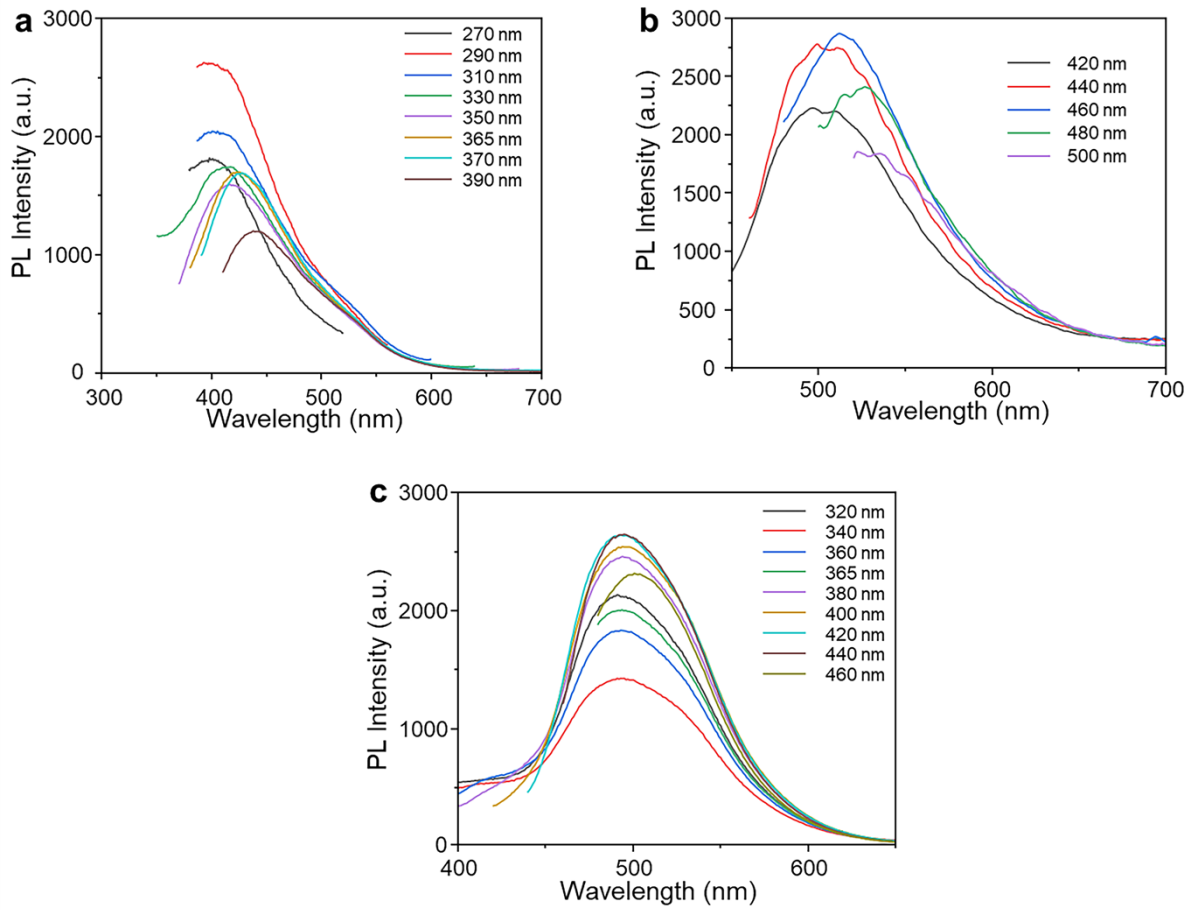

Figure S1. The photoluminescence (PL) emission spectra of (a) b-CDs@CN, (b) y-CDs@CN and (c) g-CDs@CN under the excitation of different wavelengths.

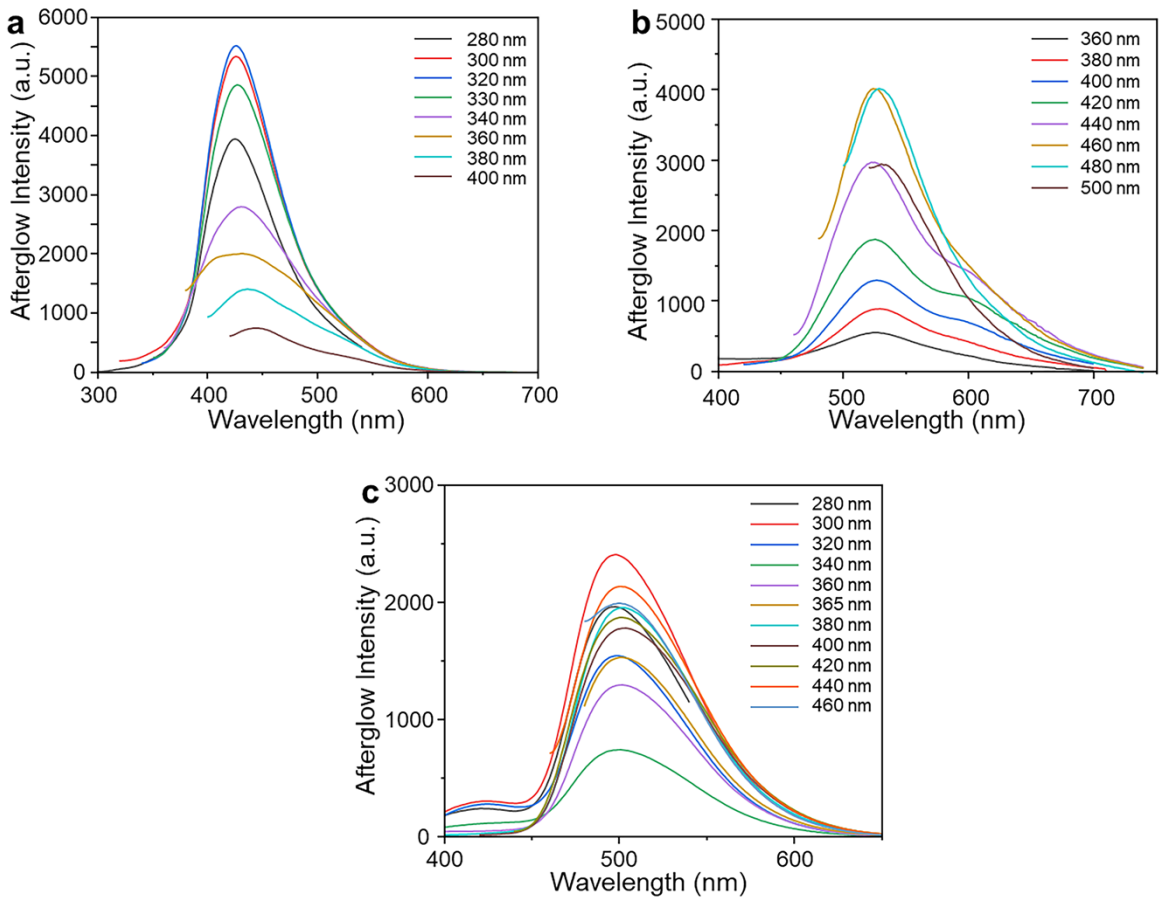

Figure S2. The afterglow emission spectra of (a) b-CDs@CN, (b) y-CDs@CN and (c) g-CDs@CN under the excitation of different wavelengths.

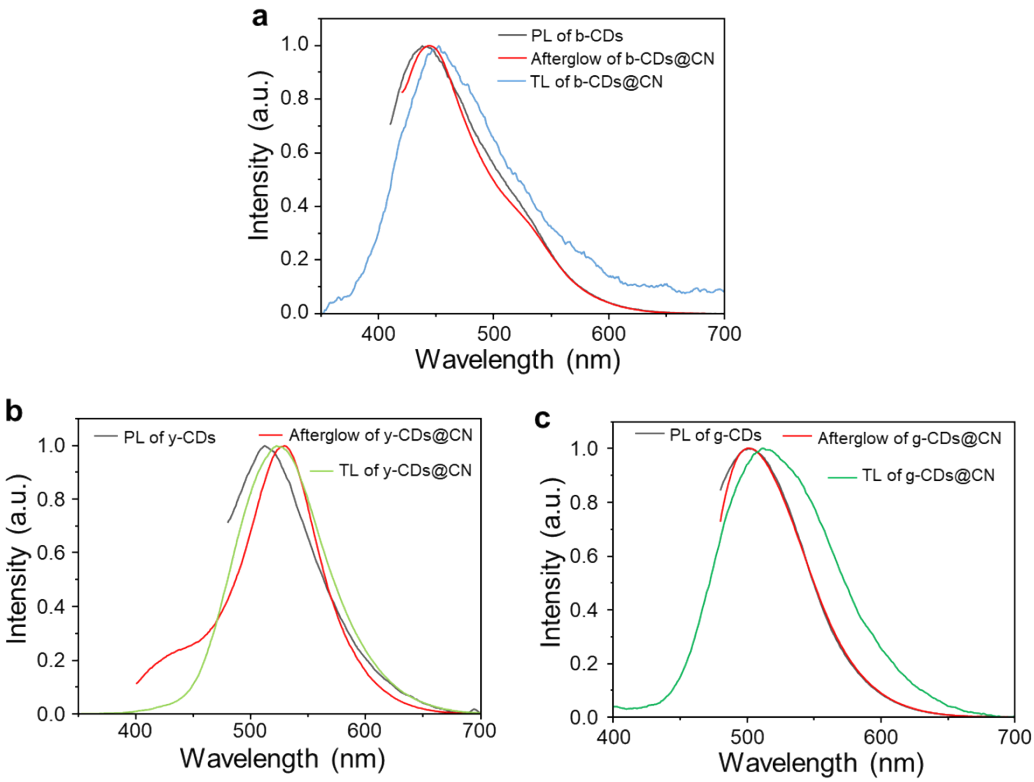

Figure S3. The TL and afterglow emission spectra of (a) b-CDs@CN, (b) y-CDs@CN and (c) g-CDs@CN and the PL emission spectra of the corresponding CDs (i.e., b-CDs, g-CDs and y-CDs).

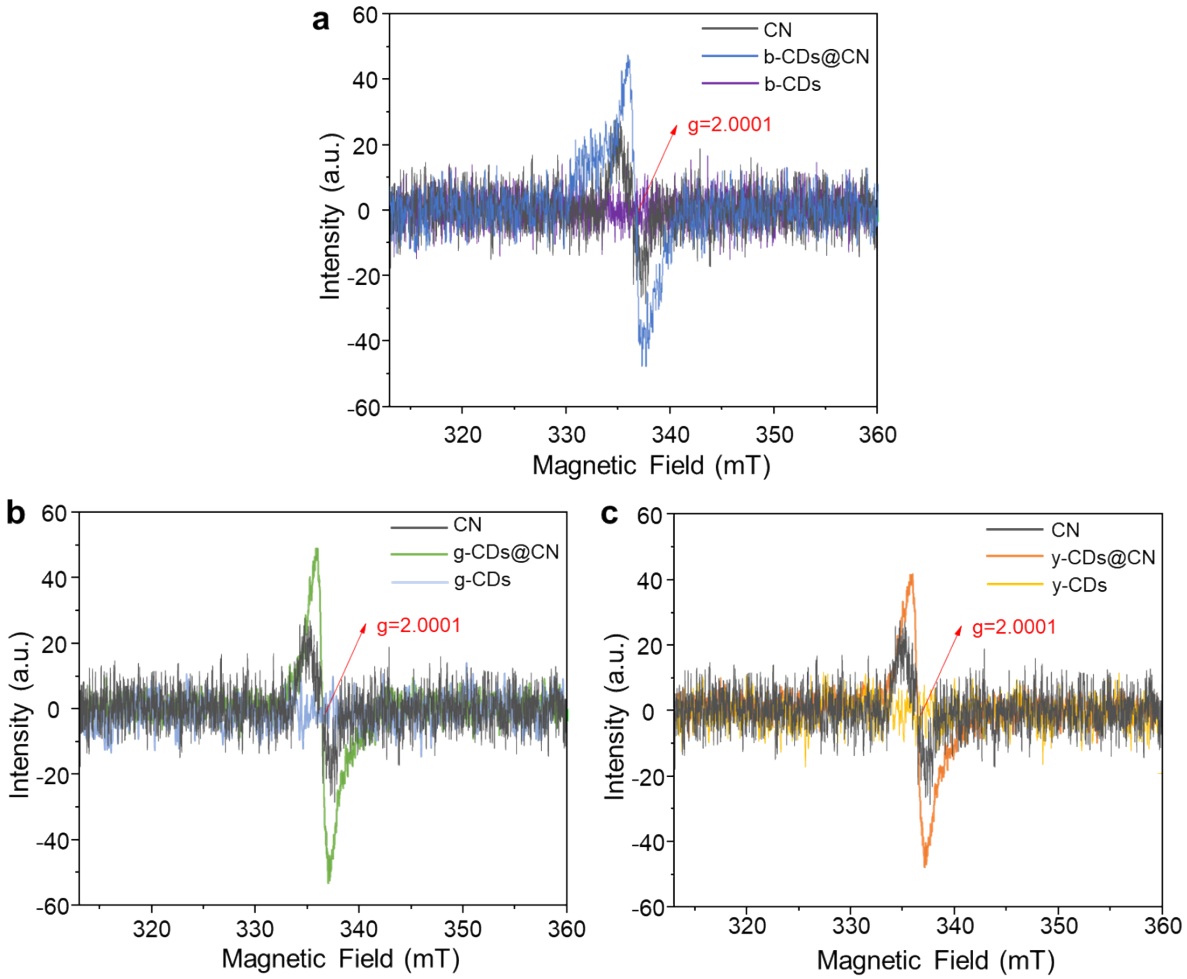

Figure S4. The ESR spectra of (a) b-CDs, CN, and b-CDs@CN, (b) g-CDs, CN, and g-CDs@CN, (c) y-CDs, CN, and y-CDs@CN.

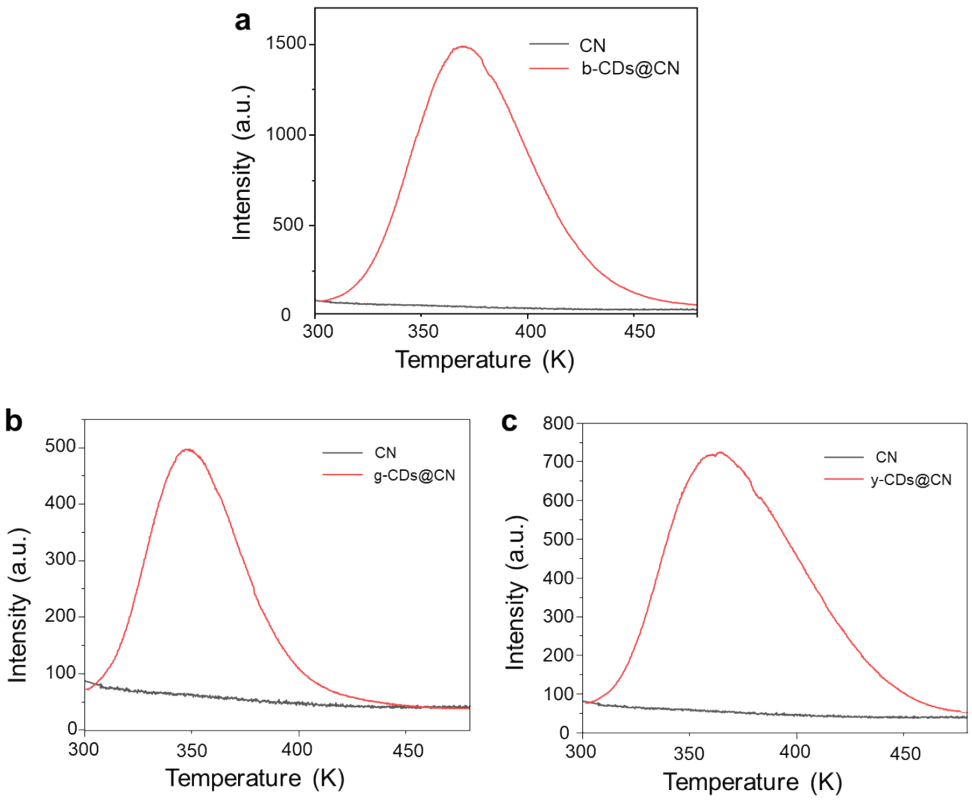

Figure S5. The TL glow curve of (a) b-CDs@CN, (b) g-CDs@CN and (c) y-CDs@CN and pristine CN (black line)

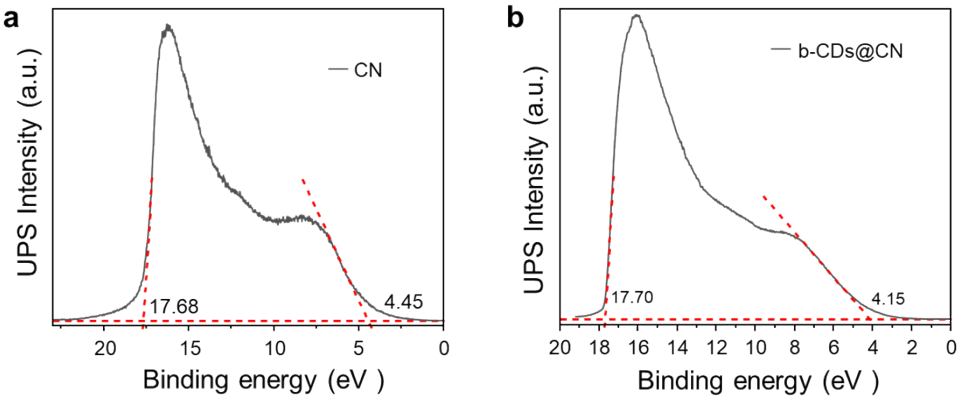

Figure S6. The UPS spectra of pristine CN and the b-CDs@CN.

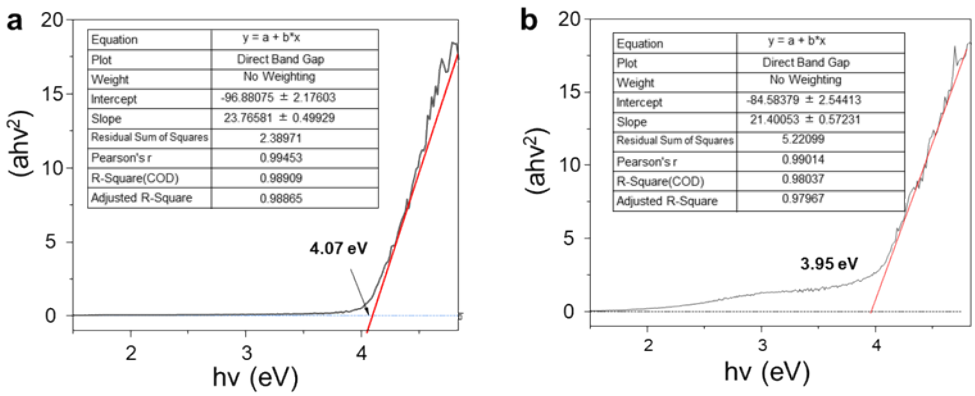

Figure S7. The UV–vis DRS spectra of pristine CN and the b-CDs@CN.

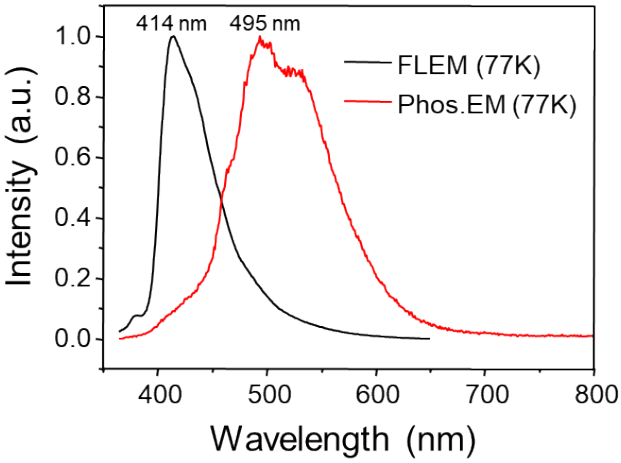

Figure S8. The low temperature (77 K) fluorescence (FL) and phosphorescence (Phos.) emission spectra of b-CDs.

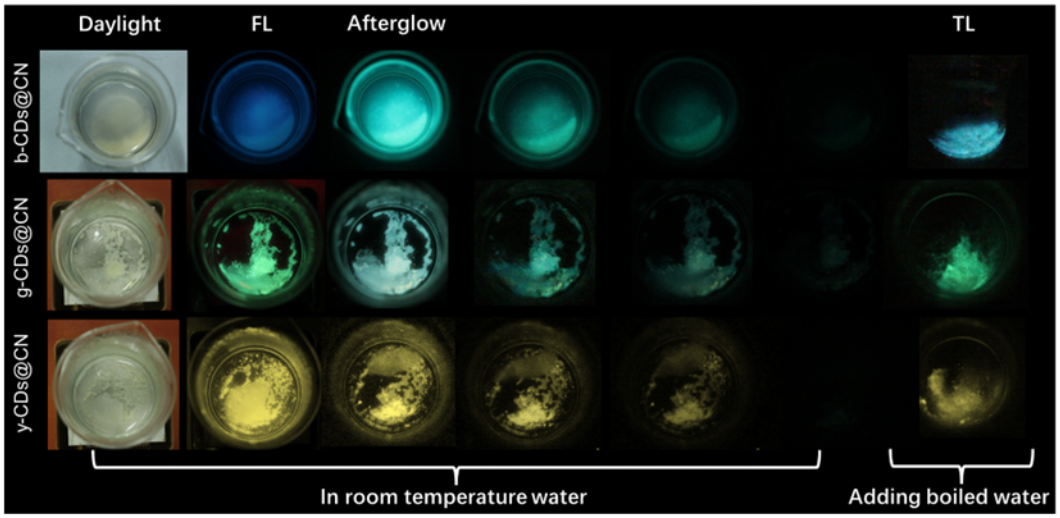

Figure S9. Photographs of three CDs@CNs in room temperature water under daylight, fluorescence, afterglow, and TL when boiled water is adding.

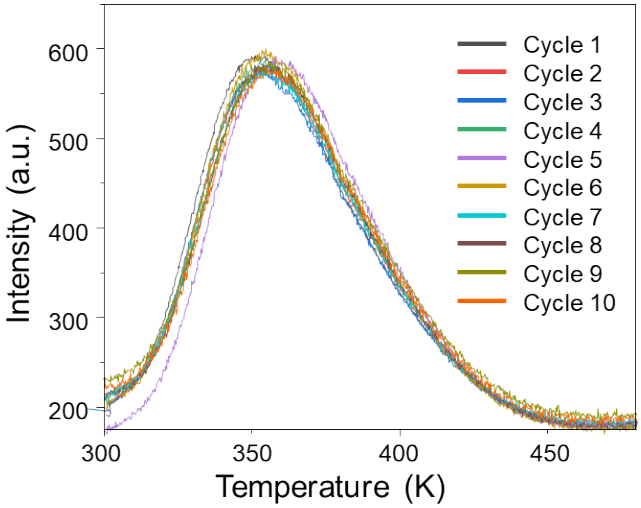

Figure S10. The TL glow curves of b-CDs@CN of 10 repeated excitation–capture–detrapping cycles.

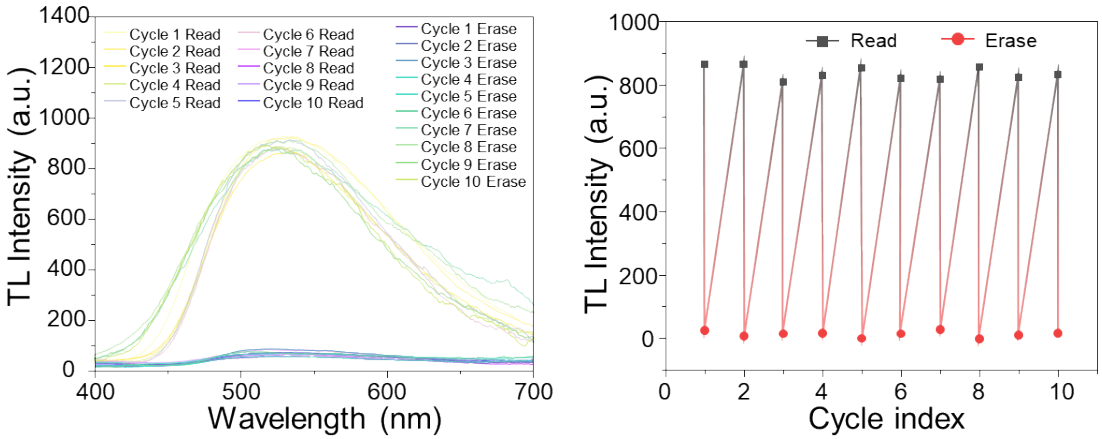

Figure S11. The TL emission spectra and intensity of b-CDs@CN corresponding to 10 repeated excitation–capture–detrapping cycles.

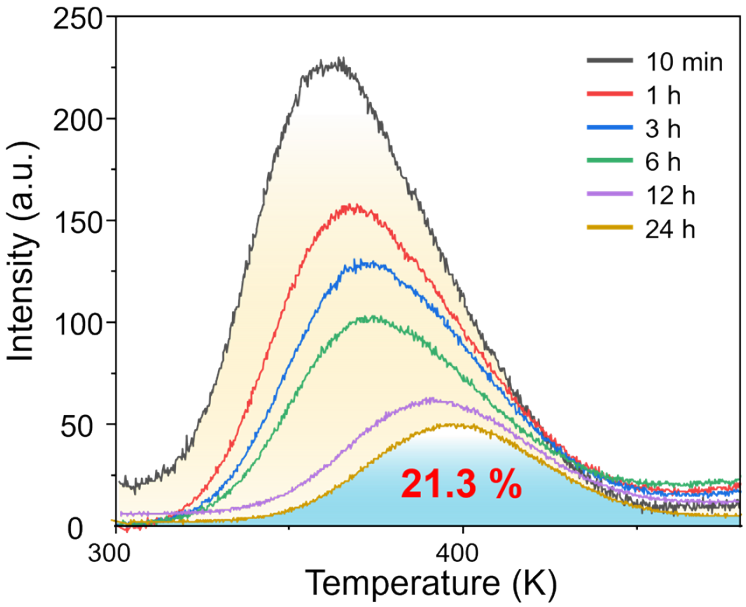

Figure S12. TL glow curves of CDs@CN after excitation with a 365 nm UV lamp for 2 minutes, followed by storage at room temperature for different periods of time..

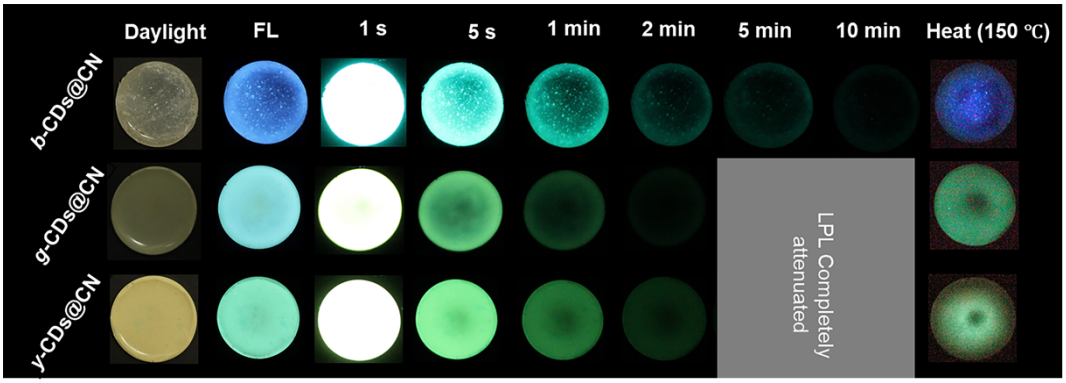

Figure S13. Photographs of three CDs@CNs-based silicone films taken under daylight and UV (365 nm) and after the irradiation source was removed for varying afterglow durations, and the images captured of phosphors after 30 minutes of decay when heated at 150 °C on a hot plate (excitation wavelength ($\lambda_{esc.}$), 365 nm; excitation power, 16 W; excitation time, 2 minutes; and temperature, 298.15 K). FL denotes fluorescence.

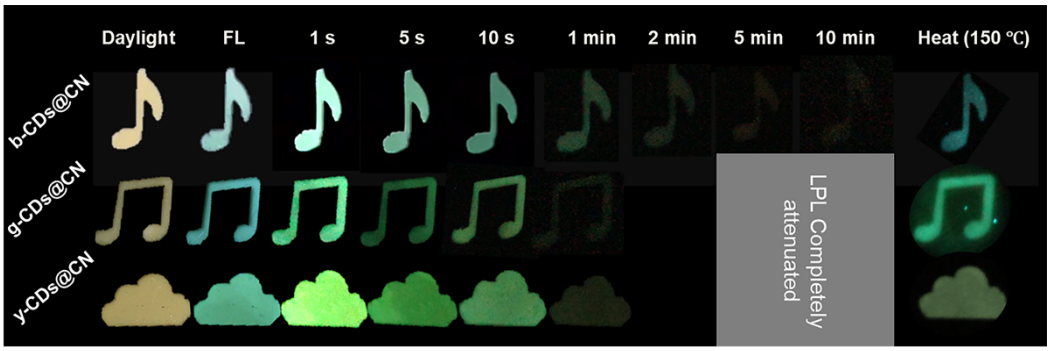

Figure S14. Photographs of different tags and codes which were imprinted on the LPL films through UV light (365 nm) excitation by altering the masks. Phtographs were taken under daylight and UV (365 nm) and after the irradiation source was removed for varying afterglow durations, and images captured of films after 30 minutes of decay when heated at 150 °C on a hot plate (excitation wavelength ($\lambda_{esc.}$), 365 nm; excitation power, 16 W; excitation time, 2 min; and temperature, 298.15 K). FL denotes fluorescence.

References

[1] K. Jiang, S. Sun, L. Zhang, Y. Lu, A. Wu, C. Cai, H. Lin, *Angew. Chem. Int. Ed.* 2015, **54**, 5360-5369.

[2] K. Jiang, X. Feng, X. Gao, Y. Wang, C. Cai, Z. Li, H. Lin, *Nanomaterials* 2019, **9**, 529.

[3] J. Li, H. Zhao, X. Zhao, X. Gong, *Nanoscale Horiz.* 2023, **8**, 83-94.

[4] X. Tong, Y. Wu, K. Jiang, J. Jiang, Y. Xu, L. Feng, X. Wang, J. Du, H. Lin, *Angew. Chem. Int. Ed.* 2025, **64**, e202415312.

[5] L. Feng, K. Jiang, Y. Xu, X. Tong, Z. Zhou, F. Li, X. Wang, Y. Zhang, H. Lin, *Adv. Optical Mater.* 2024, **12**, 2302821.