

Multi-wavelength excitation-dependent fluorescence with dynamic color gradients for information encryption and anti-counterfeiting

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Experimental Section

Synthesis of B-CDs and B-CDs/CaCO₃ composite: 0.2 g of citric acid and 0.8 g of urea were dissolved in 25 mL of deionized water (DI) by ultrasonic and oscillatory processing. 0.2 g of NaOH was further introduced into the above solution. After dissolution, the mixed solution was transferred to a Teflon-lined autoclave (50 mL) and then treated at 200 °C for 6 h. The raw solution was obtained after cooling down to room temperature. B-CDs were obtained when the resultant solution underwent dialysis and freeze-drying procedures. For the preparation of the B-CDs/CaCO₃ composite, 12.5 mL of raw solution was injected in a Teflon-lined autoclave (25 mL). 0.6215 g of CaCl₂ was added and dissolved fully. The mixed solution was heated at 150 °C for 12 h. The powder is washed with DI and ethanol several times. B-CDs/CaCO₃ composite was obtained when the powder after washing was dried at 80 °C.

Synthesis of G-CDs and G-CDs/SiO₂ composite: 0.2 g of citric acid and 0.1 g of resorcinol were dissolved in 20 mL of deionized water (DI) by ultrasonic and oscillatory processing. 5 mL of H₃PO₄ solution was added and formed a uniform mixed solution. The mixed solution was transferred to a Teflon-lined autoclave (50 mL) and then treated at 200 °C for 6 h. The raw solution was obtained after cooling down to room temperature. G-CDs were obtained when the resultant solution underwent dialysis and freeze-drying procedures. For the preparation of the G-CDs/SiO₂ composite, 10 mL of raw solution was injected in a Teflon-lined autoclave (25 mL). 10 mL of tetraethyl orthosilicate was added and dissolved fully. The mixed solution was heated at 150 °C for 12 h. The powder is washed with DI and ethanol several times. G-CDs/SiO₂

composite was obtained when the powder after washing was dried at 80 °C.

Synthesis of R-Eu, UCL-B, and UCL-G optical materials: the synthesis processes of R-Eu, UCL-B and UCL-G are the same except for the difference of doping elements. The designed chemical formula of R-Eu, UCL-B, and UCL-G are $\text{YVO}_4: 5\%\text{Eu}^{3+}$, $\text{YVO}_4: 2\%\text{Er}^{3+}/10\%\text{Yb}^{3+}$, and $\text{YVO}_4: 1\%\text{Tm}^{3+}/10\%\text{Yb}^{3+}$, respectively. Taking the R-Eu for example, 2.0751 g of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.1320 g of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mL of DI, recorded as solution 1. 1.3242 g of Na_3VO_4 was dissolved in 35 mL of DI, recorded as solution 2. 5.6466 g of trisodium citrate was dissolved in 30 mL of DI, recorded as solution 3. Holding a stirring condition, solution 3 was injected into solution 1, and then solution 2 was further introduced. After forming a transparent mixed solution, the mixed solution was transferred to a Teflon-lined autoclave (50 mL) and then treated at 180 °C for 12 h. White sediment was obtained after cooling down to room temperature. White sediment was washed with DI and ethanol for several times and dried at 80 °C. Finally, R-Eu was obtained when the dried white sediment was calcined at 800 °C for 2 h. For the preparation of UCL-B and UCL-G, solution 1 of the former contains $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, and another contains $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$. The other treatment procedures are not changed.

Connecting material and security inks preparation: 1.5 g of carboxymethyl cellulose V was dissolved in 30 mL DI to form the connecting material. 0.05 g of R-Eu, 0.1 g of B-CDs/ CaCO_3 composite, and 0.05 g of UCL-G was introduced in 3 mL of connecting material to form security ink 1. 0.05 g of R-Eu, 0.1 g of G-CDs/ SiO_2 composite and

0.05 g of UCL-B was introduced in 3 mL of connecting material to form security ink
2.

Characterization Method: Transmission electron microscopy images and high-resolution transmission electron microscopy images were carried out on JEM-2100 Plus, JEM-F200 and Talos L120C G2 electron microscopes. Scanning electron microscope images were recorded on a Hitachi S-4800 electron microscope. X-Ray powder diffraction data were measured on a SmartLab SE X-ray diffractometer. Fourier transform infrared spectra were tested on a FTIR5700 spectrometer. UV-Vis absorption spectra were recorded on a Lambda 950 spectrometer. X-ray photoelectron spectroscopy results were obtained on a Thermo Scientific K-Alpha spectrometer. Fluorescence, room-temperature phosphorescence, and upconversion luminescence spectra were measured on a F-4600 spectrometer.

Table S1 Comparison of some RTP materials

Materials	Emission (nm)	Phosphorescence lifetime (ms)	Decay time to the naked eye	Quantum yield	Ref.
Full color CDs/PAM	476, 502, 586, 633	637.00, 583.81, 503.23, 478.97	12, 8, 6, 2.4	46.8%, 35%, 4.4%, 9.3%	1
F-CDs-3/PVA	520	218	4	/	2
MP-CDs	535	880	< 8	18.2%	3
Zn-CDs-LDH	490	734	5	30.16%	4
CDs/KAl(SO ₄) ₂ ·x(H ₂ O)	480	655	1.5	/	5
CDs, CDs-X (X = F, Cl, Br)	525, 521, 525, 520	680, 830, 820, 810	< 8	7.43%, 8.95%, 9.49%, 8.00%	6
P-HNI, P-HNI film	523, 523	92, 704	1, 8	1%, 2.6%	7
CDs/CaCO ₃	513	237	7	2.77%	This work

Table S2 Calculated values of crystal plane index (hkl) based on the equation S1

Lattice parameters			Crystal plane index (hkl)			lattice fringe spacing
a	b	c	h	k	l	(nm)
7.1192	7.1192	6.2298	2	2	0	0.25
7.1192	7.1192	6.2298	1	0	1	0.44
7.1192	7.1192	6.2298	2	0	0	0.36
7.1192	7.1192	6.2298	1	1	2	0.26

The equation S1 is shown below:

$$d = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$$

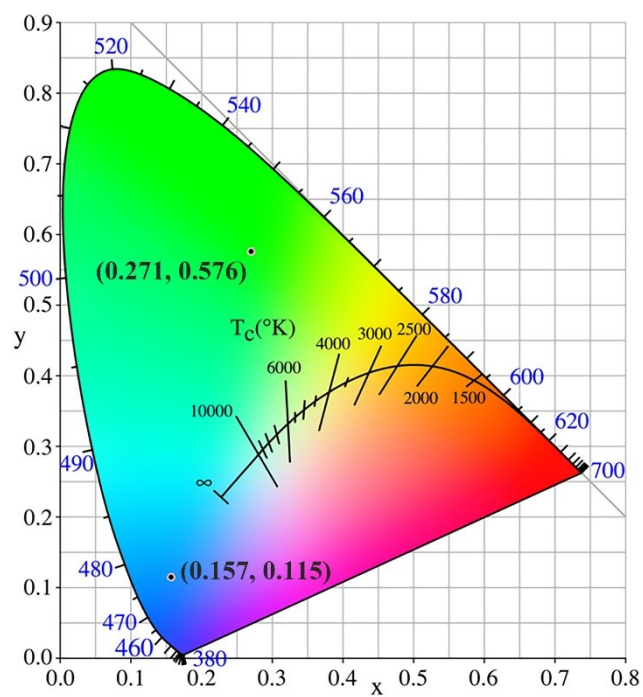


Figure S1 CIE coordinates of blue emission of B-CDs and green emission of G-CDs

under 365 nm excitation

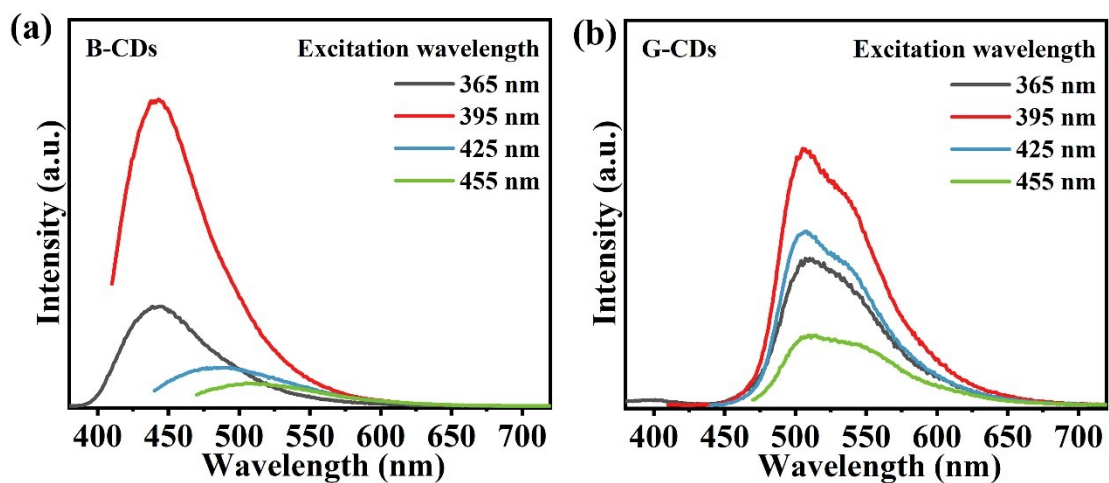


Figure S2 Emission spectra of B-CDs (a) and G-CDs (b) under 365 nm, 395 nm, 425 nm, and 455 nm excitation

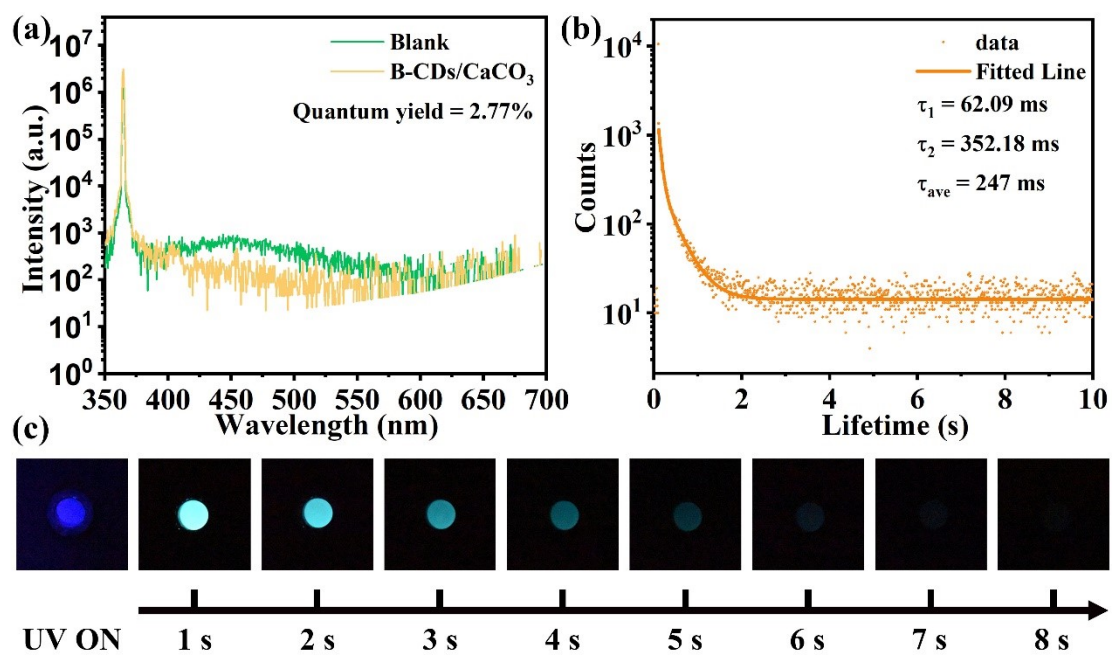


Figure S3 (a)-(c) The quantum yield, lifetime and phosphorescent decay images of B-CDs/CaCO₃ composite

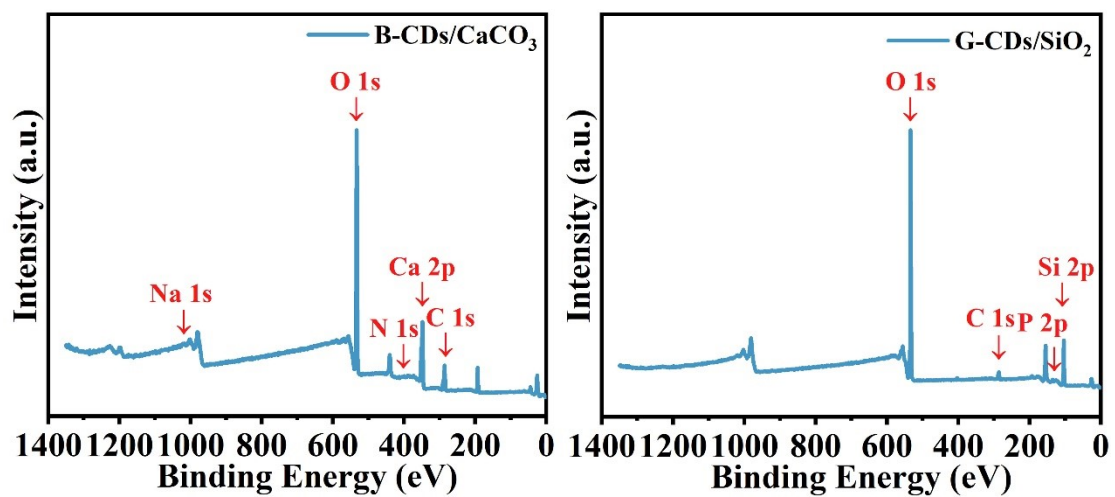


Figure S4 Full-scale XPS spectra of (a) B-CDs/CaCO₃ composite and (b) G-CDs/SiO₂ composite

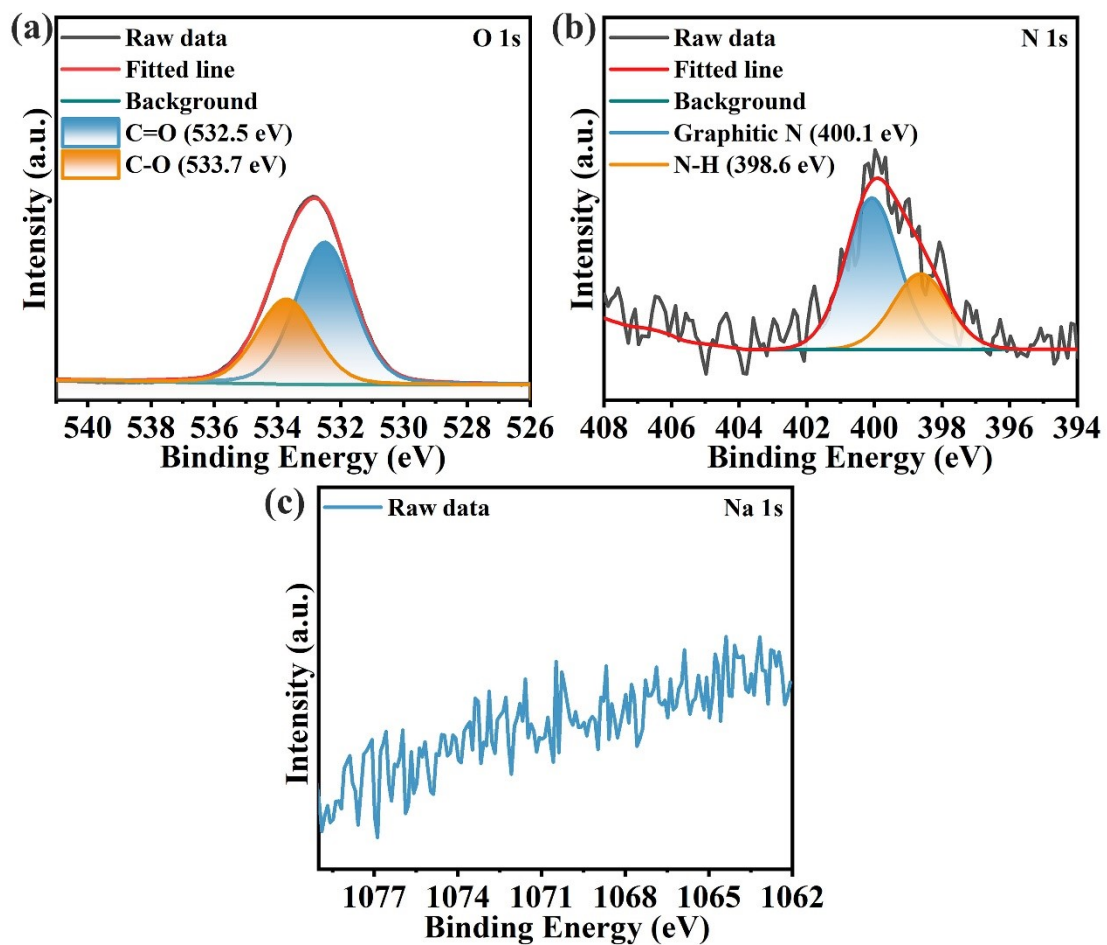


Figure S5 High-resolution O 1s, N 1s, and Na 1s spectra of B-CDs/CaCO₃ composite

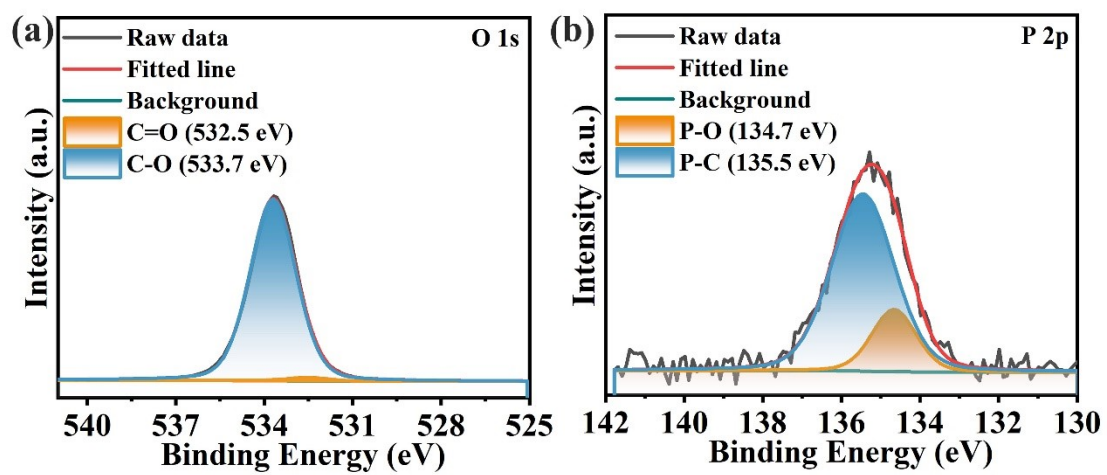


Figure S6 High-resolution O 1s and P 2p spectra of G-CDs/SiO₂ composite

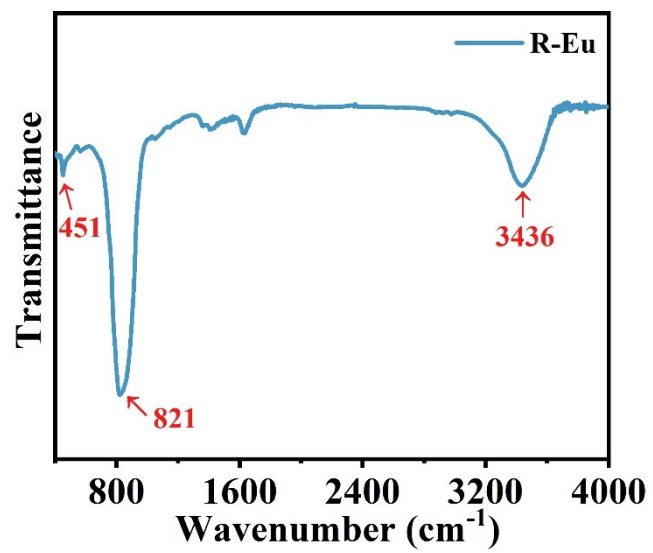


Figure S7 FT-IR spectrum of R-Eu

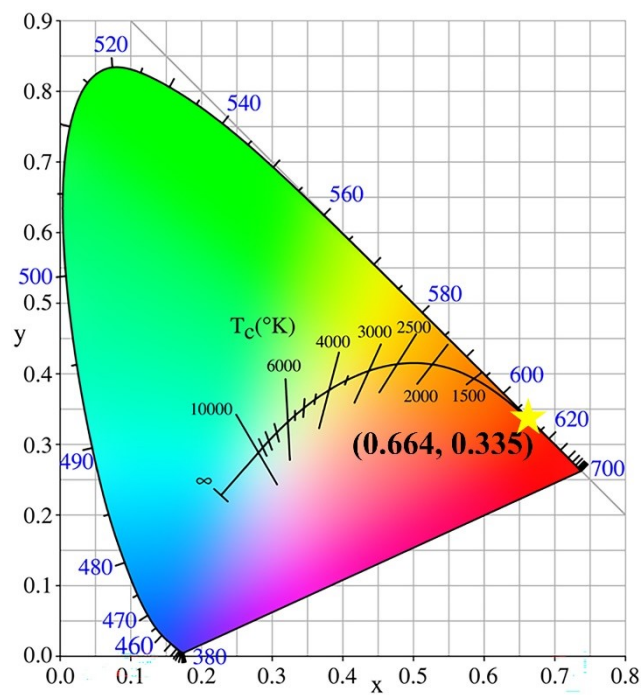


Figure S8 CIE coordinates of R-Eu under 254 nm excitation

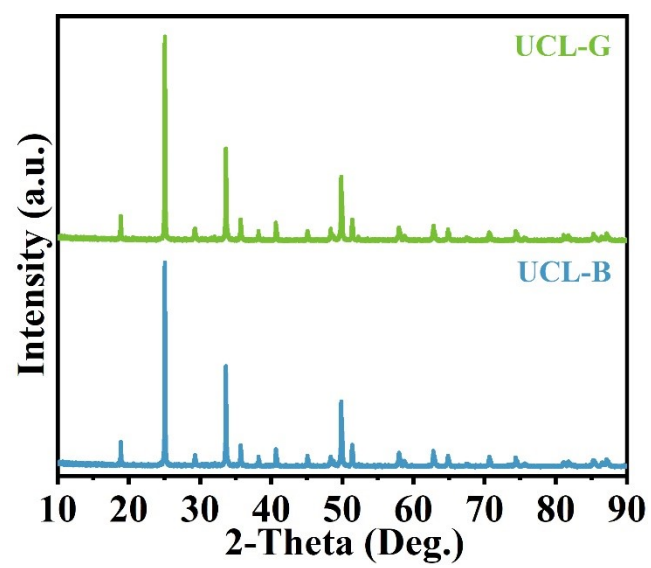


Figure S9 XRD results of UCL-B and UCL-G

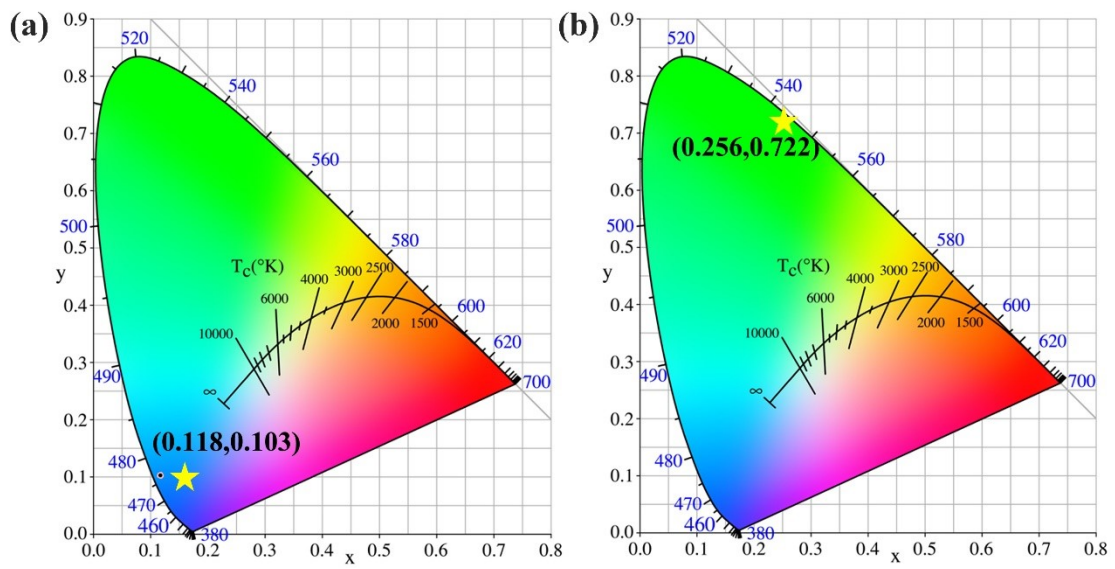


Figure S10 CIE coordinates of UCL-B ($\lambda_{\text{ex}} = 980 \text{ nm}$) and UCL-G ($\lambda_{\text{ex}} = 980 \text{ nm}$)

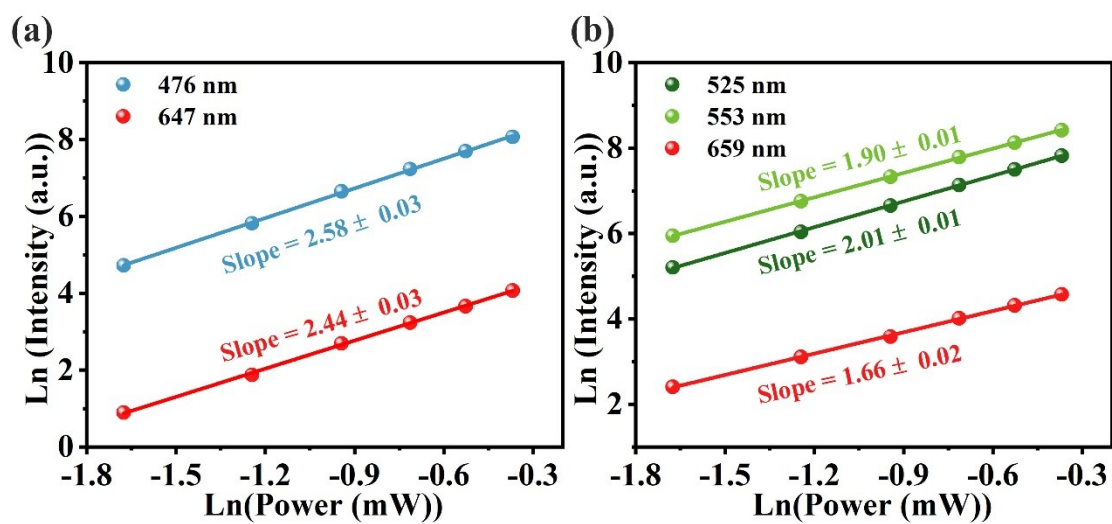


Figure S11 The log-log plots of excitation power-dependent UCL emission intensity of (a) 476 nm and 647 nm emission of UCL-B and (b) 525 nm, 553 nm, and 659 nm emission intensity of UCL-G

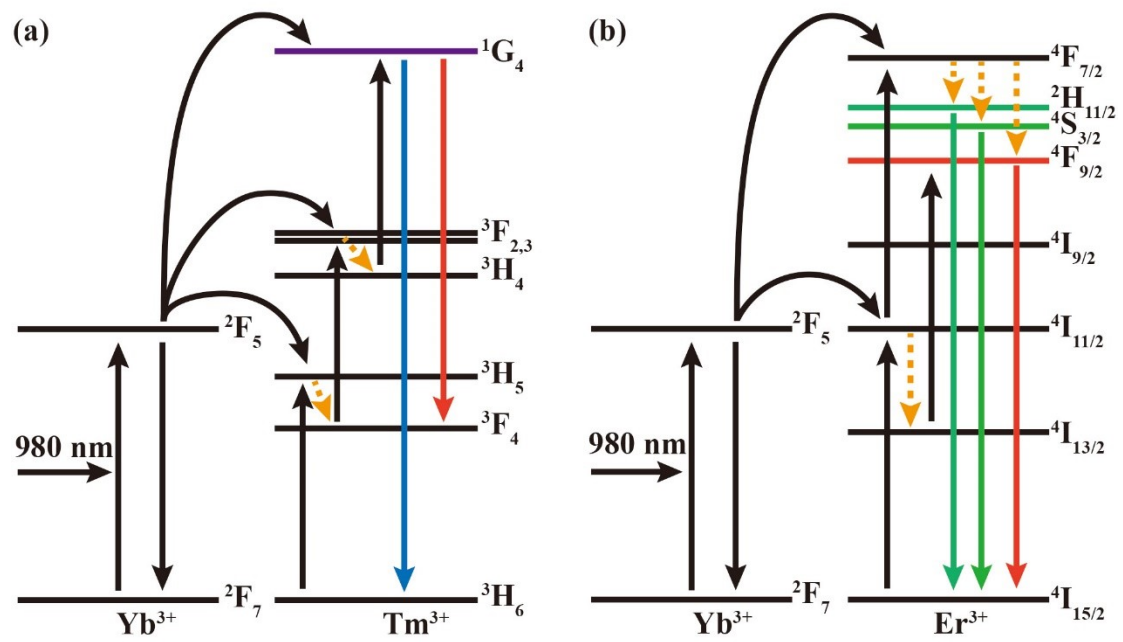


Figure S12 The UCL processes of Tm³⁺/Yb³⁺ and Er³⁺/Yb³⁺ doped YVO₄ systems

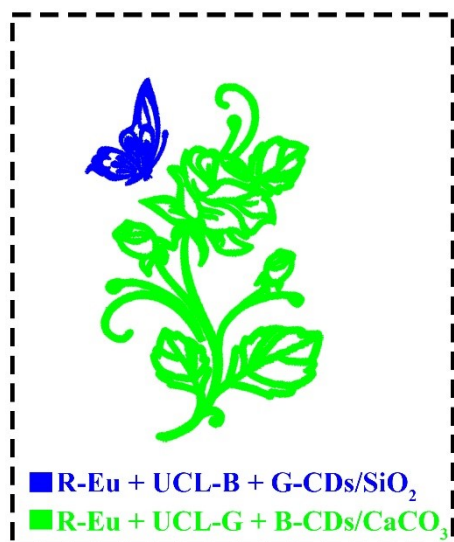


Figure 13 The schematic diagrams of the composition of functional inks used in various parts of the security pattern.

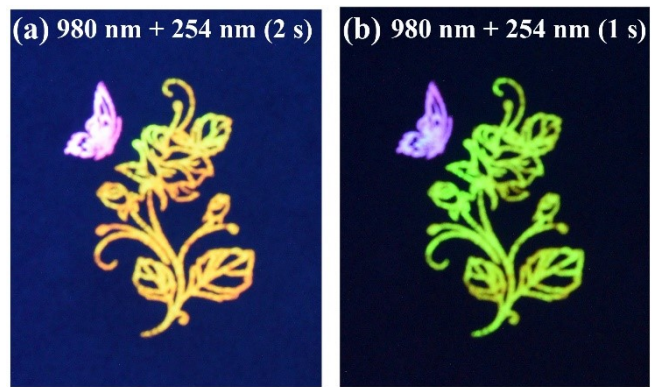


Figure S14 (a) the security labels exposed under the 980 nm and 254 nm (~ 2 s). (b) the security labels exposed under the 980 nm and 254 nm (~ 1 s).

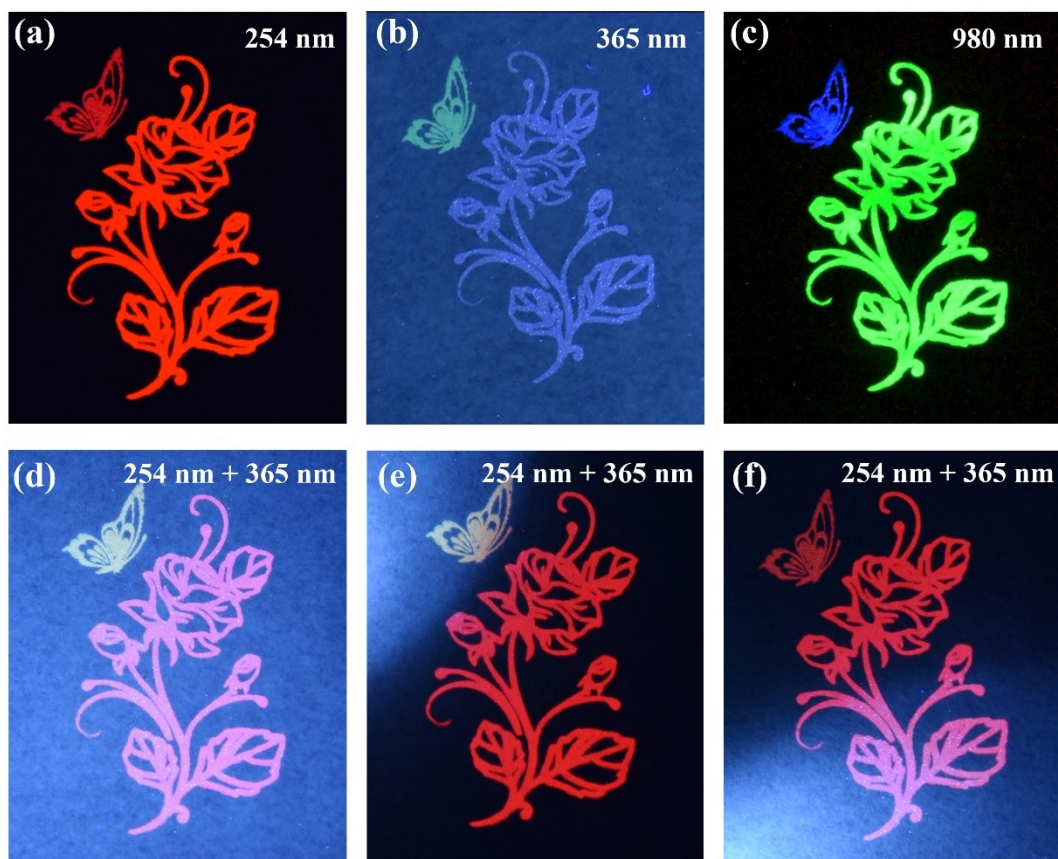


Figure S15 Images of security patterns after stored for 365 days under the excitation of (a) 254 nm, (b) 365 nm, (c) 980 nm, and (d)-(f) 365 nm and 254 nm.

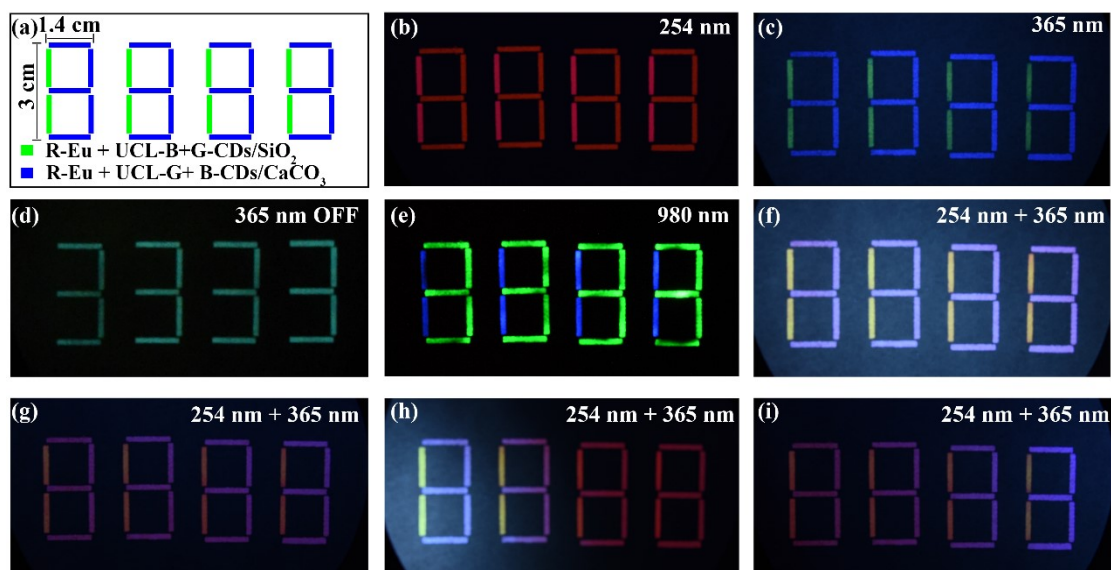


Figure S16 (a) Schematic diagram of the fabricated information coding printed using security inks. Images of the encoded information (b) under the excitation of 254 nm and (c) 365 nm, (d) after removal of 365 nm UV light, and (e) under the excitation of 980 nm. (f)-(i) The encoded information exposed in the 254 nm and 365 nm UV light.

Reference

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