Supplementary Information (SI) for Materials Chemistry Frontiers.

Supporting Information (SI)

Cs_4PbX_6-UCLNPs/PS film for multimodal anti-counterfeiting and information encryption storage upon triple strategies of water treatment, light excitation and heating/cooling

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1. Experimental

1.1 Reagents and materials

Cs_2CO_3 (99.0 %), $PbCl_2$ (99.0 %), $PbBr_2$ (99.0 %), PbI_2 (99.0 %), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), $Y(NO_3)_3{\cdot}6H_2O$ (99.5 %), $Er(NO_3)_3{\cdot}6H_2O$ (99.9 %), $Yb(NO_3)_3{\cdot}5H_2O$ (99.9 %), oleylamine (OLA, 80-90%), polystyrene (PS), CH_2Cl_2 (DCM, 99%), ethylene diamine tetraacetic acid (EDTA, 99.5 %), NaF (98 %), polyvinyl pyrrolidone (PVP, K30) were used, and all of the chemicals were of analytic grade and purchased from Aladdin reagent Co. LTD, Shanghai, China.

1.2 Characterizations

An X-ray diffractometer (XRD, made by Bruker Corporation) was used to analyze the phase components of the prepared samples. The internal structure and morphology of the products were observed by a scanning electron microscope (SEM, JSM-7610F), a light microscope (LM, CVM500E), a fluorescence microscope (FM, Nikon Ti-s), an energy-dispersive X-ray (EDX) spectroscopy and a transmission electron microscope (TEM, Tecnai G2 F30). The elemental composition, chemical state and electronic state on the surface of the samples were analyzed by an X-ray photoelectron spectroscopy (XPS, Nexsa). The photoluminescence (PL) properties of the films were studied by a Hitachi fluorescent spectrophotometer (F-7000). The UCL emission spectra of the specimens were acquired by a laser device (FC-980-500-SM) under 980-nm laser excitation. The UV-Vis absorption spectrums of the samples were measured by an ultraviolet-visible-near-infrared spectrophotometer (Shimadzu Co. UV-3600). All tests were carried out at RT.

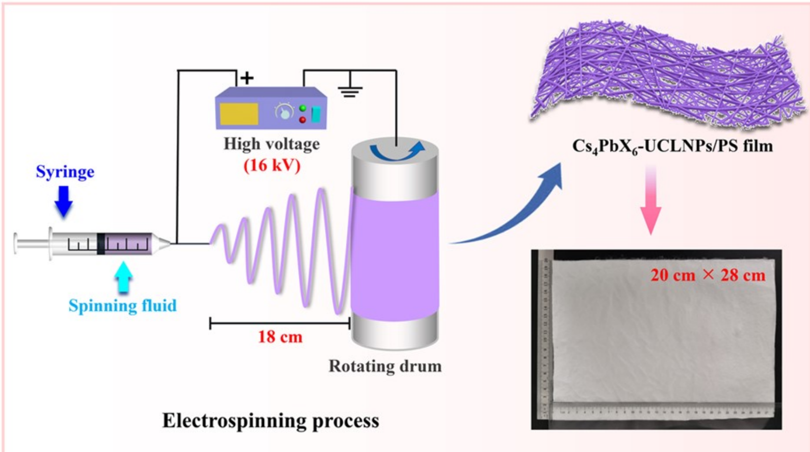

Fig. S1. Schematic Diagram of single-nozzle electrospinning process and physical photo of Cs_4PbX_6-UCLNPs/PS film obtained

2. Results and Discussion

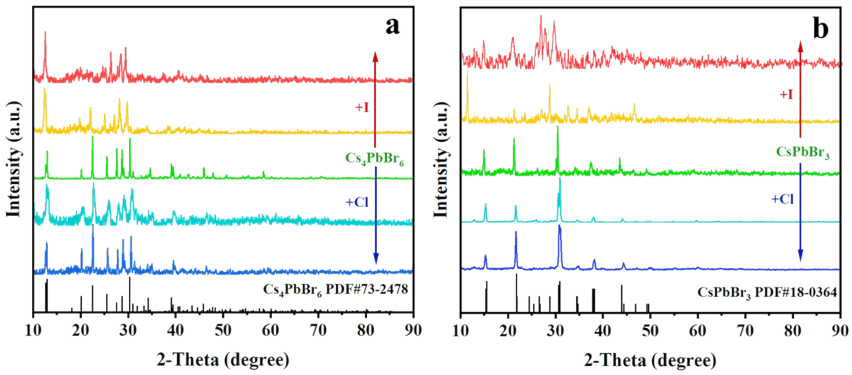

Fig. S2. XRD patterns of Cs_4PbX_6 QDs with different halide compositions before (a) and after (b) water treatment

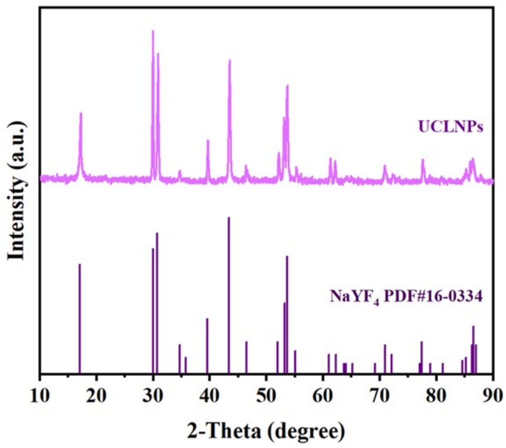

Fig. S3. XRD patterns of UCLNPs

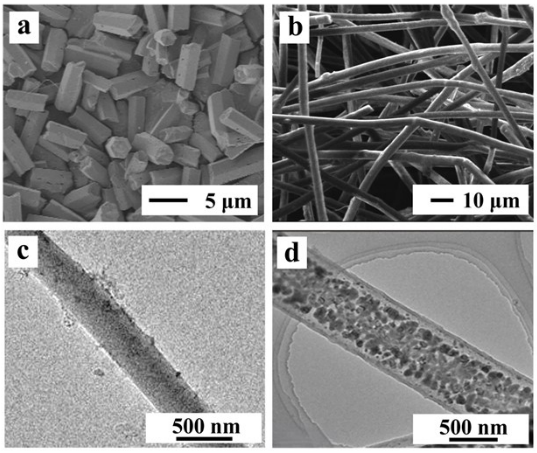

Fig. S4. SEM images of UCLNPs (a) and $CsPbBr_3$-UCLNPs/PS film (b); TEM images of Cs_4PbBr_6-UCLNPs/PS fiber (c) and $CsPbBr_3$-UCLNPs/PS fiber (d)

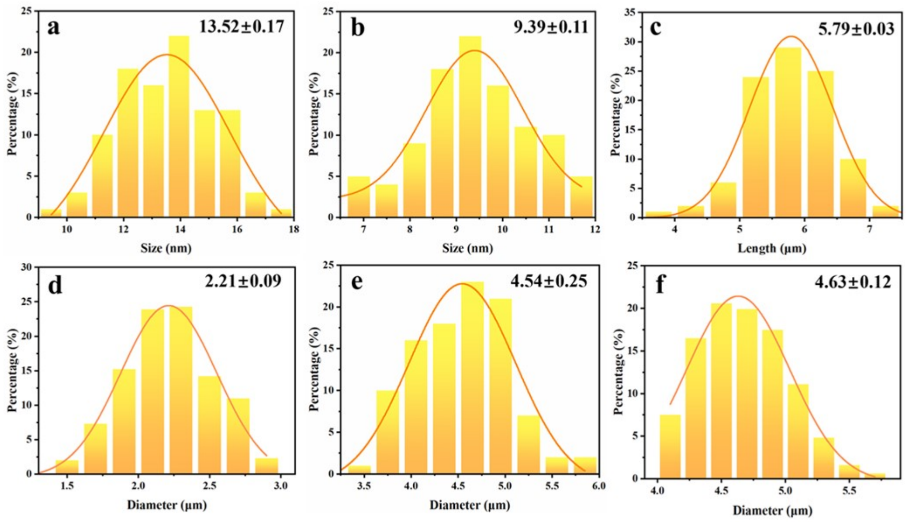

Fig. S5. Size distributions of the Cs_4PbBr_6 QDs before (a) and after (b) water treatment; Length (c) and diameter (d) distributions of the UCLNPs; Diameter distributions of fibers in Cs_4PbBr_6-UCLNPs/PS film (e) and $CsPbBr_3$-UCLNPs/PS film (f)

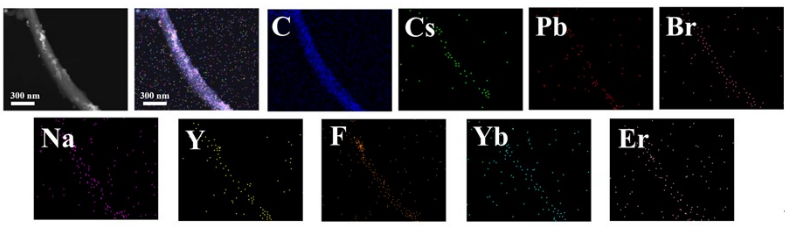

Fig. S6. High-resolution TEM image and corresponding EDX elemental mappings of Cs_4PbX_6-UCLNPs/PS fiber

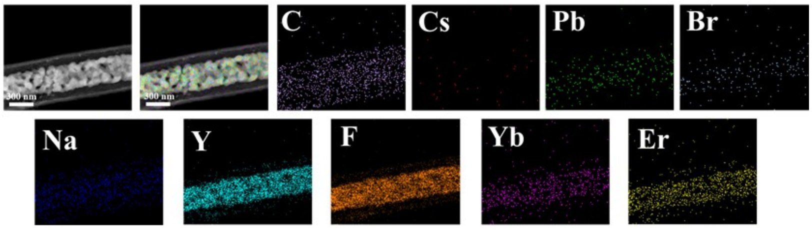

Fig. S7. High-resolution TEM image and corresponding EDX elemental mappings of $CsPbX_3$-UCLNPs/PS fiber

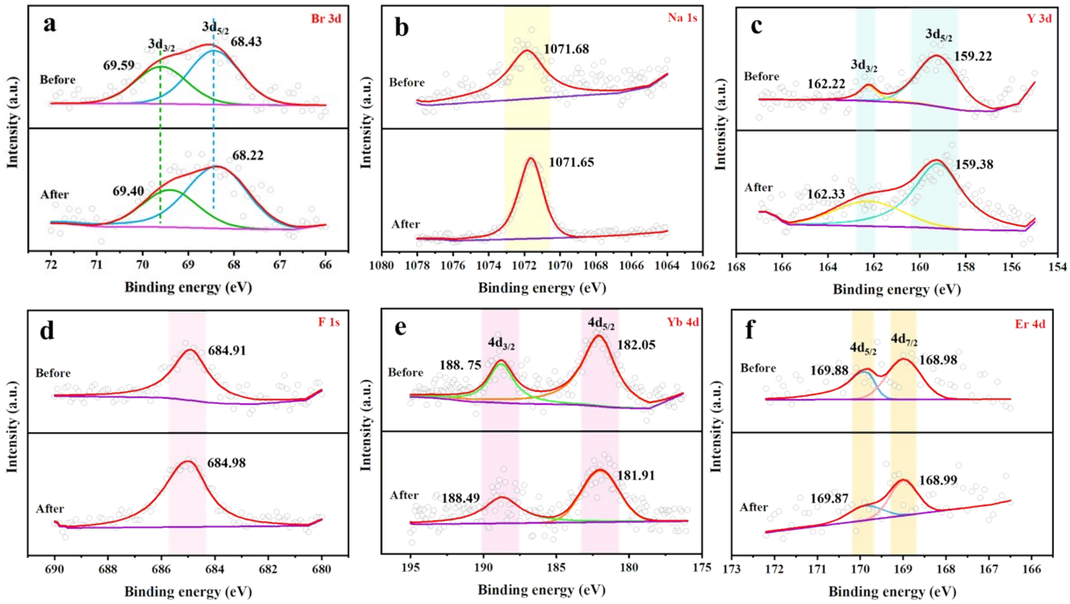

Fig. S8. Comparison of high-resolution XPS peaks for (a) Br 3d, (b) Na 1s, (c) Y 3d, (d) F 1s, (e)Yb 4d and (f) Er 4d in Cs_4PbBr_6-UCLNPs/PS film before and after water treatment

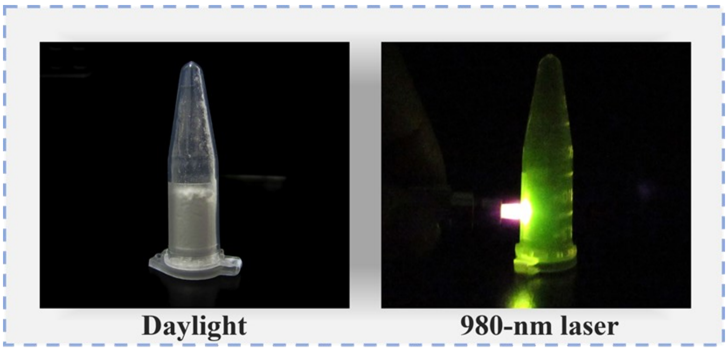

Fig. S9. Digital photos of UCLNPs under daylight and 980-nm laser illumination

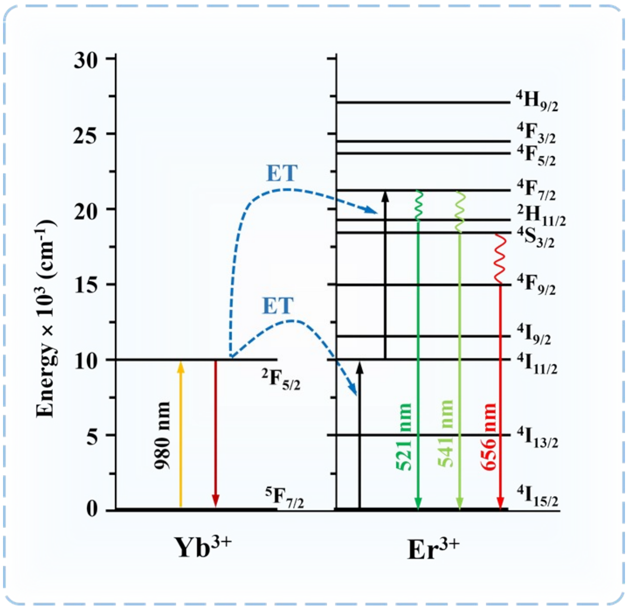

Fig. S10. A simplified energy level scheme of the UCL emission mechanism for UCLNPs in Cs_4PbX_6-UCLNPs/PS film

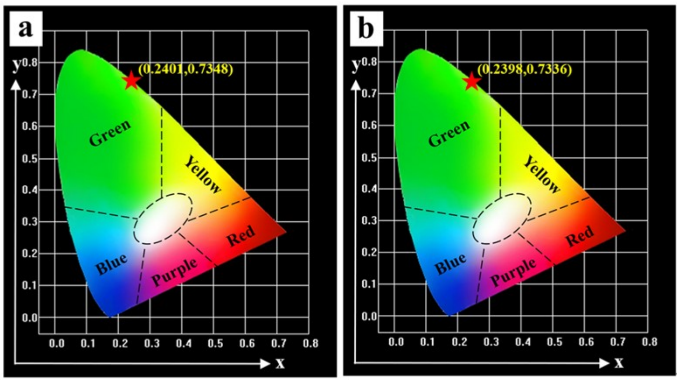

Fig. S11. CIE chromaticity coordinates diagram of Cs_4PbX_6-UCLNPs/PS film with different UCLNPs contents (a) and Cs_4PbX_6-UCLNPs/PS film with different halide compositions (b)

Table S1. CIE chromaticity coordinates of Cs_4PbX_6-UCLNPs/PS film with different UCLNPs contents

Mass percentage	CIE (x, y)
UCLNPs:PS=25%	(0.2482,0.7348)
UCLNPs:PS=50%	(0.2386,0.7357)
UCLNPs:PS=75%	(0.2393,0.7336)
UCLNPs:PS=100%	(0.2397,0.7340)
UCLNPs:PS=125%	(0.2404,0.7359)

Table S2. CIE chromaticity coordinates of Cs_4PbX_6-UCLNPs/PS film with different halide compositions

Mass percentage	CIE (x, y)
$Cs_4PbCl_3Br_3$	(0.2398,0.7336)
$Cs_4PbCl_2Br_4$	(0.2398,0.7337)
Cs_4PbBr_6	(0.2394,0.7341)
$Cs_4PbBr_4I_2$	(0.2394,0.7344)
$Cs_4PbBr_3I_3$	(0.2395,0.7344)

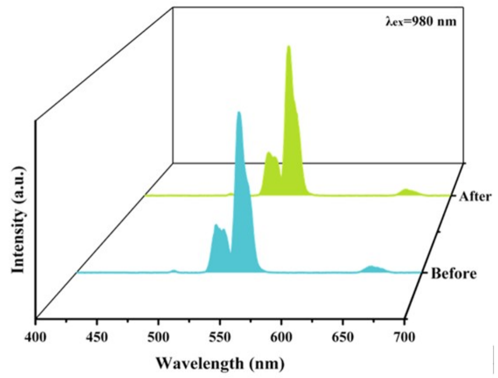

Fig. S12. UCL emission spectra of Cs_4PbX_6-UCLNPs/PS film before and after water treatment

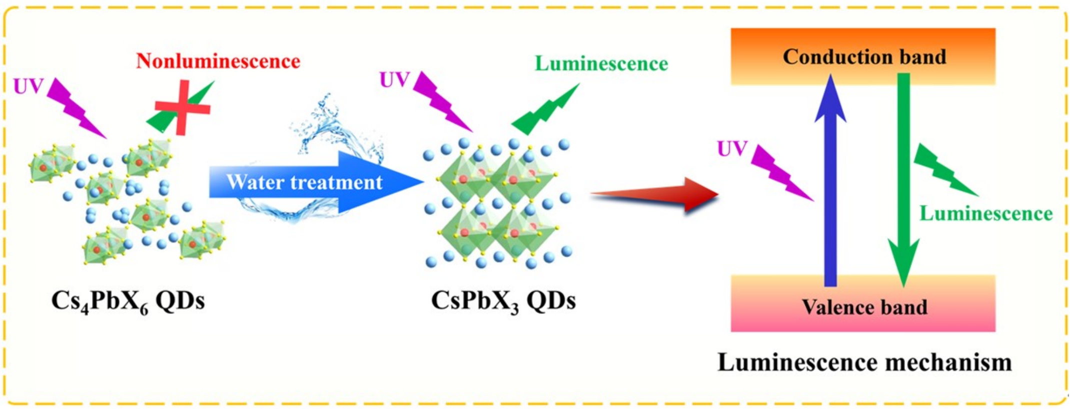

Fig. S13. Schematic diagram of the DCL mechanism of the conversion of Cs_4PbX_6 QDs to $CsPbX_3$ QDs after water treatment

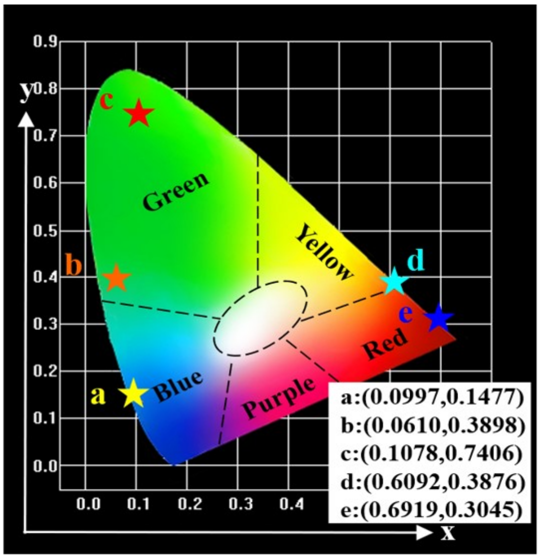

Fig. S14. CIE chromaticity coordinates diagram of $CsPbX_3$-UCLNPs/PS film after water treatment

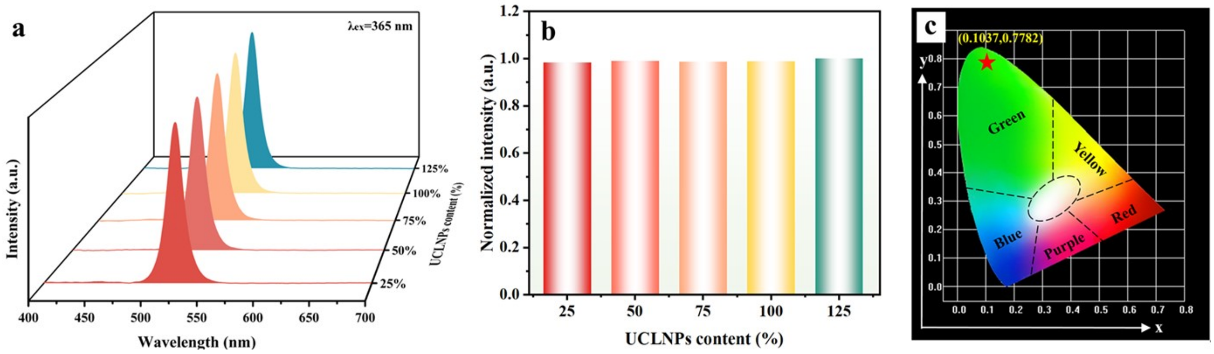

Fig. S15. DCL spectrum (a), normalized DCL intensity plot (b) and CIE chromaticity coordinates diagram (c) of $CsPbBr_3$-UCLNPs/PS film with different UCLNPs contents

Table S3. CIE chromaticity coordinates of $CsPbX_3$-UCLNPs/PS film with different UCLNPs contents

Mass percentage	CIE (x, y)
UCLNPs:PS=25%	(0.1037,0.7782)
UCLNPs:PS=50%	(0.1045,0.7793)
UCLNPs:PS=75%	(0.1036,0.7787)
UCLNPs:PS=100%	(0.1039,0.7769)
UCLNPs:PS=125%	(0.1042,0.7775)

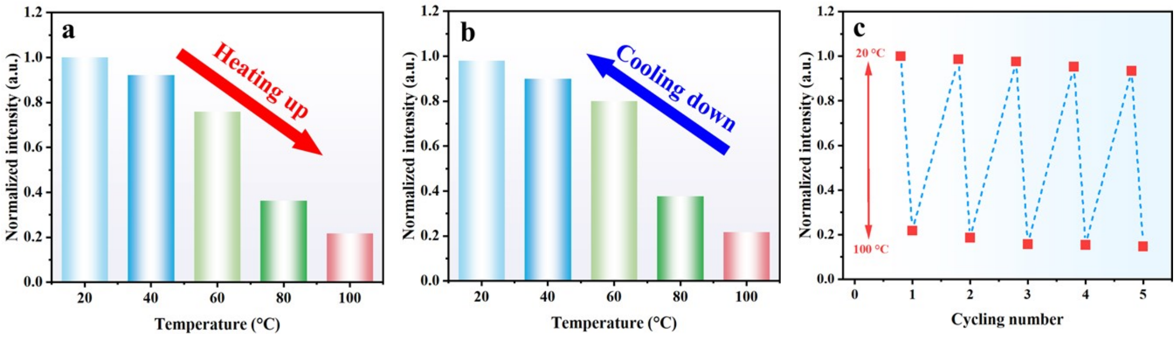

Fig. S16. Temperature-dependent normalized DCL intensity plot of $CsPbX_3$-UCLNPs/PS film during heating process (a) and cooling process (b); Plot for normalized intensity of DCL peak at 517 nm of $CsPbX_3$-UCLNPs/PS film in heating/cooling cycle at 20 °C and 100 °C (c)

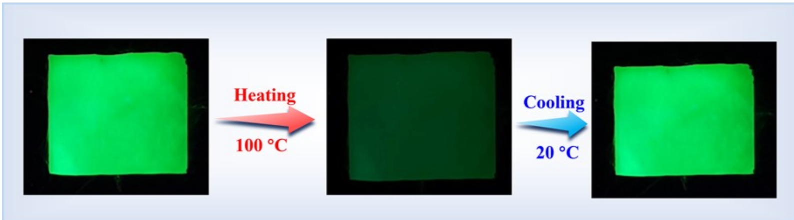

Fig. S17. Physical photos of $CsPbX_3$-UCLNPs/PS film after a heating/cooling cycle process under UV light

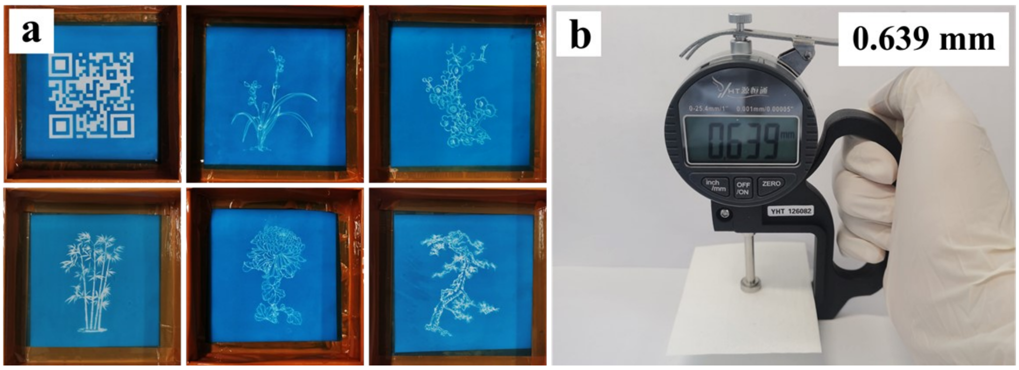

Fig. S18. Digital photos of silk-screen printing plates (a); Physical photo of the Cs_4PbBr_6-UCLNPs/PS film measured by film thickness meter (b)

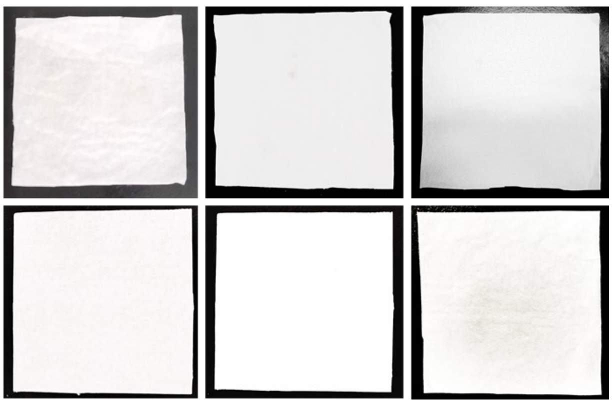

Fig. S19. Digital photos of designable patterns printed on Cs_4PbX_6-UCLNPs/PS film by using water-based ink *via* silk-screen printing technology under daylight

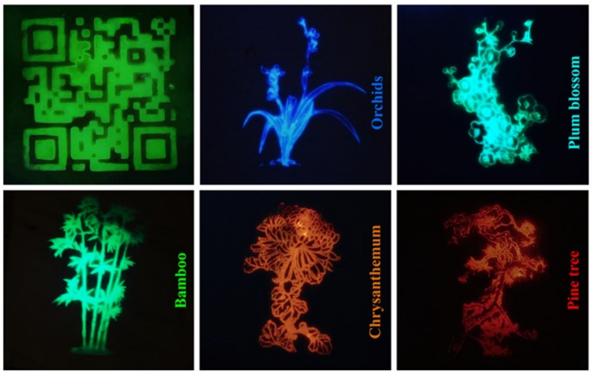

Fig. S20. Digital photos of anti-counterfeiting patterns on Cs_4PbX_6-UCLNPs/PS film placed in a natural environment for a month

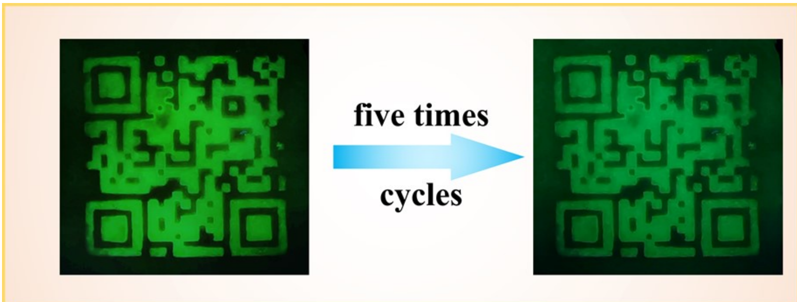

Fig. S21. Digital photos of patterns for Cs_4PbX_6-UCLNPs/PS film after five times heating/cooling cycle

Table S4. Calculated cost for synthesizing one cm^2 of Cs_4PbX_6-UCLNPs/PS film based on the prices quoted at the places of purchase

	Ingredients	**Usage amount**	**Unit price (USD/g)**	**Price (USD)**
Cs_4PbX_6-UCLNPs/PS film fabrication	Cs_2CO_3	6.96E-05 g	0.34	2.37E-05
	$PbBr_2$	1.11E-04 g	0.64	7.10E-05
	OA	2.05E-03 mL	0.014	2.87E-05
	OLA	1.78E-03 mL	0.040	7.12E-05
	ODE	0.021 mL	0.018	3.78E-04
	EDTA	1.04E-03 g	0.014	1.45E-05
	NaF	1.79E-03 g	0.008	1.43E-05
	$Y(NO_3)_3\cdot 6H_2O$	1.06E-03 g	0.048	5.08E-05
	$Yb(NO_3)_3\cdot 5H_2O$	3.21E-04 g	0.30	9.63E-05
	$Er(NO_3)_3\cdot 6H_2O$	3.29E-05 g	0.15	4.93E-06

	PS	3.57E-03 g	0.017	6.07E-05
	DCM	0.017 g	0.0085	1.44E-04
Total				0.001

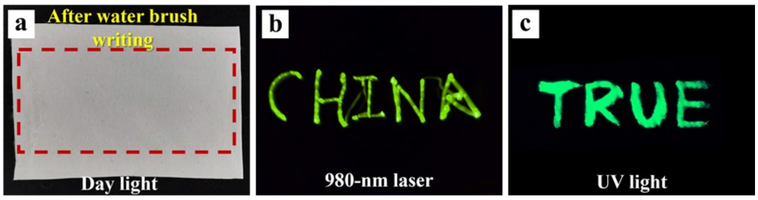

Fig. S22. Digital photos of dynamic anti-counterfeiting of Cs_4PbBr_6-UCLNPs/PS film after water brush writing

Table S5 A summary of research progress of fluorescent anti-counterfeiting and information storage encryption materials

Used component	Strategy of anti-counterfeiting	Luminescence of utilization	Preparation method	Color of luminescence	Application	Anti-counterfeiting level	Ref.
$LiYF_4$:Yb^{3+}, Ho^{3+}, Ce^{3+}/carbon QDs	980-nm laser+ 365-nm light	UCL+DCL	Hydrothermal +screen printing	Green to red (UCL) +blue (DCL)	Static anti-counterfeiting	Medium	[2]
$NaYF_4$:Yb^{3+}, Tm^{3+}-$CsPbX_3$ QDs glasses	980-nm laser+ 365-nm light	UCL+DCL	Ball milling	Bluish purple or red (UCL)+blue to green to red multicolor (DCL)	Static anti-counterfeiting+information encryption	Medium	[3]
$CsCa_2Ta_3O_{10}$：Yb^{3+}, Er^{3+}@$Cs(Pb_xMn_{1-x})(Cl_yBr_{1-y})_3$	980-nm laser+ 365-nm light	UCL+DCL	Solid state reaction	Green (UCL)+red，green and blue (DCL)	Static anti-counterfeiting+information encryption	Medium	[4]
$SrAl_2O_4$:Eu^{2+}/TPU	365-nm light	DCL	Electrospinning	Green (DCL)	Static anti-counterfeiting	Low	[8]
$Ca_2YMgScSi_3O_{12}$: Mn^{2+}	X-ray+254-nm+UV(365, 395, 463 nm) light	DCL	High-temperature solid-state reaction	Green to deep-red multicolor (DCL)	Static anti-counterfeiting	Low	[10]
$CsPbBr_3$ @mesoporous silica nanospheres	Water treatment+ 365-nm light	DCL	Hot-injection	Green (DCL)	Static anti-counterfeiting	Medium	[12]
$Bi_2Ti_4O_{11}$: Yb^{3+}, Er^{3+} @TPU film	980-nm laser	UCL	Electrospinning	Red, yellow and green (UCL)	Static anti-counterfeiting+ dynamic anti-counterfeiting	Medium	[13]
$CsPb(Br_xCl_y)_3$ (x=y)/$CsPb(Br_xCl_y)_3$ (x>y)-polymethyl methacrylate (PMMA)	Water treatment+ 365-nm light	DCL	Photolithographic patterning	Blue to green (DCL)	Static anti-counterfeiting	Low	[14]
Cs_3TbF_6:Eu^{3+}	Water treatment+ 365-nm light	DCL	Hot-injection	Green to yellow to red multicolor (DCL)	Static anti-counterfeiting	Medium	[17]
Fluorescence dyes (fluorescein isothiocyanate, rhodamine and dansyl acid-disulfide)	365-nm light	DCL	Photodynamic disulfide chemistry	Blue, green and red (DCL)	Static anti-counterfeiting+ dynamic anti-counterfeiting+information storage	Medium	[18]

$NaYF_4$:Yb/Tm@Na YF_4:Yb-$CsPbX_3$	980-nm laser+ 365-nm light	UCL+DCL	Two-step high temperature reflux method and hot-injection method	Blue to green to red multicolor (UCL)+blue to green to red multicolor (DCL)	Static anti-counterfeiting	Medium	[19]
Boric acid@carbon QDs	365-nm light+ heating/cooling	DCL	Hydrothermal	Blue to orange (DCL)	Static anti-counterfeiting+information encryption	Medium	[20]
Mn:$CsPbCl_3$ QDs and $CsPbBr_3$ QDs	365-nm light+ heating/cooling	DCL	Hot-injection	Green and orange (DCL)	Static anti-counterfeiting+information encryption+ information storage	Medium	[27]
Cs_4PbX_6 QDs	Water treatment+ 365-nm light	DCL	Inkjet printing patterned	Blue to green to red multicolor (DCL)	Static anti-counterfeiting+information encryption	Medium	[40]
Cs_4PbX_6-UCLNPs/PS film	980-nm laser+water treatment+365-nm light+ heating/cooling	UCL+DCL	Electrospinning	Green(UCL)+blue to green to red multicolor (DCL)	Static anti-counterfeiting+ dynamic anti-counterfeiting+information encryption+ information storage	High	This work