Supporting information

Solvent-Free Synthesis of Rare-Earth-Doped Zirconia Ceramic Nanofiber Films with Enhanced Luminescence for Anti-Counterfeiting and Warm White Lighting

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$$I_t = I_0 + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \#S\ (1)$$

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \#S\ (2)$$

Formula S(1) uses a double-exponential equation to fit the photoluminescence decay curve of the sample, where I_t is the intensity at time t, I_0 is the background intensity, A_1 and A_2 are the exponential coefficients, τ_1 and τ_2 are the decay times, and t is time. The average lifetime τ can be calculated using Formula S(2).

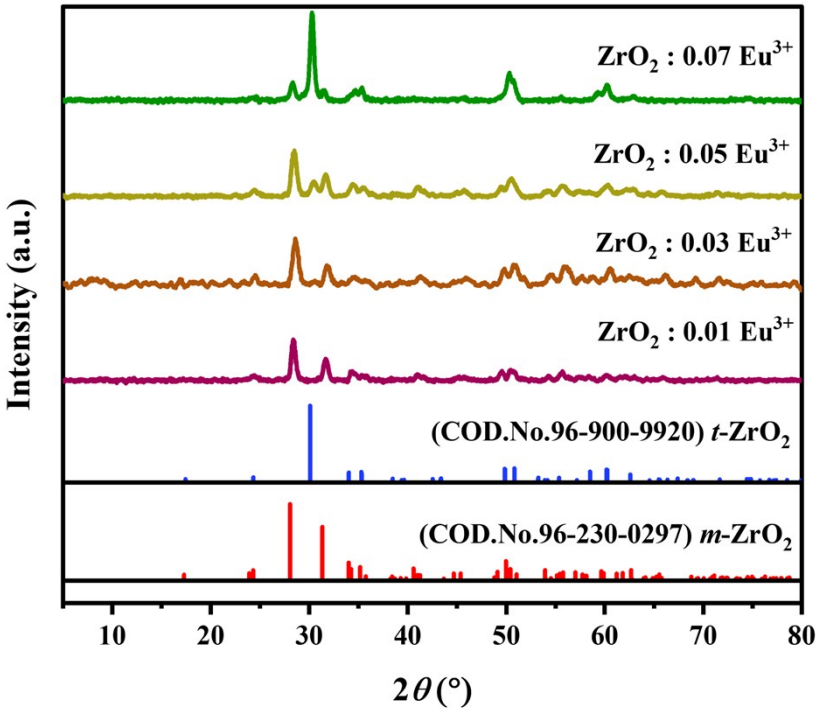

Figure S1 XRD patterns of ZrO_2:xEu^{3+} (x=0.01, 0.03, 0.05, 0.07 mmol) nanofibers.

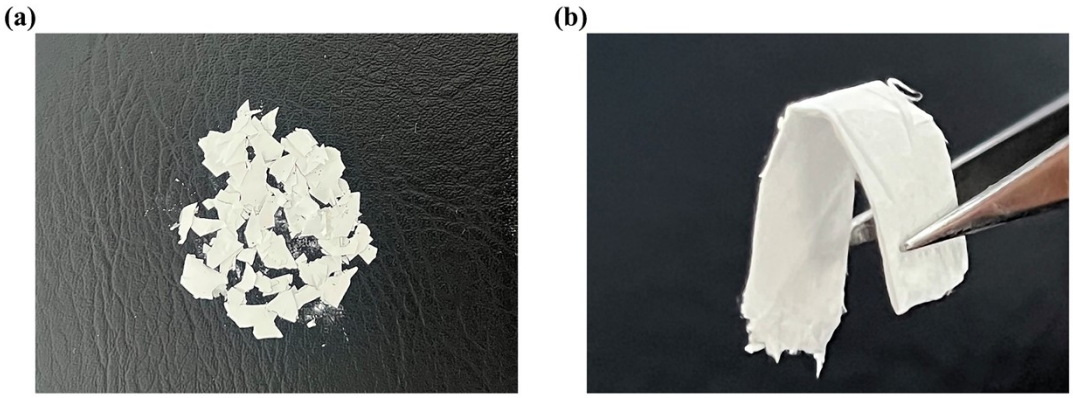

Figure S2 Physical photographs: (a) ZrO_2:0.05Eu^{3+} nanofiber, (b) ZrO_2:0.95La^{3+},0.05Eu^{3+} nanofiber films.

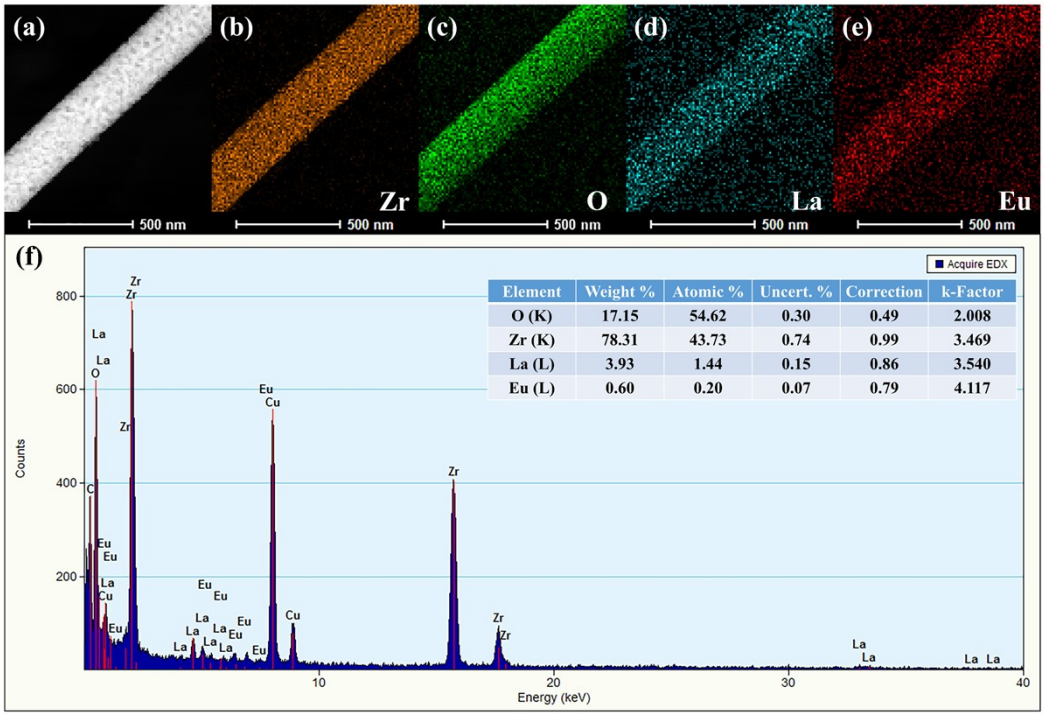

Figure S3 STEM-EDS elemental mappings of ZrO_2:0.95La^{3+},0.05Eu^{3+}nanofibers (a) HAADF image, (b-e) nanofibers for Zr, O, La, and Eu elements, respectively, (f) EDS spectra.

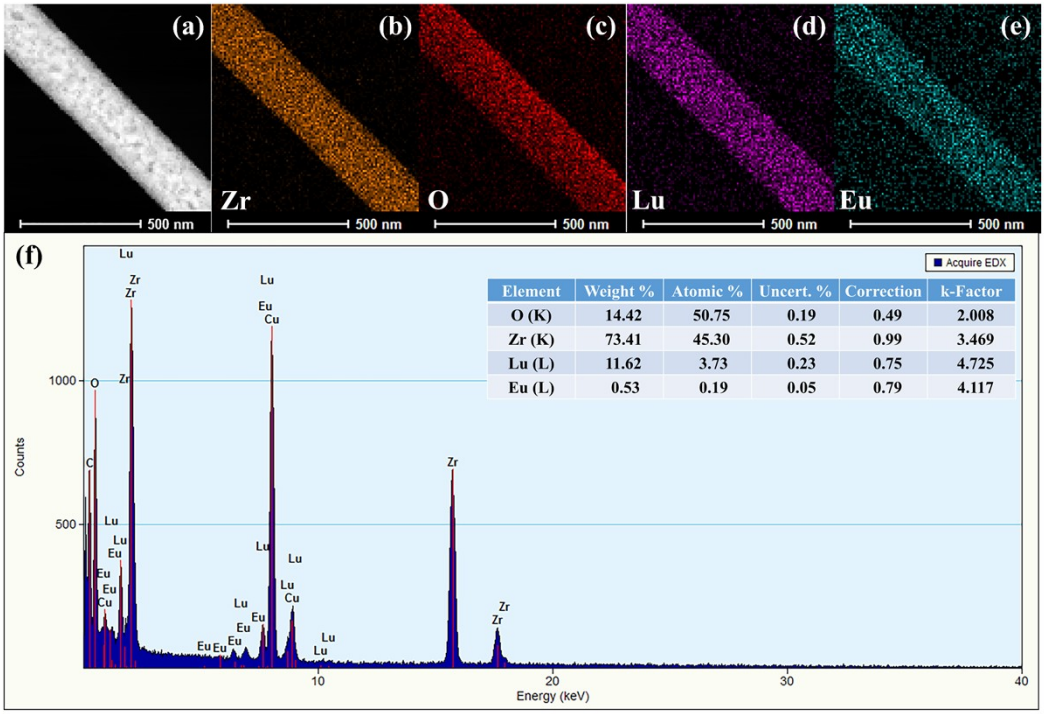

Figure S4 STEM-EDS elemental mappings of ZrO_2:1.40Lu^{3+},0.05Eu^{3+}nanofibers (a) HAADF image, (b-e) nanofibers for Zr, O, Lu, and Eu elements, respectively, (f) EDS spectra.

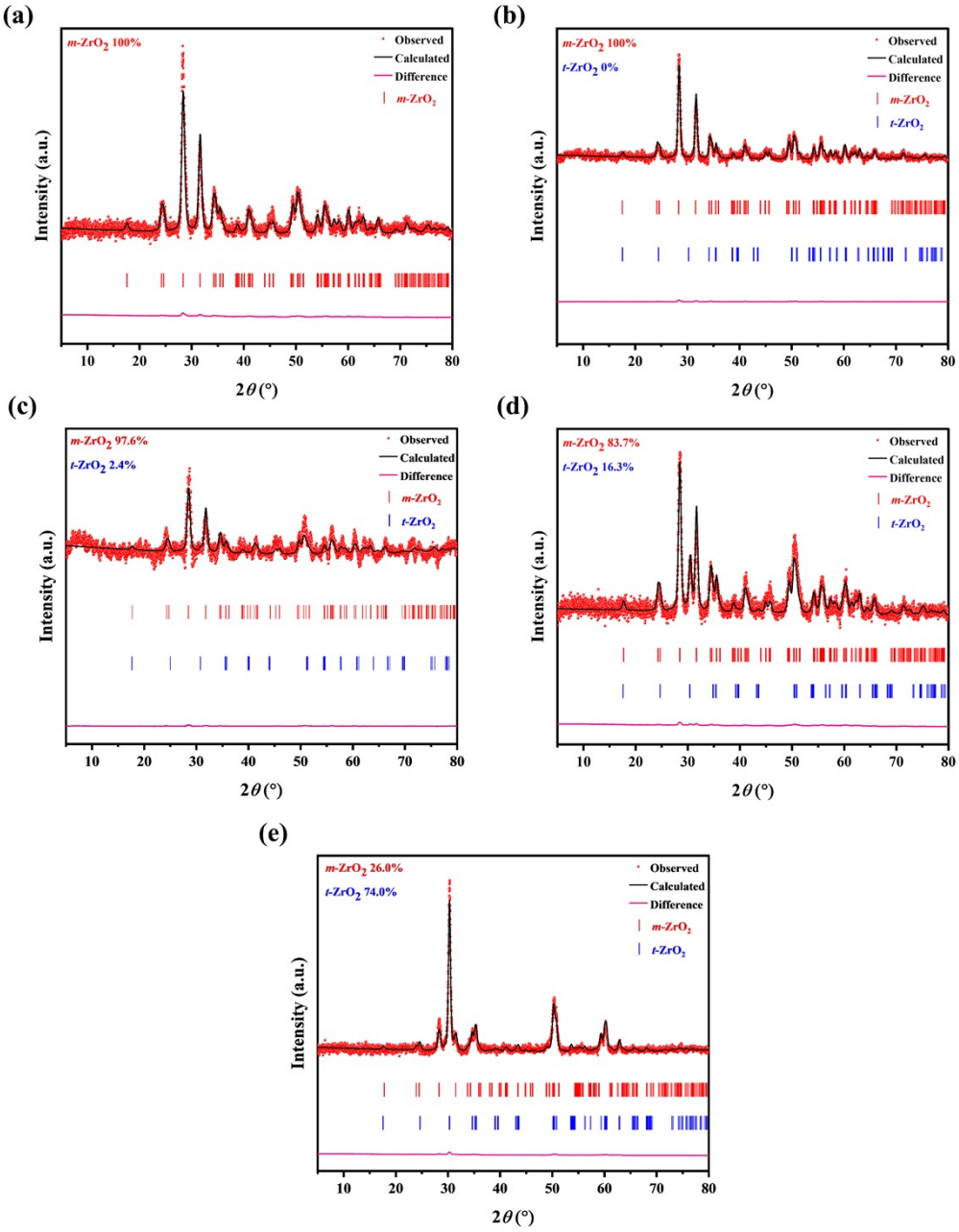

Figure S5 Refined diffraction patterns of ZrO_2:xEu^{3+} nanofibers (a) x=0 mmol, (b) x=0.01 mmol, (c) x=0.03 mmol, (d) x=0.05 mmol, (e) x=0.07 mmol.

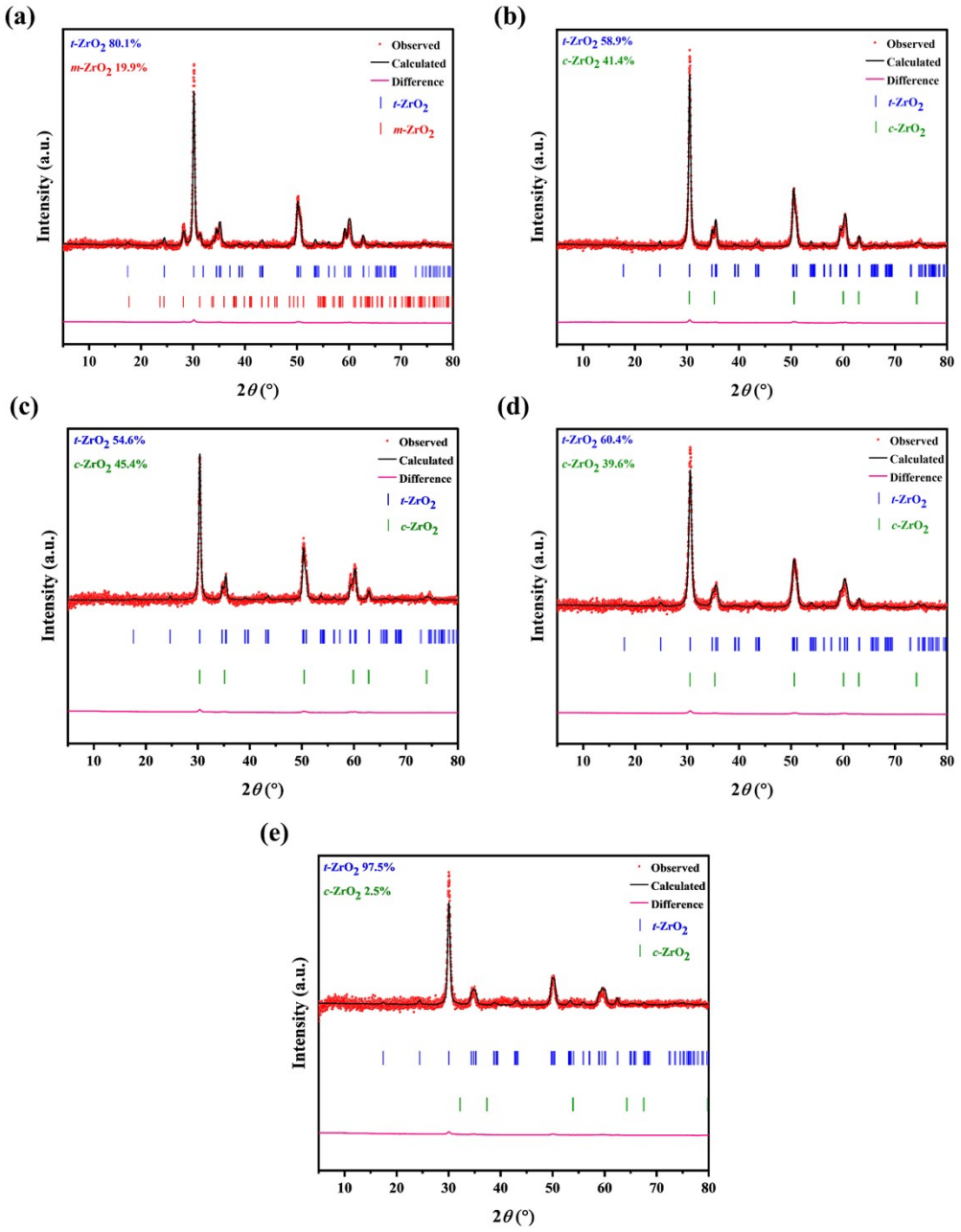

Figure S6 Refined diffraction patterns of ZrO_2:yLa^{3+},0.05Eu^{3+} nanofibers (a) y=0.50 mmol, (b) y=0.75 mmol, (c) y=0.95 mmol, (d) y=1.00 mmol, (e) y=2.00 mmol.

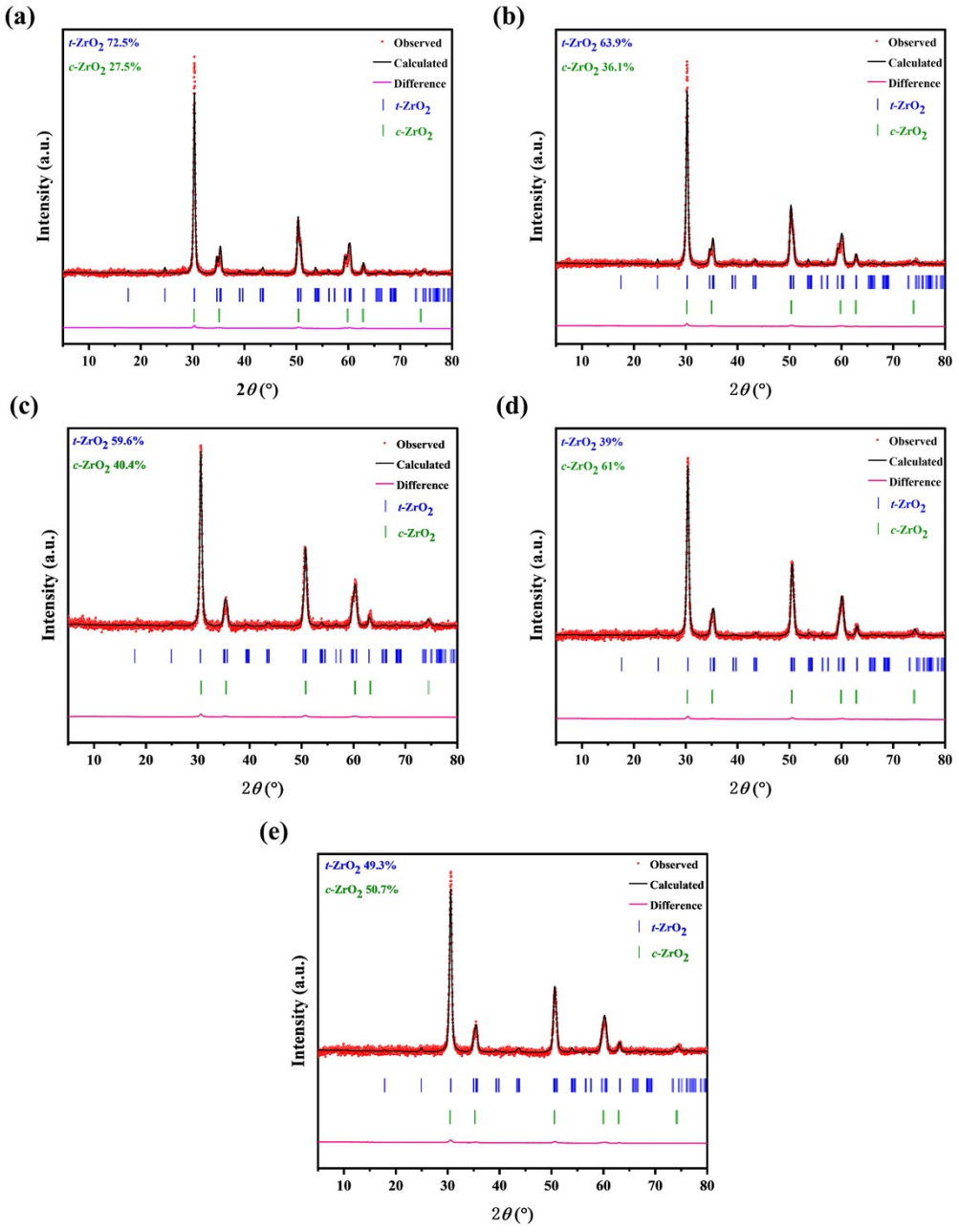

Figure S7 Refined diffraction patterns of ZrO_2:zLu^{3+},0.05Eu^{3+} nanofibers (a) z=0.50 mmol, (b) y=0.75 mmol, (c) y=1.30 mmol, (d) y=1.40 mmol, (e) y=1.50 mmol.

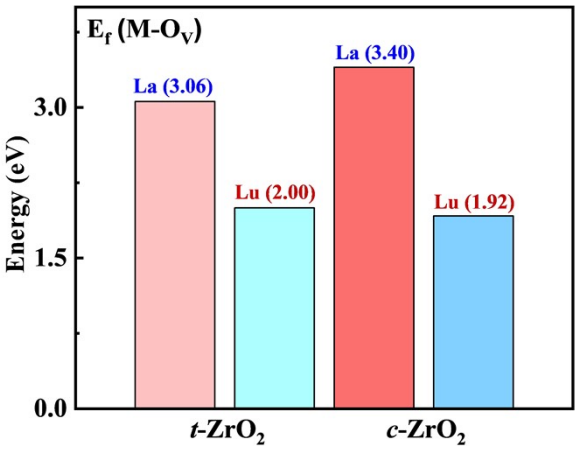

Figure S8 Formation energies E_f (M-VO) of La^{3+} and Lu^{3+} doped complex ZrO_2.

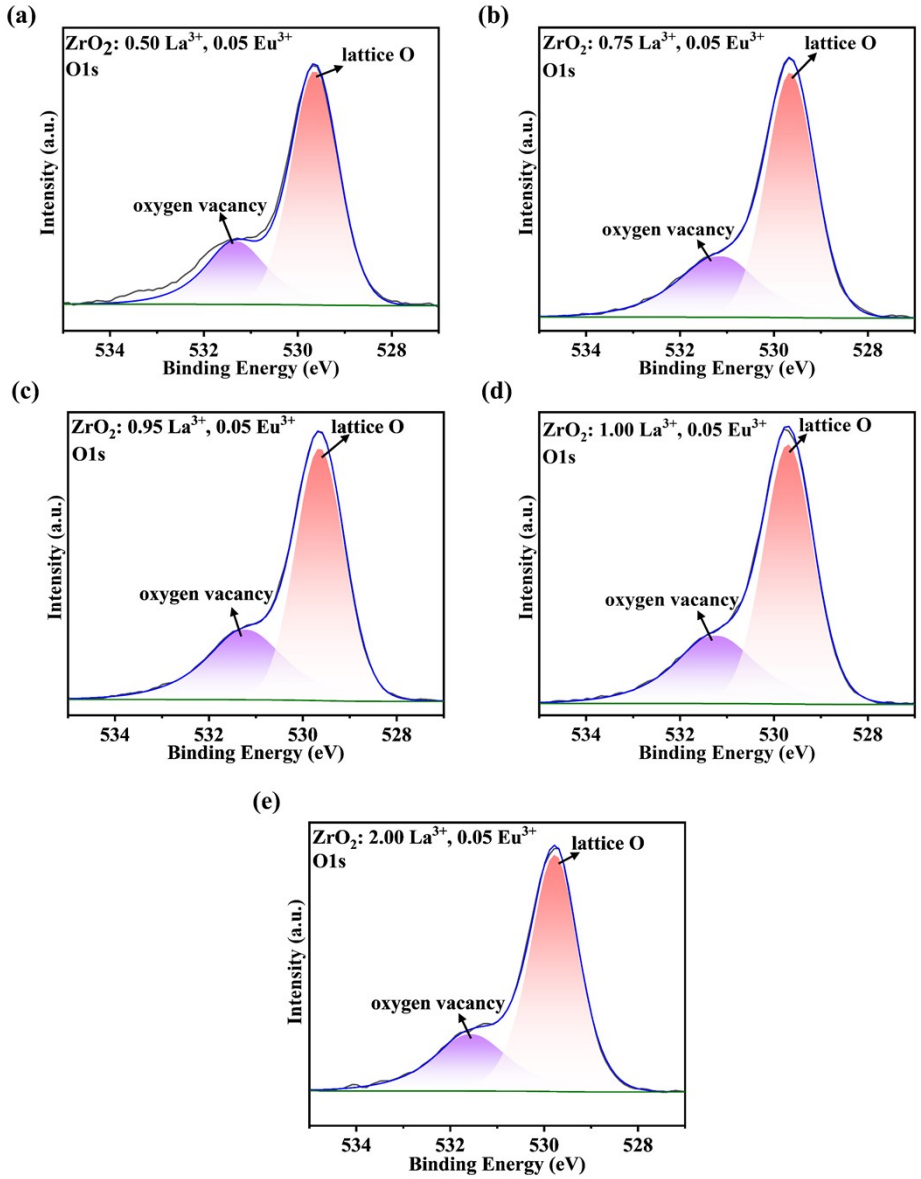

Figure S9 (a-e) O1s XPS spectra of ZrO_2:yLa^{3+},0.05Eu^{3+} (y=0.50, 0.75, 0.95, 1.00, 2.00) nanofiber films.

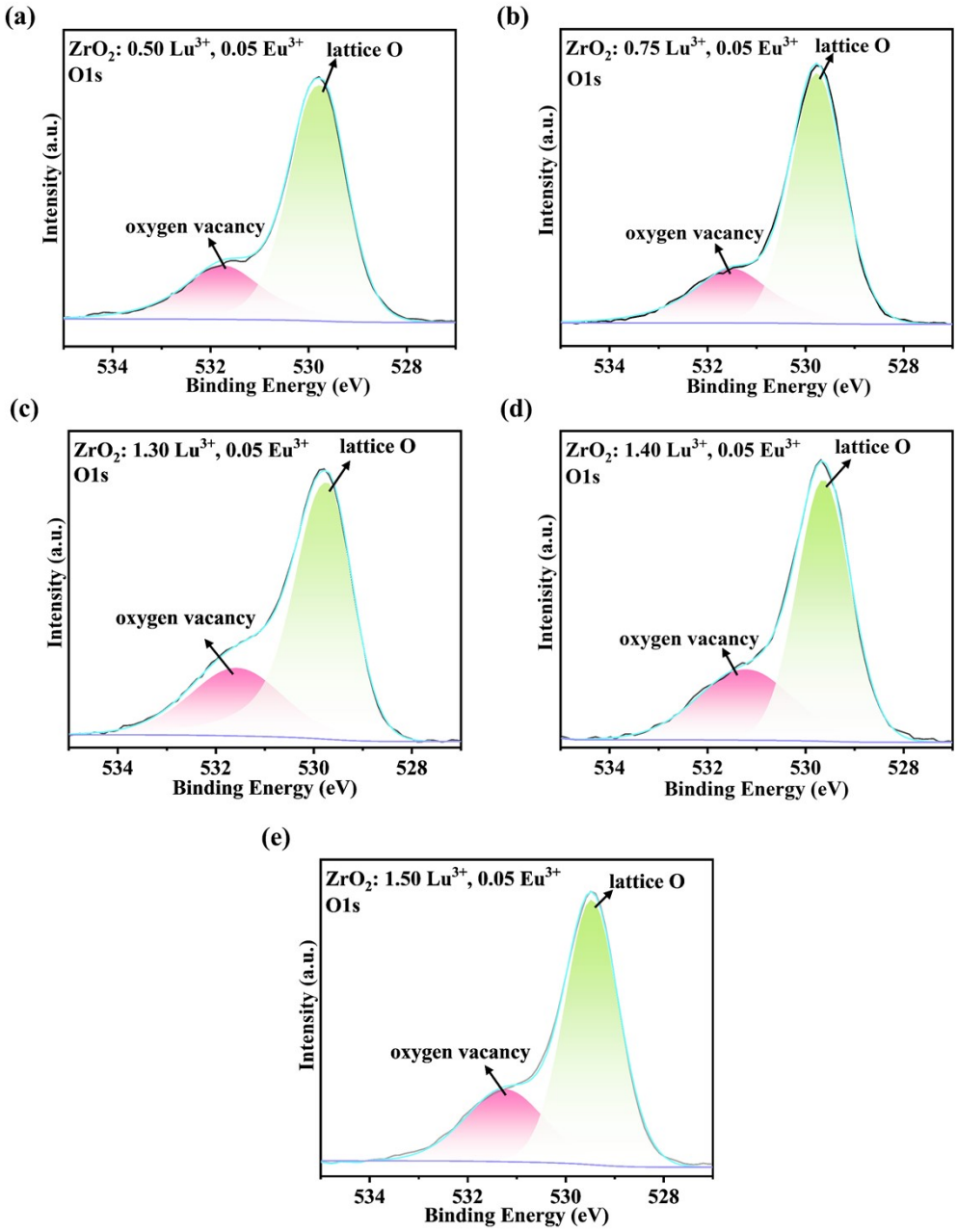

Figure S10 (a-e) O1s XPS spectra of ZrO_2:zLu^{3+},0.05Eu^{3+} (y=0.50, 0.75, 1.30, 1.40, 1.50) nanofiber films.

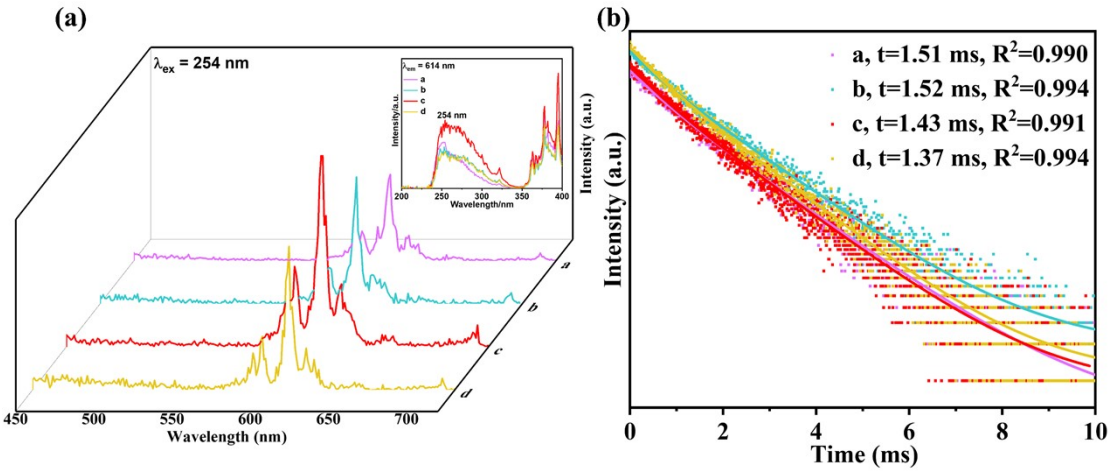

Figure S11 Luminescence properties of ZrO_2:xEu^{3+} (x=0.01, 0.03, 0.05, 0.07 mmol) nanofiber films: (a) emission and excitation spectra, (b) photoluminescence decay and fitting curves spectra.

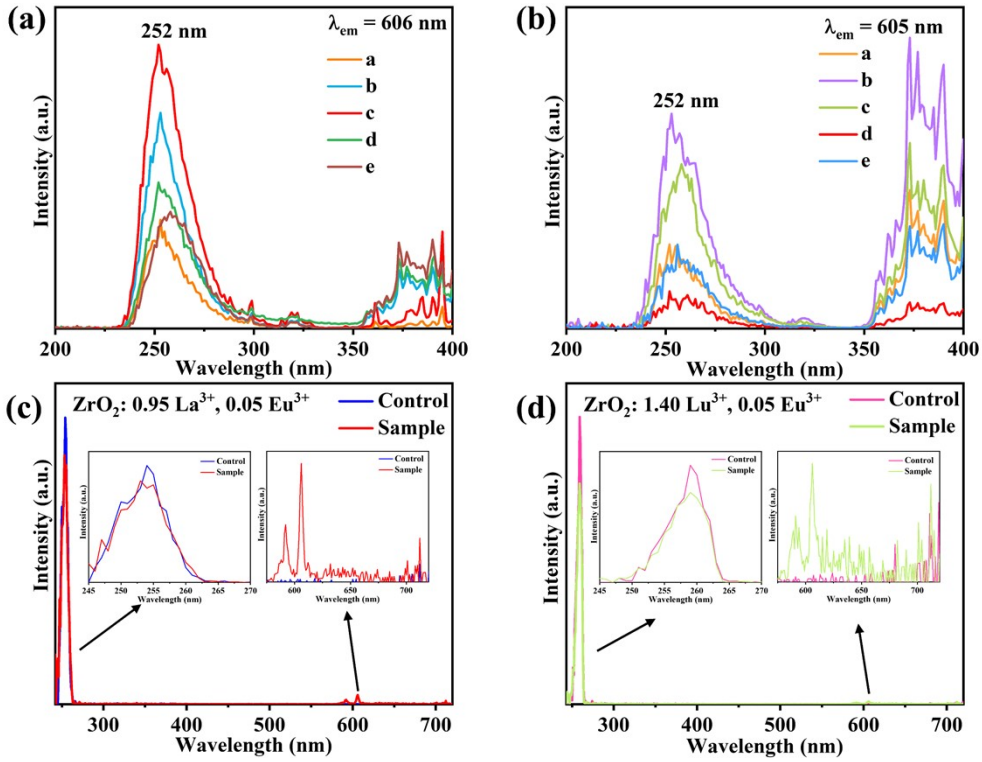

Figure S12 Excitation spectra of (a) ZrO_2:yLa^{3+},0.05Eu^{3+} (y=0.50, 0.75, 0.95, 1.00, 2.00 mmol) and (b) ZrO_2:zLu^{3+},0.05Eu^{3+} (z=0.50, 0.75, 1.30, 1.40, 1.50 mmol) nanofiber films, (b) luminescence spectrum of (c) ZrO_2:0.95La^{3+},0.05Eu^{3+} and (d) ZrO_2:1.40La^{3+},0.05Eu^{3+} nanofiber films in integrating sphere.

Figure S13 Photographs of anti-counterfeiting patterns of ZrO_2:1.40Lu^{3+},0.05Eu^{3+} nanofiber fabric: (a) under daylight, (b) on 1 day under 254 nm UV lamp, (c) after 180 days under 254 nm UV lamp.

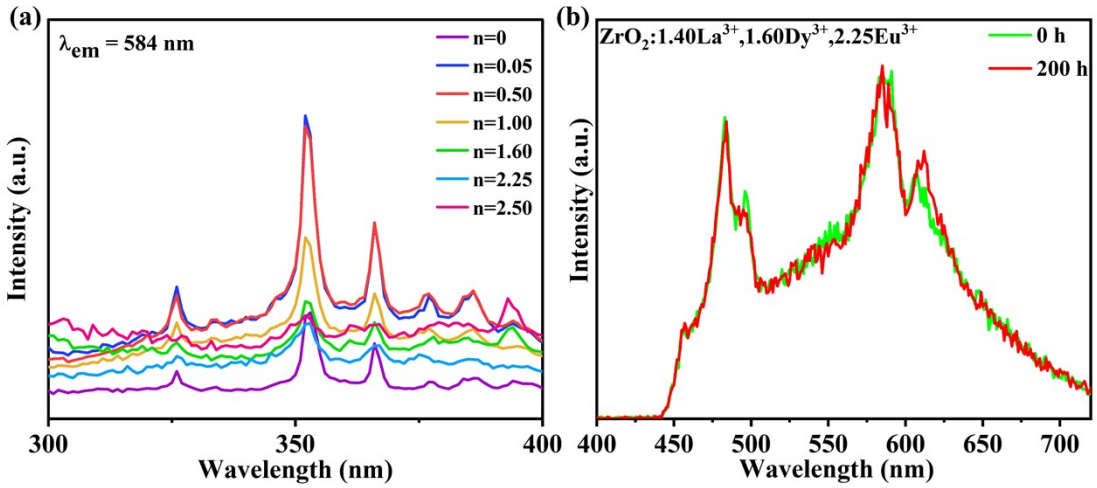

Figure S14 (a) Excitation spectra of ZrO_2:1.40Lu^{3+},1.60Dy^{3+},nEu^{3+} (n=0, 0.05, 0.50, 1.00, 1.60, 2.25, 2.50 mmol) nanofiber films, and (b) photoluminescence spectra of ZrO_2:1.40Lu^{3+},1.60Dy^{3+},2.25Eu^{3+} nanofiber films packaged WLEDs after a 200 h stability test under continuous illumination.

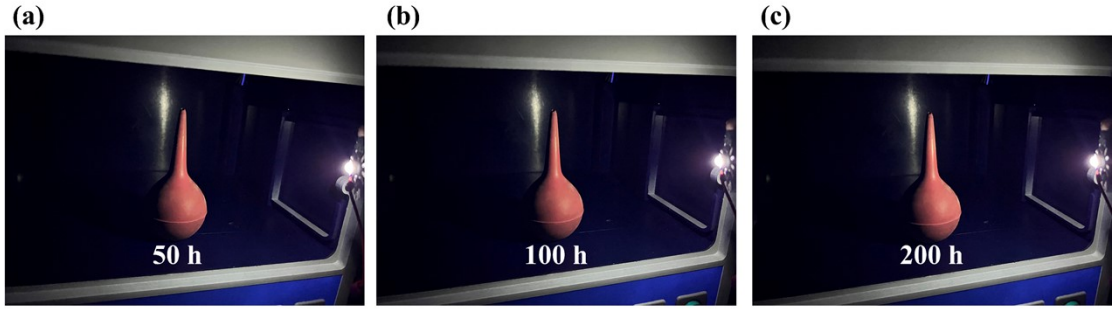

Figure S15 photographs of the continuous illumination test for ZrO_2:1.40Lu^{3+},1.60Dy^{3+},2.25 Eu^{3+} nanofiber fabric packaged WLEDs: (a) 50 h, (b) 100 h, (c) 200 h.

Table S1 List of Reliability Parameters of ZrO_2:nRE^{3+} (RE^{3+} = Eu^{3+}, La^{3+}, Lu^{3+}) Extracted from Refinement Report.

Nanofibers		R expected (R_{exp})	R profile (R_p)	Weighted R profile (R_{wp})	Goodness of fit (χ^2)
xEu^{3+}	0	2.59	1.85	2.39	0.85
	0.01	3.48	1.30	1.70	0.24
	0.03	3.51	0.83	1.07	0.09
	0.05	2.71	1.96	2.47	0.83
	0.07	2.43	1.77	2.17	0.80
yLa^{3+},0.05Eu^{3+}	0.5	2.46	2.00	2.53	1.06
	0.75	2.61	1.87	2.35	0.81
	0.95	2.32	1.56	1.92	0.69
	1.00	2.37	1.63	2.00	0.71
	2.00	1.99	1.50	1.81	0.83
zLu^{3+},0.05Eu^{3+}	0.5	2.63	2.22	3.00	1.30
	0.75	2.57	2.12	2.77	1.16
	1.30	2.60	1.74	2.23	0.73
	1.40	2.50	1.56	1.93	0.60
	1.50	2.38	1.61	1.97	0.69

Table S2 Summary of τ, PLQY, oxygen vacancy content, and radiative/non-radiative rate constants data for ZrO_2:nRE^{3+},0.05Eu^{3+} (RE^{3+} = La^{3+}, Lu^{3+}) nanofibers.

Nanofibers		τ (ms)	PLQY (%)	V_O (%)	k_r (s^{-1})	k_{nr} (s^{-1})
yLa^{3+},0.05Eu^{3+}	0.5	2.86	40.4	23.9	141.3	208.5
	0.75	3.06	58.3	26.9	190.5	136.3
	0.95	3.20	93.6	32.6	292.5	20.0
	1.00	3.00	65.6	31.5	218.7	114.7
	2.00	3.36	49.3	27.4	146.7	150.9
zLu^{3+},0.05Eu^{3+}	0.5	3.53	35.1	28.3	99.4	183.8
	0.75	3.60	40.9	29.7	113.6	164.2
	1.30	3.67	72.1	32.0	196.5	76.0
	1.40	3.61	94.7	33.3	262.3	14.7
	1.50	3.67	59.8	31.1	162.9	109.5

Table S3 CIE chromaticity coordinate of ZrO_2:1.40Lu^{3+},nEu^{3+},1.60Dy^{3+} (n=0.05, 0.50, 1.00, 1.60, 2.25, and 2.50) nanofiber films.

Nanofibers	CIE coordinate	CCT (k)	Color (white light)	CRI
ZrO_2:1.40Lu^{3+},1.60Dy^{3+},0.05Eu^{3+}	(0.3824, 0.4011)	4114	cool	39
ZrO_2:1.40Lu^{3+},1.60Dy^{3+},0.50Eu^{3+}	(0.4100, 0.4242)	3652	warm	48
ZrO_2:1.40Lu^{3+},1.60Dy^{3+},1.00Eu^{3+}	(0.4050, 0.4133)	3679	warm	53
ZrO_2:1.40Lu^{3+},1.60Dy^{3+},1.60Eu^{3+}	(0.4112, 0.4370)	3712	warm	64
ZrO_2:1.40Lu^{3+},1.60Dy^{3+},2.25Eu^{3+}	(0.4095, 0.4313)	3708	warm	72
ZrO_2:1.40Lu^{3+},1.60Dy^{3+},2.50Eu^{3+}	(0.4176, 0.4503)	3675	warm	70