Supplementary Information

Laser damage threshold of hydrophobic up-conversion carboxylated nanocellulose/SrF_2:Ho composite films functionalized with 3-aminopropyltriethoxysilane

Anna A. Luginina[a], Sergey V. Kuznetsov[a], Vladimir K. Ivanov[b], Valery V. Voronov[a], Alexey D. Yapryntsev[b], Andrey A. Lyapin[c], Elena V. Chernova[a], Aleksandr A. Pynenkov[c], Konstantin N. Nishchev[c], Radmir V. Gainutdinov[d], Alexey V. Bogach[a], Pavel P. Fedorov[a]

[a]Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilov str., Moscow 119991, Russia
[b]Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky Pr., Moscow 119991, Russia
[c]Ogarev Mordovia State University, 68 Bolshevistskaya str., Saransk, 430005, Russia

Corresponding author: P.P. Fedorov, ORCID https://orcid.org/0000-0002-2918-3926, E-mail: ppfedorov@yandex.ru; Tel: +7(499)503-87-92

This file includes Experimental methods SM1-SM2, Table S1, Figures S1−S8

Experimental method SM1: Preparation of unmodified nanocomposites films

The unmodified and modified nanocomposite films were prepared by the similar holmium content. We used $Sr_{1-x}Ho_xF_{2+x}$ powder (x = 0.08 and 0.10) of the same composition. Weighed amount of up-conversion powder for an unmodified nanocomposite film (M_{unm}, g) was necessary to reduce taking into account the content of polyaminopropylsiloxane in the modified nanocomposite film. For this, the APS was dried in a plastic beaker until a solid was formed at room temperature, then kept at 105°C for 10 minutes to undergo the APS self-condensation process. The weight loss of the APS on drying was 31.9%. Based on the difference in masses, a conversion factor K = 1.47 for APS was established, by which it is necessary to divide the mass of the APS, loaded into the dispersion, to determine its mass in the film (the molecular mass of APS is equal to 221.37 g/mol). To fulfill the $X_{unm} = X_m$ condition, where X_{unm}, wt.% and X_m, wt.% represent the content of up-conversion powder in the unmodified and modified nanocomposite films, respectively, the weighed amount of up-conversion powder in the unmodified film was calculated by the formula:

$$M_{unm} = \frac{M_m \times C}{Y_{APS}/1.47 + C} \quad , (1)$$

where M_m is the weight of $Sr_{1-x}Ho_xF_{2+x}$ for the modified nanocomposite film, g; Y_{APS} is the weight of APS, g, for a modified nanocomposite film; 1.47 is the coefficient for converting APS into polyaminopropylsiloxane, C is the dry TOCNF content in a sample of a TOCNF dispersion, g. The sample and concentration of TOCNF were the same for both films. To obtain nanocomposite films, the $Sr_{1-x}Ho_xF_{2+x}$ powder (x = 0.08 and 0.10), annealed at 750 °C, was thoroughly ground in an agate mortar. Then, a weighed portion of the powder, calculated according to formula (1), was dispersed in 10.0000 g TOCNF (1.88 wt.%) colloid suspension under sonication in ice bath for about 3-5 min with 3-4 time intervals until mixture cooling was completed (total treatment time was about 15 min). Composite films were formed by pouring the obtained colloidal suspensions into polystyrene Petri dishes, drying at room temperature for 2 days and at 105°C for 60 min, and cooling in desiccator with P_2O_5. The thickness of the films was 30–40 μm. The content of nanocellulose in the dried films varied in the range 44 - 75 wt%, and holmium content varied from 3.0 to 5.5 wt%. Obtained unmodified composite films were labeled as TOCNF:xHo, where x = wt.% Ho.

Experimental method SM2: **Determination of holmium content in modified nanocomposite film**

The holmium content in nanocomposite films was determined by titration. 0.2000-0.2500 g of a film specimen in a porcelain crucible was heated at a rate of 5°/min up to 730°C and further annealed at the same temperature during 1 hour. After cooling in a desiccator, the content of the crucible was transferred quantitatively into a glassy carbon dish. Sample was dissolved in concentrated sulfuric acid (triple H_2SO_4 treatment with complete liquid phase evaporation followed by dissolution in water) and titrated with solution of disodium ethylenediaminetetraacetate (DEDTA) in the presence of xylenol orange indicator and acetate buffer at pH = 5-6. Transition from red-violet to yellow coloration (Fedorov et al 2017) was used for an equivalency point determination. The Ho content (wt%) was calculated by formula:

$$Ho_{wt.}\% = \frac{M_{DEDTA} \times 164.93 \times (V_1 - V_0)}{\mathrm{m} \times 10}, \quad (2)$$

where M_{DEDTA} is the concentration of the DEDTA solution 0.01 mol/l; 164.930 is atomic mass of holmium; V_1 is the volume of 0.01 mol/l of the DEDTA solution used for sample titration, ml; V_0 is the volume of 0.01 mol/l of the DEDTA solution used for titration of the blank sample, ml; m is film weight, g. Relative error of the measured holmium content was 2.9% at P = 0.95 confidence interval.

Table S1 Properties of initial cellulose samples - ash free filter paper «Blue Ribbon» (Fedorov et al. 2019)

Particle size (SEM), μm		Cellulose structure	IC,%	DP	Decomposition temperature, T_{onset}/T_{endset}, °C
width	length				
50	200-1500	Iβ	68,7	1112	300/486

Supplementary Figures

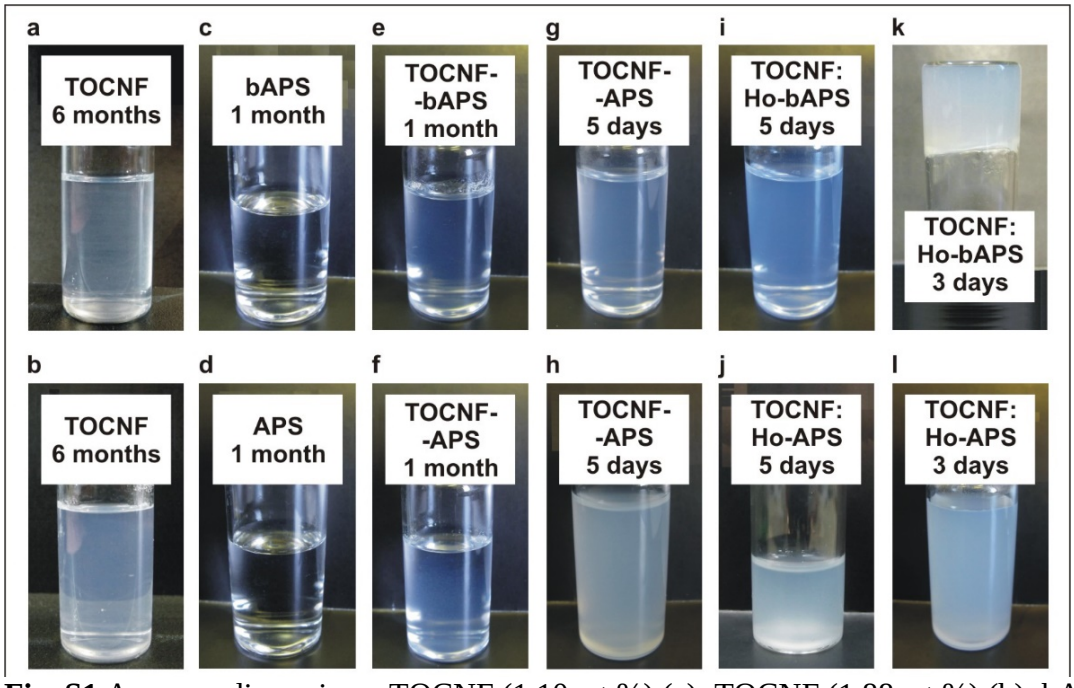
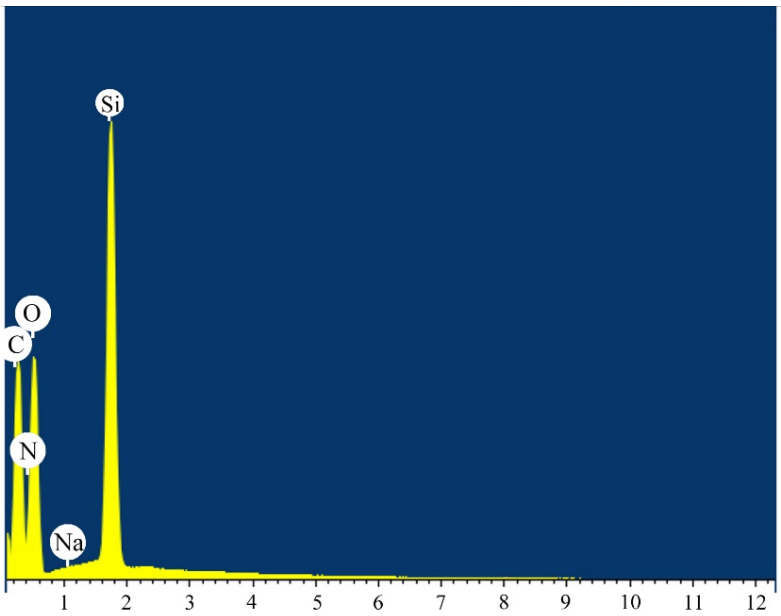


Fig. S1 Aqueous dispersions: TOCNF (1.10 wt.%) (a); TOCNF (1.88 wt.%) (b); bAPS (1.50 wt.%) (c); APS (1.50 wt.%) (d); TOCNF-bAPS (e) and TOCNF-APS (0.1% TOCNF, 0.15 wt.% APS – 6.7 mmol APS/g of dry TOCNF) (f); TOCNF-bAPS (g) and TOCNF-APS (1.10 wt.% TOCNF, 0.98 wt.% APS – 4.0 mmol APS/g of dry TOCNF) (h); TOCNF 0 wt. -bAPS:Ho (i) and TOCNF-APS:Ho (1.10 wt.% TOCNF, 0.70 wt.% APS, 0.20 wt.% $Sr_{0.90}Ho_{0.10}F_{2.10}$ – 2.9 mmol APS/g of dry TOCNF and 1.3 mmol $Sr_{0.90}Ho_{0.10}F_{2.10}$/g of dry TOCNF) (j); TOCNF-bAPS:Ho (k) and TOCNF-APS:Ho (1.10 wt.% TOCNF, 1.27 wt.% APS, 1.27 wt.% $Sr_{0.90}Ho_{0.10}F_{2.10}$ – 5.2 mmol APS/g of dry TOCNF and 8.6 mmol $Sr_{0.90}Ho_{0.10}F_{2.10}$/g of dry TOCNF) (l)

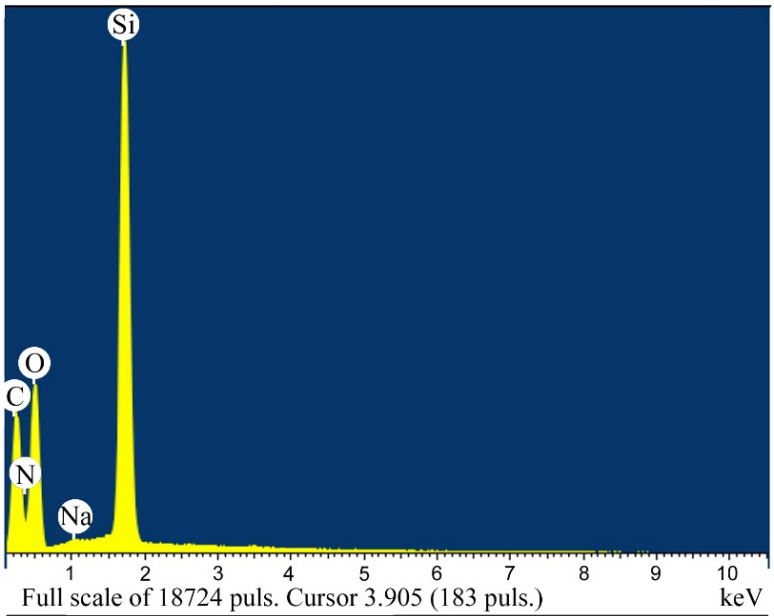


Processing parameters: Analysis of all elements (Normalized)

Spectrum	C	N	O	Na	Si
Spectrum 1	55.85	6.90	30.68	0.08	6.49
Spectrum 2	58.41	6.67	28.57	0.10	6.25
Spectrum 3	59.23	6.80	27.53	0.11	6.33
Spectrum 4	56.98	6.79	29.67	0.11	6.45
Average	57.62	6.79	29.11	0.10	6.38
Standard deviation	1.50	0.09	1.36	0.01	0.11

All results in at.%

Fig. S2 EDX analysis of TOCNF-$APS_{7.0}$ film after thermal treatment at 105°C



Processing parameters: Analysis of all elements (Normalized)

Spectrum	C	N	O	Na	Si
Spectrum 1	56.87	6.98	29.60	0.14	6.41
Spectrum 2	58.73	6.70	28.12	0.14	6.31
Spectrum 3	55.38	7.31	30.48	0.11	6.72
Spectrum 4	59.25	6.37	28.51	0.13	5.74
Average	57.55	6.84	29.18	0.13	6.30
Standard deviation	1.77	0.40	1.07	0.01	0.41

All results in at.%

Fig. S3 EDX analysis of TOCNF-b$APS_{7.0}$ film after thermal treatment at 105°C

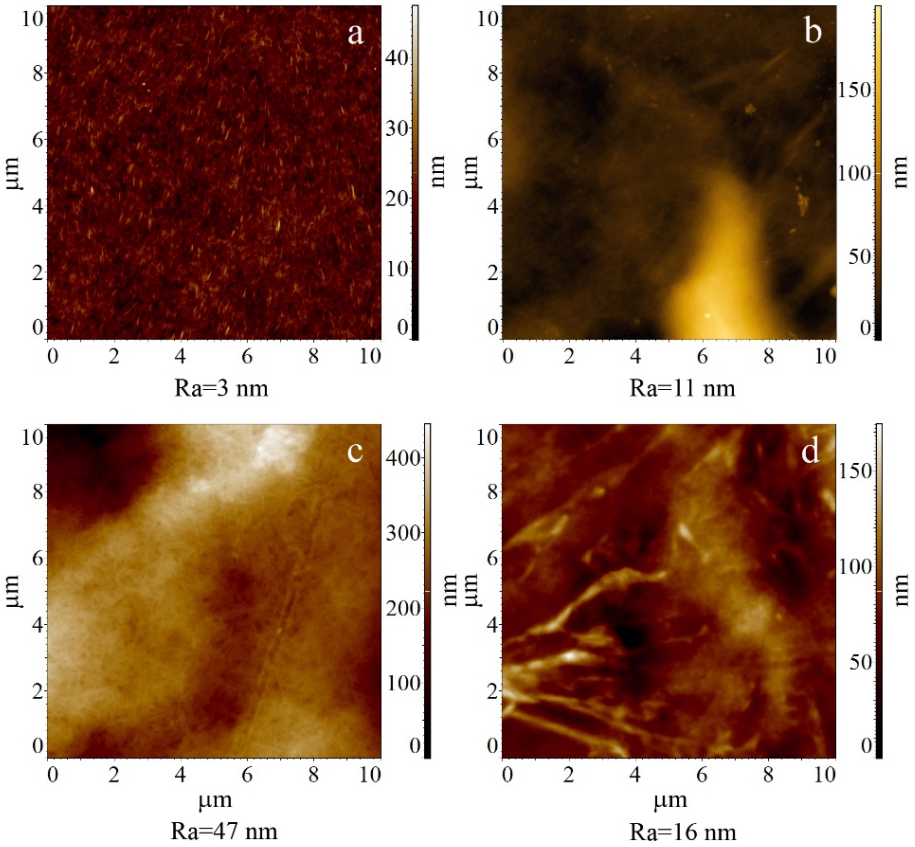


Fig. S4 AFM image of TOCNF (a), CNC (b), TOCNF-$APS_{7.0}$ (c), TOCNF-b$APS_{7.0}$ (d) films after the thermal treatment at 105°C (Ra - surface roughness value)

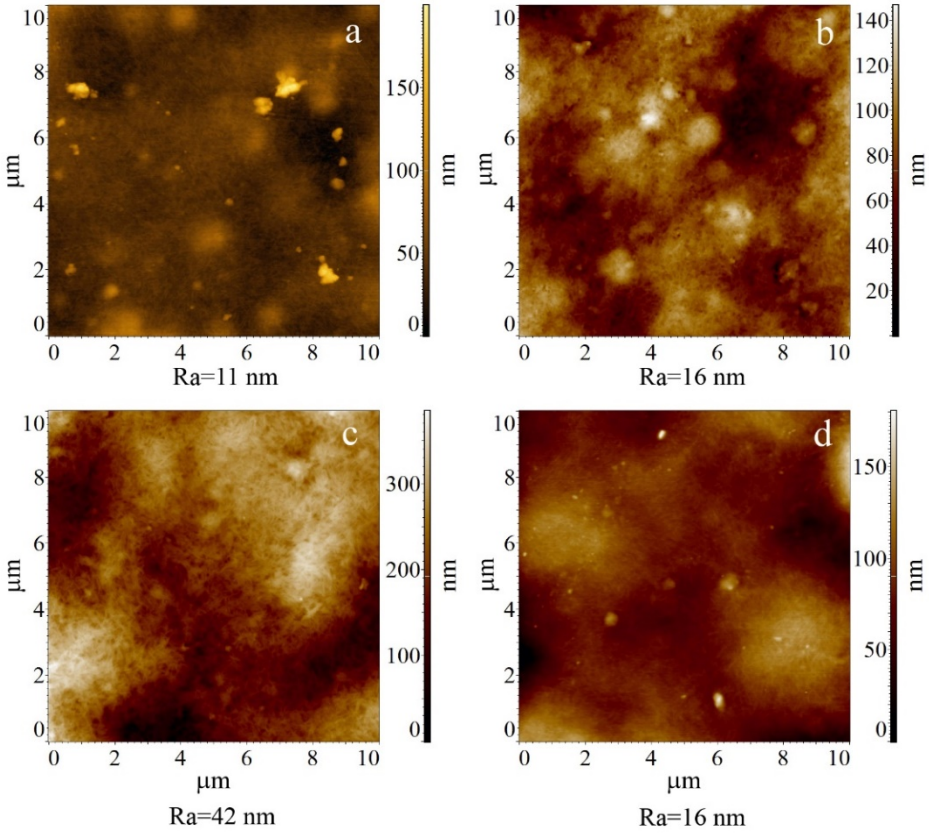


Fig. S5 AFM image of TOCNF:3.5Ho (a), TOCNF:3.5Ho-b$APS_{7.0}$ (b), TOCNF:3.5Ho-$APS_{7.0}$ (c), CNC:5.5Ho (d) composite films after the thermal treatment at 105°C (Ra - surface roughness value)

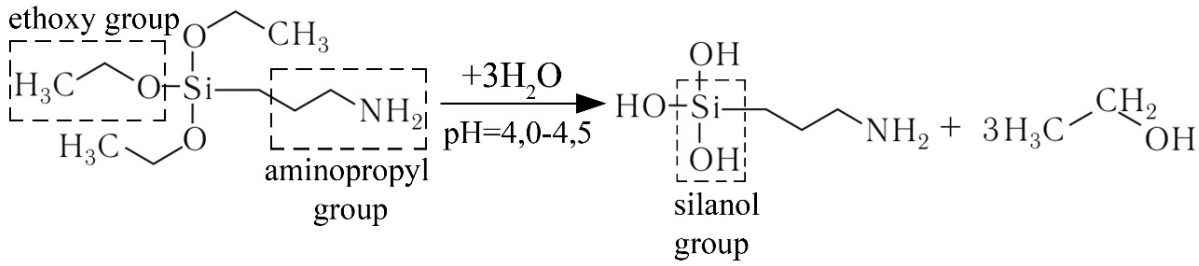
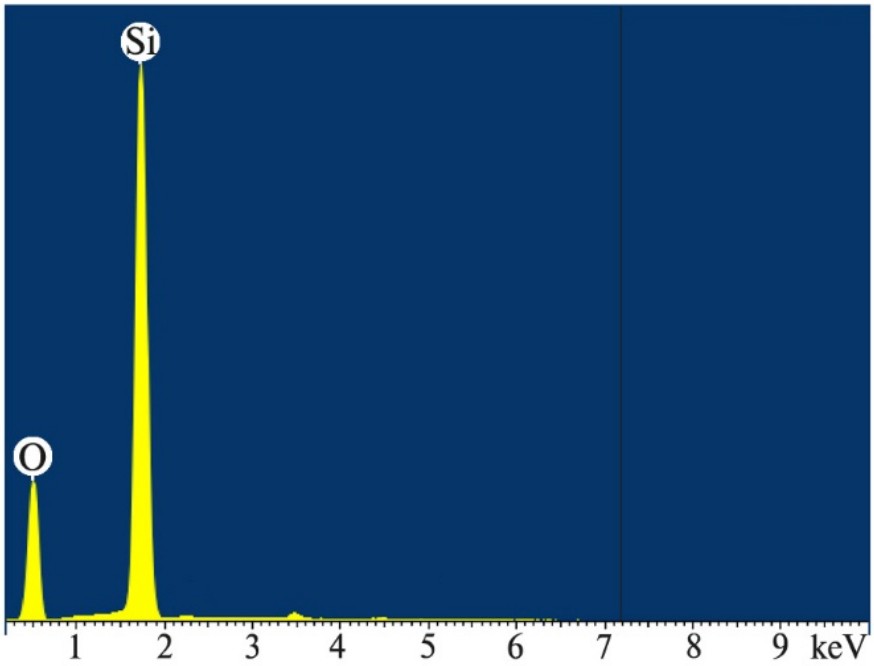


Fig. S6 Hydrolysis of APS at pH = 4.0-4.5 with the formation of 3-aminopropylsilanetriol



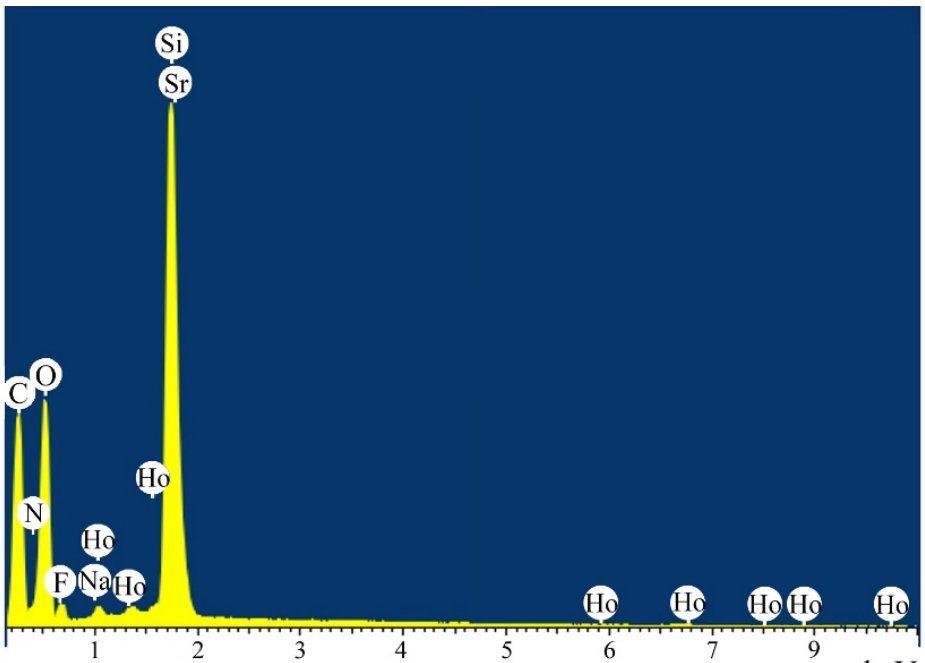
Full scale of 61796 puls. Cursor 7.194 (137 puls.)

Processing parameters: Analysis of all elements (Normalized)

Spectrum	O	Si
Spectrum 1	71.07	28.93
Spectrum 2	67.24	32.76
Spectrum 3	66.34	33.66
Spectrum 4	69.77	30.23
Spectrum 5	66.05	33.95
Average	68.09	31.91
Standard deviation	2,22	2,22

All results in at.%

Fig. S7 EDX analysis of APS after thermal treatment at 700°C



Full scale of 11781 puls. Cursor 4.675 (75 puls.)

Processing parameters: Analysis of all elements (Normalized)

Spectrum	C	N	O	F	Na	Si	Sr	Ho
Spectrum 1	50.23	4.98	25.05	12.27	0.09	4.73	2.41	0.24
Spectrum 2	49.77	4.53	23.38	14.75	0.11	4.32	2.98	0.27
Spectrum 3	50.13	4.58	23.94	13.56	0.09	4.59	2.82	0.29
Spectrum 4	50.78	4.96	29.20	7.47	0.12	4.97	2.27	0.23
Mean	50.23	4.76	25.37	12.01	0.10	4.65	2.62	0.26
Standard deviation	0.42	0.24	2.67	3.20	0.01	0.27	0.33	0.04

All results in at.%

Fig. S8 EDX analysis of TOCNF:3.3Ho-$APS_{5.0}$ (27.1 wt.% $Sr_{0.90}Ho_{0.10}F_{2.10}$) composite film after thermal treatment at 105°C

References

Fedorov PP, Luginina AA, Rozhnova YA, Kuznetsov SV, Voronov VV, Uvarov OV et al. (2017) Preparation of nanodispersed fluorite-type $Sr_{1-x}R_xF_{2+x}$ (R= Er, Yb, Ho) phases from citrate solutions. J Fluor Chem 194:8–15. https://doi.org/10.1016/j.jfluchem.2016.12.003

Fedorov PP, Luginina AA, Kuznetsov SV, Voronov VV, Lyapin AA, Ermakov AS, Pominova DV, Yapryntsev AD, Ivanov VK, Pynenkov AA, Nishchev KN (2019) Composite up-conversion luminescent films containing a nanocellulose and SrF_2:Ho particle. Cellulose 26:2403–2423. https://doi.org/10.1007/s10570-018-2194-4.