Laser damage threshold of hydrophobic up-conversion carboxylated nanocellulose/SrF₂:Ho composite films functionalized with 3-aminopropyltriethoxysilane

Anna A. Luginina · Sergey V. Kuznetsov · Vladimir K. Ivanov · Valery V. Voronov · Alexey D. Yapryntsev · Andrey A. Lyapin · Elena V. Chernova · Aleksandr A. Pynenkov · Konstantin N. Nishchev · Radmir V. Gainutdinov · Dmitrii I. Petukhov · Alexey V. Bogach · Pavel P. Fedorov

Received: 26 April 2021 / Accepted: 12 September 2021 / Published online: 1 October 2021
© The Author(s), under exclusive licence to Springer Nature B.V. 2021

Abstract Luminescent nanocomposite films, containing SrF₂:Ho up-conversion particles, were prepared by two different protocols from aqueous dispersions of TEMPO-oxidized cellulose nanofibrils (TOCNF) functionalized with 3-aminopropyltriethoxysilane (APS) without the use of organic solvents at pH = 4.0–4.5 and 9.0–9.5, respectively. Proposed synthetic protocols included the formation of the films by drying the dispersions containing pre-hydrolyzed APS adsorbed onto TOCNF and SrF₂:Ho particles followed by heating at 105 °C. Hydrophobic (water contact angle 101 ± 2°), strong, and translucent TOCNF/SrF₂:Ho-APS films were prepared by casting from a solution at pH = 4.0–4.5. Scanning electron microscopy, energy-dispersive X-ray spectroscopy with element mapping, Fourier-transform infrared spectroscopy, X-ray diffraction methods confirmed homogeneous distribution of up-conversion particles in TOCNF matrices as well as the grafting of linear polysiloxanes via the condensation of silanol groups and OH-groups on the surface of TOCNF. Differential scanning calorimetry and thermogravimetry data confirmed an increase in thermal stability of the APS modified nanocomposite films obtained at pH = 4.0–4.5. Hydrophobic TOCNF/SrF₂:Ho-APS films were prepared by casting from a solution at pH = 4.0–4.5. Scanning electron microscopy, energy-dispersive X-ray spectroscopy with element mapping, Fourier-transform infrared spectroscopy, X-ray diffraction methods confirmed homogeneous distribution of up-conversion particles in TOCNF matrices as well as the grafting of linear polysiloxanes via the condensation of silanol groups and OH-groups on the surface of TOCNF. Differential scanning calorimetry and thermogravimetry data confirmed an increase in thermal stability of the APS modified nanocomposite films obtained at pH = 4.0–4.5. Hydrophobic TOCNF/SrF₂:Ho-APS nanocomposite films exhibited an intense red luminescence in the visible spectrum range (τ₁ level excitation of Ho³⁺ ions with 1912 nm laser irradiation) as well as two-times higher laser damage threshold compared to unmodified TOCNF/SrF₂:Ho films. TOCNF/SrF₂:Ho-APS films can be used for visualization 2 μm laser radiation in medicine and long-distance atmosphere monitoring.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10570-021-04198-7.

A. A. Luginina · S. V. Kuznetsov · V. V. Voronov · E. V. Chernova · A. V. Bogach · P. P. Fedorov
Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilov Street, Moscow, Russia 119991
E-mail: ppfedorov@yandex.ru

V. K. Ivanov · A. D. Yapryntsev
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky Prospect, Moscow, Russia 119991

A. A. Lyapin · A. A. Pynenkov · K. N. Nishchev
Ogarev Mordovia State University, 68 Bolshevistskaya str., Saransk, Russia 430005

R. V. Gainutdinov
Shubnikov Institute of Crystallography, Federal Scientific Research Centre Crystallography and Photonics, Russian Academy of Sciences, 59 Leninsky Prospect, Moscow, Russia 119333

D. I. Petukhov
Department of Chemistry, Lomonosov Moscow State University, 1-3 Leninskie Gory, Moscow, Russia 119991
Keywords  TEMPO-oxidized cellulose nanofibrils · Functionalization · Nanocomposite · SrF$_2$:Ho · Up-conversion luminescence

Introduction

New generation luminescent nanocellulose-based composites and hybrid materials have found numerous application in optoelectronics (Dias et al. 2020; Vicente et al. 2018; Yang et al. 2018), organic light-emitting diodes (OLEDs) (Zhang et al. 2019), biosensors and detectors for monitoring environment and/or food quality control (Dai et al. 2020; Wang et al. 2020), biomedicine (Guan et al. 2018), latent fingerprint detection (Hai et al. 2018), anti-counterfeiting applications (Li and Hu 2019; Xiong et al. 2019; Zhang et al. 2018) and some other areas of photonics (Eichhorn 2018; Lizundia et al. 2020; Xue et al. 2018; Zhang et al. 2017). Cellulose nanofibrils (CNF), cellulose nanocrystals (CNC) and TEMPO-oxidized CNF (TOCNF) are unique matrices for the synthesis of luminescent nanocomposites because of their large surface areas, high reactivities, good optical properties, mechanical strength and colloid stability (De France et al. 2020; Kontturi et al. 2018; Thomas et al. 2018). Rare earth-based up-conversion luminophores, that efficiently transform near-infrared irradiation to visible light (Auzel 2004; Dong et al. 2013; Ovsyankin and Feofilov 1966; Qin et al. 2017; Reig et al. 2020), can be utilized for object visualization, in biomarkers, luminescent tagging, solar elements, electronic displays, etc. (Brites et al. 2020; Fischer et al. 2018; Liang et al. 2019; Zhou et al. 2015); this includes twomicron laser irradiation visualizers, based on holmium luminescent transitions, implemented in medical equipment and lidars (Belyaev et al. 2016; Lyapin et al. 2017; Scholle et al. 2010; Verber et al. 1971). Metal fluorides are considered most effective lumiphore matrices because of low phonon energies and high probabilities of the anti-Stokes transitions allowing visualization of IR-irradiation (Fedorov et al. 2011).

Composites based on nanocellulose and up-conversion luminophores have allowed developing the novel optical devices because of the synergy between the components. For example, the combination of CNC and 2.8 wt% NaYF$_4$:Yb:Er cubic phase was used for chiral up-conversion luminescent films preparation by evaporation-induced self-assembly (EISA) technique (Jiang et al. 2016). Up-conversion luminescent films, retaining tunable photonic chiral activity, have been obtained by self-assembly of CNC and polyvinyl alcohol (PVA)-stabilized hexagonal NaYF$_4$:Yb,Er nanorods (Nguyen et al. 2017). Up-conversion luminescent nanopaper, comprising cellulose nanofibrils (CNF) functionalized with NaYF$_4$:Yb,Er nanoparticles, have been synthesized for applications in sensors and anti-counterfeiting labels (Zhao et al. 2014).

Laser damage threshold (Wood 2014) and thermal stability (Delone 1993) are important criteria of nanocomposite films stability and their applicability as IR-irradiation visualizers. Earlier, we have developed flexible semitransparent CNC and CNC/CNF composite films with up-conversion SrF$_2$:Ho particles (Fedorov et al. 2019) and hydrophobic TOCNF-based alkyl ketene dimer (AKD) modified composite films with up-conversion MF$_2$:Ho (M = Ca, Sr) particles (Fedorov et al. 2020). These composites demonstrated intense red luminescence under Ho$^{3+}$ excitation with 1912 nm laser irradiation.

Considering that nanocomposite films have to be flexible and thermally stable, in this work, TOCNF
was used as the matrix for the incorporation of SrF₂:Ho nanoparticles. Significant amount of OH⁻ and COO⁻ groups on TOCNF surface opens opportunity for the surface modification, including increasing TOCNF thermal stability and hydrophobization of TOCNF surface (Rol et al. 2019), for example, by silylation. CNF silylation is carried out with various silylating agents, including methyltrichlorosilane (Orsolini et al. 2018), trimethylchlorosilane (Sai et al. 2015), chlorodimethylisopropylsilane (Andresen et al. 2006), 3-aminopropyltriethoxysilane (APS) (Peresin et al. 2017) in organic solvents. Salon et al. (2007) studied modification of microcrystalline cellulose with APS in ethanol/water and established that APS hydrolysis with the formation of silanol groups was required in order to enhance cellulose grafting, but covalent bonding of silanol groups with cellulose hydroxyls occurred only after the thermal treatment at 100–110 °C. Also, Robles et al. (2018) studied CNF silylation with APS in ethanol, water, and ethanol/water media and observed formation of hydrophobic CNF-APS films when water was used as a reaction solvent. Khanjanzadeh et al. (2018) performed CNC silylation with APS in aqueous solutions: at the beginning, APS was hydrolyzed in water, adsorbed onto CNC with hydrogen bond formation, covalently bound to CNC by forming Si–O–C bonds with CNC surface after reaction between silanol groups and CNC hydroxyls, resulting in an increase in thermal stability (by ~ 10 °C) of silylated CNC compared to untreated material. There is only a single report of TOCNF silylation with APS in ethanol/water solutions in the literature (Indarti et al. 2019). Whereas silylation of CNC and CNF is an efficient way of their hydrophobization, and some authors (Khanjanzadeh et al. 2018; Sai et al. 2015) mentioned an increase in thermal stability of organosilylated CNC and CNF, similar effects for TOCNF have not been reported yet.

In this paper, a readily available and inexpensive bifunctional APS monomer with primary amino-group and easily hydrolyzable ethoxysilyl moiety was chosen as silylating agent because of its high reaction capability, good solubility in water and low toxicity. The purpose of the present study was to develop up-converting nanocomposite TOCNF/SrF₂:Ho-APS films with hydrophobic properties and enhanced thermal stability as well as increased laser damage threshold compared to composite films reported earlier (Fedorov et al. 2019, 2020). TOCNF/SrF₂:Ho-APS nanocomposite films were obtained by mixing aqueous TOCNF dispersion, up-conversion SrF₂:Ho particles and aqueous APS in different weight ratios followed by casting, drying under air, and thermal treatment. The hydrophobicity, morphological, structural, and thermal properties of the composite films were studied depending on the pH of the reaction medium, the content of up-conversion particles and APS. Optical and luminescent properties of obtained composite films as well as their laser damage threshold were also studied.

Materials and methods

Starting materials

Ash free filter paper (FP) “Blue Ribbon” (State Standard 12,026–76) supplied by Prime Chemicals Group (Russia) was used as a precursor material for TOCNFs production. TEMPO (99% pure) was purchased from NIOCH SB RAS (Russia). 3-aminopropyltriethoxysilane (97% pure) was purchased from PENTA-91 Company (Russia). 19 wt% sodium hypochlorite solution (grade A, State Standard 11,086–76) was supplied by Prime Chemicals Group. Sodium bromide, sodium hydroxide, glacial acetic acid and hydrochloric acid (chemically pure grade) were supplied by Chimmed (Russia). Dialysis tubing (12–14 kDa molecular weight cut-off, Orange Scientific, Belgium) was purchased from Rosmedbio (Russia). Sr₁−ₓHoₓF₂+x (x = 0.08 and 0.10) fluoride luminophores were prepared by the technique proposed earlier (Fedorov et al., 2017). The characteristics of the FP cellulose samples are given in Table S1.

TOCNF preparation

TOCNF was prepared by the previously reported technique (Jiang et al. 2013) with some modifications (see Supplementary Information, Sect. 1). The content of TOCNF in the dispersion was determined by gravimetry as an average of two independent analyzes.

Preparation of silylated TOCNF

In this paper APS/dry TOCNF 0.44, 0.66, 1.11, 1.22, 1.33, 1.44, 1.48 and 1.55 weight ratio that corresponds
to APS loading of 2.0, 3.0, 5.0, 5.5, 6.0, 6.5, 6.7 and 7.0 mmol/g dried TOCNF was used. TOCNF modification was carried out in an aqueous medium at pH = 9.0–9.5 and pH = 4.0–4.5; silylation was performed as reported elsewhere (Khanjanzadeh et al. 2018; Robles et al. 2018; Tan et al. 2016), see protocols 1 and 2, respectively.

**Silylation in water at pH 9–9.5 (Protocol 1)**

This protocol was based on the report of Tan et al. (2016). APS aqueous solutions (1.19–4.16 wt%) were prepared by adding APS to bidistilled water under intense stirring in fluoroplastic beaker for 10 min. Then, 10.0000 g of TOCNF dispersion (1.88 wt%) were added dropwise to APS solution and stirred with a magnetic stirrer at room temperature for 30 min, while maintaining pH value in 9.0–9.5 range by adding dropwise 0.1 wt% NaOH. APS concentration was increased from 0.49 to 1.71 wt%, while TOCNF concentration was constant (about 1.10 wt%). The films were formed by pouring the obtained mixture in polystyrene Petri dishes, drying at room temperature for 2 days and at 105°C for 60 min (Khanjanzadeh et al. 2018). Obtained films (45–55 micron thickness) were cooled in P2O5—dried desiccator in order to prevent the formation of bicarbonated amino groups through the reaction with water and atmospheric carbon dioxide. The films were designated TOCNF-bAPSn, where b is means pH = 9.0–9.5 of the reaction medium, and n is APS loading equal to the ratio of APS to dried TOCNF, mmol/g.

**Silylation in water at pH 4–4.5 (Protocol 2)**

This protocol was based on the report of Khanjanzadeh et al. (2018) with the same precursor content/concentration as in Protocol 1; while the synthesis was carried out at pH = 4.0–4.5. pH value was corrected with glacial acetic acid, and obtained modified films were labeled as TOCNF-APSn.

**Preparation of modified nanocomposite films**

In order to obtain nanocomposite films, Sr1-xHoxF2+x (x = 0.08 ± 0.10) powder, annealed at 750°C, was thoroughly ground in an agate mortar. 0.1000–0.2900 g of ground powder were dispersed in 10.0000 g TOCNF (1.88 wt%) colloid suspension under ultrasonication in an ice bath for 3–5 min until complete mixture (total treatment time was about 15 min). Unmodified nanocomposite films with the same holmium content were prepared under the same conditions (see Supplementary Information, Sect. 2). Obtained dispersion was added dropwise to APS solution prepared by protocol 1 or 2 and stirred with a magnetic stirrer at room temperature for 30 min, while maintaining the pH value of 9.0–9.5 or 4.0–4.5, respectively. Composite films (50–60 micron thickness) were formed by pouring the obtained mixture in polystyrene Petri dishes, drying at room temperature for 2 days and at 105°C for 60 min and cooling in desiccator with P2O5. The dried films contained 30–56 wt% nanocellulose and 3.0–5.5 wt% Ho. Films obtained at pH = 9.0–9.5 and pH = 4.0–4.5 were labeled as TOCNF:xHo-bAPSn and TOCNF:xHo-APSn, respectively, where x is holmium wt% content.

**Characterization methods**

X-ray diffraction patterns were recorded with Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany; CuKα-radiation; 8–60° 2θ range, 0.02° 2θ step). The 22.7° 2θ diffraction peak was used for TOCNF crystallinity index (IC, %) calculation by Segal’s method (Fedorov et al. 2019). The carboxylate content (mmol/g) in TOCNF was determined by a conductometric titration technique according to the protocol described elsewhere (Jiang et al. 2013). The conductivity values were recorded at room temperature using an Expert-002 conductometer as the mean value of three measurements. The degree of oxidation of primary hydroxyl groups (DO) was determined by Eq. 1 (Habibi et al. 2006):

\[
DO = \frac{162 \times (V_1 - V_0) \times C_{NaOH}}{m - 36 \times (V_1 - V_0) \times C_{NaOH}}
\]

where \(V_1\) and \(V_0\) are the equivalent volumes of NaOH standard solution added (in L); \(C_{NaOH}\) is the exact concentration of NaOH standard solution (mol/L); \(m\) is dry TOCNF weight in TOCNF dispersion (g); and coefficients 162 and 36 correspond to the molecular weight of anhydroglucose unit (AGU) and the difference between molecular weights of AGU and sodium anhydroglucuronate moiety, respectively.

The particle size distributions in the films were analyzed by simultaneous use of scanning electron
microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) (NVision 40 microscope, Carl Zeiss NTS GmbH, Germany, with X-Max detector, Oxford Instruments, UK). The surface morphology, size, and shape of TOCNF particles and the morphology of the composite films were also analyzed using SEM. A drop of dilute aqueous dispersion of 0.01 wt% TOCNF was applied onto a single crystal silicon substrate and air-dried for the further SEM analysis. Particle size, size of nanofibrils, and pore size were calculated using the ImageJ software as a mean value in 25 independent measurements.

The surface morphology and roughness were investigated using NTEGRA Prima atomic force microscope (NTMDT Spectrum Instruments, Russia) in a tapping mode. All experiments were carried out under controlled conditions maintained by a TRACK-PORE ROOM-05 measuring complex (purity class 5 ISO (100), the accuracy of maintaining air temperature in the range of 23 ± 0.05 K, the relative air humidity is 55 ± 1%). The average roughness (Ra) was measured using the atomic force microscopy (AFM) images for 10 μm × 10 μm scanning areas and was determined as the average of 5 independent measurements.

Zeta potential (ζ-potential) values of the dispersions were measured by electrophoretic light scattering technique using the phase analysis light scattering (PALS) on the Photocor Compact-Z analyzer at room temperature. The resulting ζ-potential values are mean values in five consecutive measurements.

The degree of polymerization (DP) was assessed by viscosity measurements using diluted solutions of dry nanocellulose films in Cadoxen (cadmium ethylenediamine) (Voronova et al. 2017). DP was determined as an average of two independent measurements.

The thickness of each film was determined by a micrometer (MKTS-25 0.001, Kalibron, Russia) as the mean value for seven randomly selected locations.

Fourier transform infrared spectroscopy (FTIR) studies were performed on an INFRALUM FT-08 spectrometer equipped with ATR unit (Pike) in the range from 400 to 4000 cm⁻¹ with spectral resolution of 4 cm⁻¹.

The transmission spectra were recorded in the 250–3000 nm range using a Cary 5000 spectrophotometer.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on a Netzsch DSC 404 F1 Pegasus and Netzsch TG 209 F1 Libra devices in the range from 25 to 800 °C with a 5 °C/min heating rate under air.

The water contact angle was measured on a FTA1000 Drop Shape Instrument B Frame System. The test sample was placed on a horizontal holder. The water was applied onto the surface of the test sample by a special microdosing syringe. The droplet volume was 100 μL. The images were recorded using a 640 × 480 pixel CCD detector. Images were obtained in 1 s and 60 s after the application of droplets. The measurements were performed at room temperature (24 ± 2 °C) and repeated for 5 times on various fresh surfaces.

In order to determine holmium content in the synthesized nanocomposite films, they were heated at 730 °C. Obtained annealed fluoride powder residue was converted to sulphates, which were dissolved in water and titrated with disodium ethylenediaminetetraacetate (xylene orange indicator) (see Supplementary Information, Sect. 3). The holmium content was determined as an average of two independent analyzes.

The up-conversion luminescence spectra were recorded with a Horiba FHR 1000 spectrophotometer with OL IS-670-LED integrating sphere (Gooch & Housego). A continuous solid-state LiYF₄:Tm laser, operating at 1912 nm, was used as the excitation source for Ho³⁺ ions. The beam diameter and excitation power of incident laser radiation were 300 μm and 960 mW, respectively.

The damage threshold, being the characteristic of laser radiation durability, was detected visually by observation of the film destruction under 1940 nm laser irradiation with focused laser beam of 1500 μm diameter. Fiber TLM-10 laser (IPG Photonics) was used as an excitation source. The measurements of the laser damage threshold were repeated 5 times on various fresh surfaces.

Results and discussion

Morphology and hydrophobic properties of unmodified and modified TOCNF films

Obtained transparent aqueous TOCNF dispersions (1.20 ± 0.05 mmol/g carboxyl group content; oxidation degree DO = 0.20) maintained their stability for
at least 6 months (Figs. S1a, b). The colloidal stability was confirmed by ζ-potential value (−50 ± 2 mV) and was due to the electrostatic repulsion of COO− functional groups. HCl hydrolysis followed by TEMPO oxidation lowered TOCNF degree of polymerization down to 123 ± 3 (Table S1), i.e., by about an order of magnitude. SEM images of TOCNF samples confirm the presence of entangled nanofibrils (20 ± 6 nm width, 809 ± 98 nm length) forming porous network (Fig. 1a); this is in a good agreement with AFM data. CNC films obtained by previously reported protocol (Fedorov et al. 2019), consist of short needle-type rods with 14 ± 2 nm width and 107 ± 38 nm length aligned in the same direction (Fig. 1b).

TOCNF silylation with APS in aqueous medium was carried out according to two protocols. APS aqueous solutions maintained their stability at pH 9.0–9.5 and/or pH 4.0–4.5 for at least one month (Figs. S1c, d). 0.10 wt% TOCNF and 0.15 wt% APS mixed dispersions were also stable within the same time periods (−30 ± 3 mV and −17 ± 2 mV ζ-potentials for TOCNF-bAPS6.7 and TOCNF-APS6.7 dispersions, respectively; Figs. S1e, f). The decrease in the absolute value of ζ-potential for TOCNF-APS6.7 in comparison with TOCNF-bAPS6.7 was probably caused by amino-group protonation, leading to the increase in the ionic strength of the system and contraction of the double electric layer. 1.10 wt% TOCNF and 0.98 wt% APS dispersions maintained their stability without flocculation and/or sedimentation for at least 5 days (Figs. S1g, h). These dispersions were more transparent and viscous at pH 9.0–9.5 than at pH 4.0–4.5, due to their three-dimensional

---

**Fig. 1** SEM images of 0.01 wt% dispersions air-dried on a single-crystal silicon substrate: TOCNF (a), CNC (b). SEM images of the films after thermal treatment at 105 °C: TOCNF-APS7.0 (c), TOCNF-bAPS7.0 (d). Insets show the corresponding film images obtained by AFM (1 μm × 1 μm scanning area)
structure formed as a result of self-condensation of the partially hydrolyzed APS (Beari et al. 2001; Salon et al. 2007, 2010).

TOCNF-APS\textsubscript{7.0} films consisted of thickened well-distinguishable nanofibrils (width up to 27 ± 6 nm). Size increase of fibrils is apparently due to their coating with linear polysiloxane network (Fig. 1c), whereas the nanofibrils in TOCNF-bAPS\textsubscript{7.0} had their width decreased down to 25 ± 7 nm and exhibited the tendency to glue to each other (Fig. 1d). AFM images of the TOCNF-bAPS\textsubscript{7.0} surfaces show 3D siloxane “islands” formed as a result of self-condensation of the hydrolyzed APS (Fig. 1d, inset). EDX results showed more uniform distribution of elements in TOCNF-APS\textsubscript{7.0} film compared to TOCNF-bAPS\textsubscript{7.0} film (Figs. S2 and S3). Si/N ratio in the modified films was close to the same ratio for APS molecules. X-ray diffraction pattern of TOCNF film contained diffraction peaks at 20 = 22.5° and 20 = 14.8 – 16.8° (double peak) that corresponded to the (200), (110) and (110) crystallographic planes of monoclinic I\textsubscript{\textbeta} cellulose (Jiang et al. 2013) (Fig. 2a).

X-ray diffraction study of TOCNF-bAPS\textsubscript{7.0} and TOCNF-APS\textsubscript{7.0} films did not show any essential changes in their TOCNF crystal structure after modification: whereas line intensities changed, the diffraction angles remained the same as for the starting TOCNF films (Fig. 2b, c). Changes in amorphous halo could be explained by amorphous nature of APS attached to TOCNF. The same explanation could also be given for the crystallinity degree decrease in TOCNF-bAPS\textsubscript{7.0} and TOCNF-APS\textsubscript{7.0} films (Table 1).

Some changes in the diffraction line intensities of I\textbeta cellulose in the modified composite films could be attributed to the presence of the fluorite phase (Fig. 2d–f). The cubic unit cell parameters of the fluorite phases of Sr\textsubscript{0.92}Ho\textsubscript{0.08}F\textsubscript{2.08} composition (a = 5.784(1) Å) calculated from X-ray diffraction patterns of the composite films corresponded well to the similar data for the initial Sr\textsubscript{0.92}Ho\textsubscript{0.08}F\textsubscript{2.08} powder annealed at 750 °C. Analysis of X-ray diffraction patterns of the modified composite films allows to conclude that cellulose crystal structure as well as crystal structure and unit cell parameters of upconversion powders remained unchanged in the course of the composite films preparation, i.e., only TOCNF surface underwent chemical transformations.

Correlations between water contact angles (WCA) of TOCNF-APS and TOCNF-bAPS films after thermal treatment at 105 °C, depending on the water droplet contact time, and APS loading are presented in Fig. 3. TOCNF films are more hydrophilic than CNC films (Fig. 3a, b). Such difference in the films properties could be explained by the difference in the chemical composition and structure of the films as well as their surface roughness (Wenzel 1936): the mean surface roughness value (Ra) for TOCNF, estimated by AFM, was more than three times lower than Ra for CNC (Table 1; Figs. S4a, b). TOCNF-APS films became hydrophobic at APS loading of 3.0–7.0 mmol/g (film surface was considered hydrophobic when WCA > 90° (Li et al. 2007), and hydrophobicity increased when APS loading grew up (Fig. 3d). The films retained their hydrophobicity when water droplet contact time was increased up to 60 s. Hydrophilicity of TOCNF-bAPS films decreased significantly after modification, but, in contrast with TOCNF-APS, these films did not become hydrophobic even at the maximum APS loading (Fig. 3d). Ra of TOCNF-APS\textsubscript{7.0} films showed the highest value and exceeded Ra of TOCNF-bAPS\textsubscript{7.0} by factor of about 2 (Table 1; Figs. S4c, d).

Hydrophobic properties of the modified composite films can be illustrated by WCA changes depending from APS loading and the preparation protocol (1 or 2), Table 2. WCAs for the heat-treated at 105 °C composite films were measured 60 s after applications of water drops on the surfaces of the films. The increase of APS loading from 3 to 6 mmol/g TOCNF led to WCA increase from 90 ± 2° to 101 ± 2° for TOCNF:Ho-APS films. The further increase of APS loading up to 7 mmol/g TOCNF did not affect WCA values for these films. After modification, TOCNF:Ho-APS films became hydrophobic. TOCNF:Ho-bAPS films remained hydrophilic even upon the increase of APS loading up to 7 mmol/g TOCNF (82 ± 2° WCA). The same trend was revealed for modified composite films based on CNC (see Table 2). Ra increased from 11 nm for TOCNF:3.5Ho (WCA 44 ± 3°) to 16 nm and 42 nm for the modified composite TOCNF:3.5Ho-bAPS\textsubscript{7.0} (WCA 82 ± 2°) and TOCNF:3.5Ho-APS\textsubscript{7.0} (WCA 101 ± 2°) films, respectively (Figs. S5a–c). Just for comparison, WCA and Ra of CNC:5.5Ho film, obtained according to the previously reported technique (Fedorov et al. 2019), were equal to 67 ± 2° (Table 2) and 16 nm (Fig. S5d), respectively. Presumably, WCA values were affected not only by the
Fig. 2 XRD patterns of the films after the thermal treatment at 105 °C (a–f) and of APS after thermal treatment at 800 °C (g).

Table 1 Physical properties of TOCNF, CNC, TOCNF-APS 7.0, TOCNF-bAPS 7.0 films after thermal treatment at 105 °C

| Sample          | Particle size (SEM), nm | Particle width (AFM), nm | Average roughness (Ra), nm | Crystallinity index (IC), % |
|-----------------|-------------------------|--------------------------|---------------------------|----------------------------|
| TOCNF           | 20 ± 6                  | 809 ± 98                 | 19 ± 5                    | 3                          | 78.2                       |
| CNC             | 14 ± 4                  | 107 ± 38                 | 13 ± 3                    | 11                         | 84.6                       |
| TOCNF-APS 7.0   | 27 ± 6                  | 818 ± 107                | 27 ± 5                    | 47                         | 72.2                       |
| TOCNF-bAPS 7.0  | 25 ± 7                  | n.d.*                    | 25 ± 7                    | 16                         | 73.7                       |

*No data

Fig. 3 Correlation between the WCA for different nanocellulose films and the water droplet contact time.
chemical modifications, but by the increase of the film surface roughness, too.

Earlier, Fedorov et al. (2019) have shown that formation of hydrogen bonds between F$^-$ ions from SrF$_2$:Ho and OH$^-$ moieties from nanocellulose is the key factor determining dispersion stability. Semitransparent bluish dispersions, formed using 1.10 wt% TOCNF, 0.70 wt% APS and 0.2 wt% SrF$_2$:Ho concentrations, were stable for at least 5-day periods (Figs. S1i-j). The increase in APS concentration up to 1.27 wt%, and SrF$_2$:Ho concentration up to 1.27 wt%, resulted in the formation of viscous opaque TOCNF:Ho-bAPS gels (Fig. S1k). Opaque TOCNF:Ho-APS dispersions, stable for a 3-day period, were formed under the similar conditions without any signs of flocculation or sedimentation (Fig. S1l): stability of TOCNF:Ho-APS dispersions was the key factor for the homogeneous distribution of the up-converting particles in the films casted from solutions.

Analysis of experimental results obtained confirmed the influence of film modification on the morphology and wettability of TOCNF surfaces: TOCNF-APS and TOCNF:Ho-APS acquired hydrophobicity in contrast with TOCNF-bAPS and TOCNF:Ho-bAPS films.

Characterization of chemical structures and thermal properties of TOCNF/SrF$_2$:Ho-APS and TOCNF/SrF$_2$:Ho-bAPS composite films

FTIR spectrum of TOCNF (Fig. 4a) and CNC (Fig. 4b) comprises absorption bands typical for cellulose macromolecules (see Supplementary Information, Sect. 4). FTIR spectrum of TOCNF differs from the spectrum of CNC by the presence of the band at 1606 cm$^{-1}$ corresponding to COO$^-$ stretching in sodium form (Jiang et al. 2013). FTIR spectrum of TOCNF:3.5Ho composite film (Fig. 4c) is similar to that of TOCNF except for a small shift from 3273 to 3282 cm$^{-1}$ of 3282 − 3338 cm$^{-1}$ band for the composite film; this confirms the formation of interfacial hydrogen bonds between F$^-$ ions of the up-conversion

### Table 2 The effect of APS loading on water contact angle and transmittance coefficient of TOCNF:Ho-APS composite films

| Sample          | Sr$_{1-x}$Ho$_x$F$_{2-x}$ content, wt% | Ho content*, wt% | WCA, (deg) | Transmittance at 650 nm (%) |
|-----------------|----------------------------------------|------------------|------------|-----------------------------|
| TOCNF:3.3Ho     | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 27.1             | 3.27 ± 0.09 | 40 ± 3                     | 23.6 |
| TOCNF:3.3Ho-APS$_{3.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 27.1             | 3.25 ± 0.09 | 90 ± 2                      | 23.5 |
| TOCNF:3.3Ho-APS$_{3.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 27.1             | 3.26 ± 0.09 | 96 ± 2                      | 21.4 |
| TOCNF:3.3Ho-APS$_{6.7}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 27.1             | 3.25 ± 0.09 | 101 ± 2                     | 19.1 |
| TOCNF:3.3Ho-bAPS$_{6.7}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 27.1             | 3.24 ± 0.09 | 82 ± 2                      | −   |
| TOCNF:3.5Ho     | Sr$_{0.92}$Ho$_{0.08}$F$_{2.08}$       | 35.2             | 3.47 ± 0.10 | 44 ± 3                      | 20.0 |
| TOCNF:3.5Ho-APS$_{6.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 40.1             | 3.46 ± 0.12 | 97 ± 2                      | 18.5 |
| TOCNF:3.5Ho-APS$_{5.5}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 40.1             | 3.45 ± 0.10 | 101 ± 2                     | 15.7 |
| TOCNF:3.5Ho-bAPS$_{7.0}$ | Sr$_{0.92}$Ho$_{0.08}$F$_{2.08}$       | 35.2             | 3.45 ± 0.10 | 82 ± 2                      | −   |
| TOCNF:4.9Ho     | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 40.1             | 3.47 ± 0.14 | −                          | 17.2 |
| TOCNF:4.9Ho-APS$_{5.5}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 40.1             | 3.46 ± 0.14 | 98 ± 2                      | 15.4 |
| TOCNF:5.5Ho     | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 40.0**           | 5.46 ± 0.15 | −                          | 12.3 |
| TOCNF:5.5Ho-APS$_{6.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 45.0             | 5.45 ± 0.15 | 101 ± 2                     | 8.7  |
| CNC:5.5Ho       | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 45.0**           | −            | 67 ± 2                      | 22.0 |
| CNC:5.5Ho-bAPS$_{6.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 45.0             | −            | 79 ± 2                      | −   |
| CNC:5.5Ho-APS$_{3.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 45.0             | −            | 92 ± 2                      | −   |
| CNC:5.5Ho-APS$_{6.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 45.0             | −            | 103 ± 2                     | −   |
| CNC:5.5Ho-APS$_{7.0}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 45.0             | −            | 103 ± 2                     | −   |
| TOCNF:4.9Ho-AKD$_{30}$ | Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$       | 40.0***          | −            | 123 ± 2                     | 11.3 |

*Ho content was determined by chemical analysis (see Supplementary Information, Sect. 3)

**Fedorov et al. (2019)

***Fedorov et al. (2020)
particles and OH groups of TOCNF (Fedorov et al. 2019).

Modification of TOCNF:3.5Ho-APS$_{7.0}$ film resulted in appearance of additional adsorption bands in FTIR spectrum (Fig. 4d), namely two weak bands at 2928 cm$^{-1}$ and 2860 cm$^{-1}$ corresponding to asymmetric and symmetric stretching of CH$_2$ fragment of APS aminopropyl groups (Kim et al. 2011; Masmoudi et al. 2013); strong 1550 cm$^{-1}$ band corresponding to N–H bending vibration of primary amine groups (Khanjanzadeh et al. 2018; Robles et al. 2018); and weak 1626 cm$^{-1}$ band corresponding to the deformation mode of NH$_2$ groups that are hydrogen-bonded to the OH groups of cellulose. Such band assignment is in an agreement with previously reported data regarding treatment of SiO$_2$ and copper surfaces with APS (Culler et al. 1985; Masmoudi et al. 2013). The presence of 1606 cm$^{-1}$ band (COO$^-$Na$^+$) allowed us to assume that non-oxidized primary and secondary OH groups took part in the condensation reaction, whereas oxidized C6 primary hydroxyls did not participate in the latter process. Also, 1333 cm$^{-1}$ and 1231 cm$^{-1}$ bands correspond to C–N bond bending modes (Hokkanen et al. 2014); and 1465 cm$^{-1}$ weak band correspond to CH$_2$ bending of the aminopropyl groups (Ishida et al. 1982; Pavia...
et al. 2009). The absence of 1575 cm⁻¹ and 1485 cm⁻¹ absorption bands, corresponding to the vibrational modes of bicarboxylic amino groups associated with atmospheric water and carbon dioxide confirmed removal of moisture and CO₂ after the thermal treatment at 105 °C followed by drying in desiccator (Kim et al. 2011). Essential intensity increase of the bands within 1000–1150 cm⁻¹ indicated formation of Si–O–Si siloxane bonds and covalent Si–O–C_	ext{cellulose} bonding. However, overlapping of strong absorption bands, corresponding to C–O–C stretching and pyranose ring skeletal vibrations of cellulose, prevented the unequivocal identification of the typical Si–O–Si and Si–O–C_	ext{cellulose} bonds giving absorption bands in the same spectrum range. According to the previous reports (Masmoudi et al. 2013; Vandenberg 1991), the presence of Si–O–Si absorption band at higher frequencies (ca. 1148 cm⁻¹ and above) is caused by formation of three-dimensional siloxane units, while lower frequency band (1034–1050 cm⁻¹) indicated formation of long linear Si–O–Si chains, and 1000–1012 cm⁻¹ bands pointed out at the very low degree of self-condensation. Thus, appearance of the new absorption band at 1002 cm⁻¹ in the TOCNF:3.8Ho-APS 7.0 spectrum, shift of the other band from 1055 to 1050 cm⁻¹ along with its intensity increase confirmed the formation of linear Si–O–Si chains with various degree of condensation (chain length). Shift of 1028 cm⁻¹ band up to 1030 cm⁻¹ was caused by Si–O–Si linear self-condensation and covalent Si–O–C_	ext{cellulose} bonding (Rachini et al. 2012). Very low intensity of 920 cm⁻¹ band, corresponding to Si–O stretching, indicated an insignificant content of Si–OH groups (Masmoudi et al. 2013). The latter observation, as well as ethoxy group absence, is in agreement with existing data (Beari et al. 2001; Salon et al. 2007, 2010) indicating that lowering pH down to 4.0–4.5 promoted APS hydrolysis and delayed Si–OH self-condensation (Fig. S6).

TOCNF:3.8Ho-bAPS 7.0 FTIR spectrum (Fig. 4e) differed from the spectrum of TOCNF:3.8Ho-APS 7.0 by the absence of 1626 cm⁻¹ and appearance of 1644 cm⁻¹ weak absorption band, corresponding to the bending vibrations of adsorbed water molecules (Fedorov et al. 2019), and 1391 cm⁻¹ absorption band, corresponding to deformation vibrations of CH₃ methoxy groups from -O-CH₂CH₃ moieties (Kim et al. 2011). Intensity increase of 1150 cm⁻¹ weak band and the absence of 1030 cm⁻¹ in TOCNF:3.5Ho-bAPS 7.0 film spectrum confirmed the formation of the three-dimensional siloxane units along with linear oligomers. Analysis of FTIR spectrum of the thermally treated at 105 °C TOCNF:3.5Ho-APS films confirmed the presence of the linear APS oligomers and formation Si–O–C_	ext{cellulose} covalent bonds as a result of the condensation with TOCNF hydroxyls. Ethoxy group presence in TOCNF:3.5Ho-bAPS 7.0 films indicated the presence of oligomers of partially hydrolyzed APS (Fig. S7).

Both primary and secondary hydroxyl groups of cellulose can participate in the silylation reaction (Pereira et al. 2020), whereas, in TEMPO oxidation, only primary hydroxyls can undergo chemical transformations (Okita et al. 2010). Schematic structure of TOCNF:Ho-APS films is presented in Fig. 5.

Data obtained indicate clearly that pH value of the first step of the silylation reaction in aqueous medium significantly affected hydrophobic properties of the modified composite APS films. The hydrophobicity of TOCNF:Ho-APS films was probably caused by evenly distributed layer of chemisorbed linear polysiloxane, and hydrogen bonds formation between NH₂ moieties of aminopropyl groups and OH groups of TOCNF. The latter bands changed the APS configuration at the film surface: aminopropyl groups were bent, and their polar NH₂ moieties were oriented toward TOCNF surfaces, whereas propyl fragments were oriented along the surface (Culler et al. 1985; Indarti et al. 2019; Masmoudi et al. 2013; Rachini et al. 2012).

According to TGA data, solid APS, obtained by drying under air at 25 °C and further annealing at 105 °C (see Supplementary Information, Sect. 2), loses about 16.4% of its weight at 150 °C (Fig. 6a). DSC curve comprised endo-effects at 84 °C and 131 °C, corresponding to the evaporation of ethanol formed during the hydrolysis of residual APS, as well as adsorbed water. The further heating at 150–270 °C accompanied with additional weight loss of 5.8% and exo-effect at 265 °C, which corresponding to self-condensation process, Si–O–Si bond formation, and oxidation of amino groups to imino-groups. Heating at 270–700 °C caused additional 38% weight loss, and it was accompanied by the three exo-effects at 416, 470 and 606 °C associated with aminopropyl group oxidation, oxidative thermal decomposition with Si–O–Si bond cleavage and oxidation of residual carbon (Peña-Alonso et al. 2005; Qiao et al. 2015). The residue after
700 °C annealing was about 39.8% of the initial weight. EDX analysis of this residue indicated the presence of O and Si only with O:Si ratio being to 2:1 (Fig. S8). XRD has confirmed that the residue was single-phase amorphous SiO$_2$ (Fig. 2g).

According to TGA and DSC data, onset thermal degradation ($T_{\text{onset}}$) of TOCNF:3.3Ho and TOCNF:3.3Ho-APS$_{6.7}$ films under air started at 204 °C and 216 °C, respectively (Fig. 6b and c). At the first step (25–150 °C), TOCNF:3.3Ho film demonstrated only a little weight loss (about 4.4%) because of evaporation of adsorbed water (Fig. 6b). The higher weight loss for TOCNF:3.3Ho-APS$_{6.7}$ film (about 5.7%) was caused by additional water evaporation produced by the condensation of remaining silanol groups (Fig. 6c). The weight loss of TOCNF:3.3Ho film was about 39% in the 150–330 °C temperature range. It was accompanied by two exothermic effects in DSC curve at 240 °C and 304 °C (Fig. 6b), that corresponded to the thermal degradation of cellulose due to decarboxylation of TOCNF, depolymerization and cleavage of glycosidic linkages of cellulose (Fukuzumi et al. 2010; Lichtenstein and Lavoine 2017). The third exothermic effect at 472 °C was due to the residual carbon oxidation. The weight loss of TOCNF:3.3Ho film at the third stage of decomposition (330–510 °C) was about 29.5%. According to TGA, the residue weight after the decomposition of TOCNF:3.3Ho film under air was 27.1%, which corresponds to the initial content of up-conversion powder in the composite film (as confirmed by
quantitative chemical analysis for holmium content, Table 2).

For TOCNF:3.3Ho-APS_{6.7} film, TGA study showed 23.4\% weight loss in 150–380 °C temperature range (Fig. 6c). The weight loss in this temperature range was multi-stage, and it was accompanied by several exothermic effects, which occurred almost simultaneously. These complicated processes corresponded to the oxidative destruction of cellulose and amino-group oxidation with imino-group formation. The further 29.9\% weight loss of TOCNF:3.3Ho-APS_{6.7} film at 380–650 °C proceeded in a multi-step manner and was accompanied with four exothermal effects at 406, 416, 440 and 468 °C, which were related to the aminopropyl group oxidation, Si–O–Si bond cleavage and oxidation of residual carbon. According to TGA, the residue weight after the decomposition of TOCNF:3.3Ho-APS_{6.7} film under air was 41.3\%, which included Sr_{0.90}Ho_{0.10}F_{2.10} and SiO_{2}. The holmium content in TOCNF:3.3Ho-APS_{6.7} film was 3.25 ± 0.09 wt\% as determined by quantitative chemical analysis (Table 2), which corresponded to the initial 27.1 wt\% content of Sr_{0.90}Ho_{0.10}F_{2.10} powder in the composite film. The difference between the residue after the decomposition of TOCNF:3.3Ho-APS_{6.7} film (41.3\%) and the content of Sr_{0.90}Ho_{0.10}F_{2.10} powder in the composite film (27.1\%) was 14.2\% and corresponded to SiO_{2} content of the residue after the film decomposition. The value of 14.2\% SiO_{2} corresponded to its theoretical content calculated on the basis of the initial APS loading during the preparation of the composite film (the theoretical calculation took into account the drying weight loss of APS at 105 °C; (see Supplementary Information, Sect. 2).

TGA data for TOCNF:3.3Ho-bAPS_{6.7} film decomposition included 7.4\% weight loss at 150 °C (Fig. 6d) and 4.6\% at 150–200 °C (i.e., 12.0\% weight loss at 200 °C). Endo-effect at 173 °C corresponded to the evaporation of ethanol, formed in the course of hydrolysis of remaining APS, as well as the evaporation of the adsorbed water and physically adsorbed APS (Peña-Alonso et al. 2005; Qiao et al. 2015). TOCNF:3.3Ho-bAPS_{6.7} film lost 19.7\% weight at 200–380 °C. Two exothermal effects at 232 °C and 300 °C were attributed to the beginning of cellulose oxidative destruction and amino-group oxidation with imino-group formation. The thermal decomposition of TOCNF:3.3Ho-bAPS_{6.7} film started at about T_{\text{onset}} of 200 °C. Weight loss of TOCNF:3.3Ho-bAPS_{6.7} film at 380–650 °C (27.1\%) was accompanied by two exo-effects at 450 °C and 536 °C related to aminopropyl group oxidation, Si–O–Si bond cleavage and residual carbon oxidation. According to the TGA data, the residue after thermal decomposition of TOCNF:3.3Ho-bAPS_{6.7} film (41.2\%) is very close to TOCNF:3.3Ho-APS_{6.7} film (41.3\%).

Thus, TGA/DSC data confirmed an increase in the thermal stability of TOCNF:3.3Ho-APS_{6.7} modified
film compared to the thermal stability of the unmodified film.

Optical properties and morphology of TOCNF:Ho-APS composite films

Flexible and transparent TOCNF, TOCNF-APS$_{3.0}$ and TOCNF-APS$_{7.0}$ films were produced without cracks (Figs. 7a–c). Their transmittance coefficients at 650 nm decreased with the increase in APS loading from 89.4%, and 70.0% to 61.9% (Figs. 8a–c, Table S2).

The transmittance coefficients of the films depended on both the APS loading and the content of the up-conversion powder (Table 2). Comparison of the transmission spectra of the composite films with the same content of up-conversion powder (27.1 wt% Sr$_{0.90}$Ho$_{0.10}$F$_{2.10}$), TOCNF:3.3Ho and TOCNF:3.3Ho-APS$_{3.0}$ at a loading of 3.0 mmol APS per 1 g of dried TOCNF, showed that the decrease in transmittance was mainly due to the upconversion powder content (Fig. 8d, e). The further increase of APS content exhibited affected the film transmission spectra in a more complicated way. Comparison of the transmission spectra of TOCNF:3.5Ho and TOCNF:3.5Ho-APS$_{7.0}$ films with the same content of up-conversion powder (35.2 wt% Sr$_{0.92}$Ho$_{0.08}$F$_{2.08}$) revealed decreasing of the transmittance of the modified films with increasing APS loading (Fig. 8f, g; Table 2). Composite films with an APS loading of 3–7 mmol/g TOCNF were of yellowish color, homogeneous, strong, flexible and translucent (Fig. 7g–i). Content of the up-conversion powder affected the composite film transmittance at higher extent than the APS loading.

![Fig. 7 Appearance of the films: TOCNF (a), TOCNF-APS$_{3.0}$ (b), TOCNF-APS$_{7.0}$ (c) TOCNF:3.3Ho (d), TOCNF:3.5Ho (e), TOCNF:5.5 Ho (f), TOCNF:3.3Ho-APS$_{3.0}$ (g), TOCNF:3.5Ho-APS$_{7.0}$ (h), TOCNF:5.5Ho-APS$_{6.0}$ (i)]
The modified TOCNF films had a UV absorption band at 295–301 nm (Fig. 8b, c). Moreover, TOCNF:3.3Ho-APS3.0 and TOCNF:3.5Ho-APS7.0 (Fig. 8e, g) blocked UV irradiation in the wavelength range below 345 nm, exhibiting the better UV-protection of the modified composite films. The UV blocking ratios (R) of these samples at 295 and 345 nm, respectively, were evaluated using equation (S3) (see Supplementary Information, Sect. 5) and summarized in Table S2. The TOCNF:Ho-APS films possessed enhanced UV-blocking properties, and showed almost complete absorption of UV rays in both the UVB (280–315 nm) and the UVA (315–400 nm) regions.

The morphology of surface and cross-sections of the films, distribution of up-conversion particles and elements (N, Si) in the hydrophobic nanocomposite TOCNF:Ho-APS films were analyzed by SEM and EDX. Compared to unmodified TOCNF films (20 ± 8 nm nanofibril width, Fig. 1a), TOCNF:3.3Ho-APS5.0 films retained the fibrillar structure of TOCNF with thickened nanofibrils (27 ± 7 nm nanofibril width) due to continuous and uniform coverage with a polysiloxane network with up-conversion particles located between fibrils (Fig. 9a). The cross-section of the TOCNF:3.3Ho-APS5.0 film had a mesoporous structure with a pore size of 51 ± 20 nm (Fig. 9c). Cracks on the film cleavage were formed as a result of mechanical action during the film splitting. Samples of the TOCNF:3.3Ho-APS5.0 composite film had a homogeneous morphology with uniformly distributed up-conversion particles, which was confirmed by the film surface and the cross-section Z-contrast imaging (Fig. 9b, d). The size of most up-conversion particles ranged from 30 to 79 nm with a small amount of agglomerates (154 ± 34 nm). The uniformity of N, Si and Ho element distribution in TOCNF:Ho-APS films was confirmed by elemental mapping (Fig. 9e–g) and EDX analysis (Fig. S9). EDX analysis indicated that the measured Sr/Ho atomic ratio in the composite films was very close to that measured in Sr0.90Ho0.10-F2.10 powder. The EDX results confirmed the presence of N = 4.8 ± 0.2 at% and Si = 4.7 ± 0.4 at%.

The surface morphology and cross-section of TOCNF:3.3Ho-bAPS5.0 films were formed by dense layers of glued nanofibrils (Fig. 9h, i), in contrary above-mentioned TOCNF:3.3Ho-APS5.0 films.

Composite films TOCNF:Ho-APS with an optimal combination of hydrophobic, optical and mechanical properties were obtained with an up-conversion powder content of up to 45 wt% and an APS loading of 5.0–6.0 mmol/g TOCNF.
Luminescent properties and laser damage threshold of TOCNF:Ho-APS films

The upconversion luminescence spectra of Ho$^{3+}$ ions in nanocomposite TOCNF:Ho-APS films are recorded upon excitation of $5I_7$ level. Emission transitions of Ho$^{3+}$ ions in composite films ($^5F_5 \rightarrow ^5I_8$, $^5S_2(^5F_4) \rightarrow ^5I_8$, $^5F_3 \rightarrow ^5I_8$) are shown in Fig. S10. Analysis of the up-conversion luminescence spectra of hydrophobic TOCNF:Ho-APS films and hydrophilic TOCNF:Ho films after heat-treatment at 105 °C showed that the films with the same amount of holmium demonstrated similar luminescence intensity (Fig. 10a, S11). The luminescence intensity of the hydrophobic TOCNF:Ho-APS films increases with an increase in holmium content from 3.5 wt% to 5.5 wt% (Fig. 10b). Luminescence intensities of TOCNF:5.5Ho-APS films coincided with that of TOCNF:5.5Ho-AKD (Fig. 10c) and CNC:5.5Ho films (Fig. 10d). The most intense luminescence of Ho$^{3+}$ ions is in the red region (630–680 nm, $^5F_5 \rightarrow ^5I_8$ transition) for all the films. This confirms the possibility of their use for visualizing two-micron laser...
radiation. The chemical modification had a small impact on the chromaticity coordinates of the composite films (Fig. S12).

The laser damage threshold (LDT) (Wood 2014) as the radiation intensity leading to irreversible changes in the film was determined by visual observation of damage/darkening spots ($\lambda = 1940$ nm, beam diameter $1500 \mu$m) for five up-conversion composite films. 1940 nm wavelength was selected based on the location of the holmium absorption maximum for SrF$_2$:Ho solid solution (Lyapin et al 2017). The highest laser radiation durability (104.71 W/cm$^2$) was registered for a TOCNF:5.5Ho-APS$_{6.0}$ composite film (Table 3).

LDT depends on the optical, mechanical, thermal properties, morphology of the irradiated material, and the presence of absorbing inclusions (Emmert and Rudolph 2014). For materials made from unmodified cellulose, the predominant cause of damage is thermal degradation due to the evaporation of moisture and

**Table 3** Laser damage threshold of composite films based on CNC and TOCNF

| Sample | H$_2$O content determined by drying at 150 °C, wt% | Onset thermal degradation $T_{\text{onset}}$, °C | The power at which the film burns or darkens, W | LDT, W/cm$^2$ | Transmittance at 650 nm (%) |
|--------|-----------------------------------------------|-----------------------------------|----------------------------------------|-------------|--------------------------|
| TOCNF:5.5Ho | 4.4 | 204 | 0.84 | 47.3 | 12.3 |
| CNC:5.5Ho | 2.3* | 157* | 0.80 | 45.3 | 22.0* |
| TOCNF:4.9Ho-AKD$_{30}$ | 3.0** | 210** | 0.95 | 53.7 | 11.3*** |
| TOCNF:5.5Ho-bAPS$_{6.0}$ | 7.4 | 200 | 0.83 | 47.3 | – |
| TOCNF:5.5Ho-APS$_{6.0}$ | 5.7 | 216 | 1.85 | 104.7 | 8.7 |
| TOCNF-APS$_{7.0}$ | 5.7 | 216 | > 3 | > 168 | 61.9 |
| TOCNF | 4.4 | 204 | 1.845 | 104.4 | 89.4 |

*Fedorov et al. (2019)
**Fedorov et al. (2020)

Fig. 11 Images of composite films after laser irradiation with a power of 0.84 W: CNC:5.5Ho (a); TOCNF:5.5Ho (b); TOCNF:5.5Ho-bAPS$_{6.0}$ (c); TOCNF:5.5Ho-APS$_{6.0}$ (d)
subsequent charring of the films in the illuminated spot (Emmert and Rudolph 2014). For the composite films subjected to 0.84 W irradiation, the damage was not observed for the TOCNF:5.5Ho-APS$_{6.0}$ film only (Fig. 11d).

The reasons for the lowest laser radiation durability of the CNC:5.5Ho films were low $T_{\text{onset}}$ and low H$_2$O content. However, LDT of CNC:5.5Ho films slightly differed from LDTs of TOCNF:5.5Ho and TOCNF:5.5Ho-bAPS$_{6.0}$ films, despite the significant difference in their thermal stability. The difference in surface roughness was not so important because the nanoroughness (measured by AFM) was too low compared to the laser wavelength (1940 nm) to cause significant scattering and absorption of laser radiation. The optical properties of the composite films with the same content of up-conversion particles differed insignificantly (Table 3). The highest transmittance coefficient was observed for unmodified TOCNF film (89.4%) with LDT 104.4 W/cm$^2$. The highest LDT value of 168 W/cm$^2$ belonged to modified non-composite TOCNF-APS$_{7.0}$ film. The presence of absorbing SrF$_2$:Ho particles greatly reduces the LDT of composite films. The functionalization of TOCNF films by APS significantly increases their durability to laser radiation.

The main factors affecting the LDT value of nanocellulose-based nanocomposite films were the surface morphology, the presence of a uniform amorphous, thermostable coating, and the formation of a mesoporous film structure. As it has already been mentioned, the surface of TOCNF:3.3Ho-bAPS$_{5.0}$ films exhibited the tendency of gluing nanofibrils together and form 3D siloxane islands as a result of self-condensation of the hydrolyzed APS, and the film cross-section was formed by layers with a dense structure (Fig. 9h, i). In contrast to these films, on the surface of thickened nanofibrils of the TOCNF:3.3Ho-APS$_{5.0}$ film, a homogeneous polysiloxane layer was formed mainly due to linear oligomers grafted on the TOCNF surface. Mesopores are clearly visible in the film cross-section (Fig. 9a, c). Such a coating has increased resistance to thermal oxidative degradation. A similar phenomenon in the study of laser damage to antireflection SiO$_2$ coatings was reported earlier (Li et al. 2014). Thus, the up-conversion hydrophobic nanocomposite TOCNF:Ho-APS films have been developed, which possess comparable luminescence intensity to the CNC/SrF$_2$:Ho and TOCNF:SrF$_2$:Ho-AKD films obtained earlier (Fedorov et al. 2019, 2020), while having the higher resistance to laser radiation.

Conclusions

Novel preparation technique of luminescent composite cellulose films has been developed. The films were prepared by solution casting technique from precursor dispersion (SrF$_2$:Ho up-conversion particles in APS-modified aqueous TOCNF solution at pH = 4.0–4.5) followed by the thermal treatment at 105 °C. This technique produced thin (50–60 microns), hydrophobic (WCA = 97 ± 2°–101 ± 2°), strong, and flexible semitransparent composite TOCNF:Ho-APS$_{6.0}$ films with a uniform distribution of up-conversion particles (30–45 wt% SrF$_2$:Ho content, and APS loading of 5.0–6.0 mmol/g dry TOCNF). TOCNF:Ho-APS$_{6.0}$ film hydrophobicity has been caused by evenly distributed layer of chemisorbed linear polysiloxane on TOCNF surface as well as by changed configuration of aminopropyl groups that bent and oriented their polar NH$_2$ moieties toward the surface, being driven by the formation of hydrogen bonds with TOCNF hydroxyls, whereas propyl hydrophobic fragments were oriented along the film surface. Luminescence intensities of TOCNF:Ho-APS$_{6.0}$ films (Ho$^{3+}$ $^5$I$_7$ level excitation with 1912 nm laser irradiation) coincided with that of CNC/SrF$_2$:Ho and TOCNF:SrF$_2$:Ho-AKD films (Fedorov et al. 2019, 2020). The thermal decomposition ($T_{\text{onset}}$ 216 °C) and LDT (104.7 W/cm$^2$) for TOCNF:Ho-APS$_{6.0}$ film were higher than CNC/SrF$_2$:Ho (157 °C; 45.3 W/cm$^2$) and TOCNF:SrF$_2$:Ho-AKD (210 °C; 53.7 W/cm$^2$) films. TOCNF:Ho-APS$_{6.0}$ films are eco-friendly, and they can be used for visualization of 2 μm laser radiation in medicine and long-distance atmosphere monitoring. In addition, TOCNF:Ho-APS$_{6.0}$ films exhibited UV-blocking effect in both UVA and UVB regions.

Acknowledgements This work was supported by the Ministry of Science and Higher Education within the State assignment to Prokhorov General Physics Institute of the Russian Academy of Sciences and FSRC Crystallography and Photonics RAS. The equipment of the Shared Research Center supported by the Ministry of Science and Higher Education (RFMEFI62114X0005) was used in experiments. Authors express their sincere gratitude to Dr. Arthur I. Popov for his most kind assistance in the preparation of the present manuscript and Dr. Vladimir N. Kuryakov for zeta potential measurements.
Author contributions The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Human and animals rights This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent The authors have no statements about informed consent as this research does not involve human participants.

References

Andersen M, Johansson LS, Tanem BS, Stenius P (2006) Properties and characterization of hydrophobized microfibrillated cellulose. Cellulose 13:665–677. https://doi.org/10.1007/s10570-006-9072

Auzel F (2004) Upconversion and anti-Stokes processes with f and d ions in solids, Chem Rev 104(1):139–174. https://doi.org/10.1021/cr020357g

Beari F, Brand M, Jenkner P, Lehnert R, Metternich HJ, Mon-Auzel F, Andresen M, Johansson LS, Tanem BS, Stenius P (2006) Cellulose nanofibres for photonics and plasmonics. Current Opin Green Sustain Chem 12:1–7. https://doi.org/10.1016/j.cogsc.2018.03.010

Belyaev AN, Chabushkin AN, Khrushchalina SA, Kuznetsova OA, Lyapin AA, Romanov KN, Ryabochkina PA (2016) Investigation of endovenous laser ablation of varicose veins in vitro using 1.885 μm laser radiation. Lasers Med Sci 31:503–510. https://doi.org/10.1007/s10301-016-1877-z

Brites CDS, Kuznetsov SV, Konyshevsk VA, Nakladov AN, Fedorov PP, Carlos LD (2020) Simultaneous measurement of the emission quantum yield and local temperature: the illustrative example of SrF2:Yb3+/Er3+ single crystals. Eur J Inorg Chem 17:1555–1561. https://doi.org/10.1002/ejc.202000113

Culler SR, Ishida H, Koenig JL (1985) Structure of silane coupling agents adsorbed on silicon powder. J Colloid Interface Sci 106(2):334–346. https://doi.org/10.1016/s0021-9797(85)80007-2

Dai L, Wang Y, Zou X, Chen Z, Liu H, Ni Y (2020) Ultrasensitive physical, bio, and chemical sensors derived from 1-, 2-, and 3-D Nanocellulosic materials. Small 16(13):1906567. https://doi.org/10.1002/smll.201906567

De France K, Zeng Z, Wu T, Nyström G (2020) Functional materials from nanocellulose: utilizing structure-property relationships in bottom-up fabrication. Adv Mater. https://doi.org/10.1002/adma.202000657

Delone NB (1993) Basics of interaction of laser radiation with matter. Editions Frontieres, France

Dias OAT, Konar S, Leião AL, Yang W, Tjong J, Sain M (2020) Current state of applications of nanocellulose in flexible energy and electronic devices. Front Chem 8:420. https://doi.org/10.1002/smll.201906567

Dong H, Sun L-D, Yan C-H (2013) Basic understanding of the lanthanide related upconversion emissions. Nanoscale 5:5703–5714. https://doi.org/10.1039/C3NR34069D

Eichhorn SJ (2018) Cellulose nanofibres for photonics and plasmonics. Current Opin Green Sustain Chem 12:1–7. https://doi.org/10.1016/j.cogsc.2018.03.010

Emmert LA, Rudolph W (2014) Femtosecond laser-induced damage in dielectric materials. In: Ristau D (ed) Laser-induced damage in optical materials. Taylor & Francis Group, Milton Park, pp 127–152

Fedorov PP, Luginina AA, Kuznetsov SV, Osiko VV (2011) Nanofluorides. J Fluor Chem 132:1012–1039. https://doi.org/10.1016/j.jfluchem.2011.06.025

Fedorov PP, Luginina AA, Rozhnova YA, Kuznetsov SV, Voronov VV, Uvarov OV, Pynenkov AA, Nishchev KN (2017) Preparation of nanodispersed fluorite-type Sr1-xRxF2:Ho particle. Cellulose 26:2403–2423. https://doi.org/10.1007/s10570-018-2194-4

Fedorov PP, Luginina AA, Kuznetsov SV, Voronov VV, Lyapin AA, Ermakov AS, Pominova DV, Yaprntysev AD, Ivanov VK, Pynenkov AA, Nishchev KN (2019) Composite up-conversion luminescent films containing a nanocellulose and SrF2: Ho particle. Cellulose 26:2403–2423. https://doi.org/10.1007/s10570-018-2194-4

Fischer S, Ivaturi A, Jakob P, Kramer KW, Martin-Rodriguez R, Mejerink A et al (2018) Upconversion solar cell measurements under real sunlight. Opt Mater 84:389–395. https://doi.org/10.1016/j.optmat.2018.05.072

Fukuzumi H, Saito T, Okita Y, Isogai A (2010) Thermal stabilization of TEMPO-oxidized cellulose. Polym Degrad Stab 95(9):1502–1508. https://doi.org/10.1016/j.polymdegradstab.2010.06.015

Guang Q, Song R, Wu W et al (2018) Fluorescent CdTe-QD-encoded nanocellulose microspheres by green spraying method. Cellulose 25:7017–7029. https://doi.org/10.1007/s10570-018-2065-2

Habibi Y, Chanzy H, Vignon MR (2006) TEMPO-mediated surface oxidation of cellulose whiskers. Cellulose 13(6):679–687. https://doi.org/10.1007/s10570-006-9075-y

Hai J, Li T, Su J, Liu W, Ju Y, Wang B, Hou Y (2018) Reversible response of luminescent terbium(III)-nanocellulose hydrogels to anions for latent fingerprint detection and encryption. Angew Chem Int Ed 57(23):6786–6790. https://doi.org/10.1002/anie.201800119
Hokkanen S, Repo E, Suopajärvi T et al (2014) Adsorption of Ni(II), Cu(II) and Cd(II) from aqueous solutions by amino modified nanostructured microfibrillated cellulose. Cellulose 21:1471–1487. https://doi.org/10.1007/s10570-014-0240-4

Indarti E, Marwan RR, Wanrosli WD (2019) Silylation of TEMPO oxidized nanocellulose from oil palm empty fruit bunch by 3-aminopropyltriethoxysilane. Int J Biol Macromol 135:106–112. https://doi.org/10.1016/j.ijbiomac.2019.05.161

Ishida H, Chiang C, Koenig JL (1982) The structure of amionic-functional silane coupling agents: 1. γ-Aminopropyltriethoxysilane and its analogues. Polymer 23(2):251–257. https://doi.org/10.1016/0032-3861(82)90310-x

Jiang F, Han S, Hsieh YL (2013) Controlled defibrillation of rice straw cellulose and selfassembly of cellulose nanofibrils into highly crystalline fibrous materials. RSC Adv 3(30):12366–12375. https://doi.org/10.1039/c3ra41646a

Jiang H, Zhou D, Qu D, Chu G, Xu W, Song H, Xu Y (2016) Self-organized helical superstructure of photonic cellulose loaded with upconversion nanoparticles showing modulated luminescence. RSC Adv 6:76231–76236. https://doi.org/10.1039/C6RA13894B

Johansson LS, Tammelin T, Campbell JM, Setälä H, Östberg M (2011) Experimental evidence on medium driven cellulose surface adaptation demonstrated using nanofibrillated cellulose. Soft Matter 7:10917–10924. https://doi.org/10.1039/C1SM06073B

Khanjanadeh H, Behroz R, Bahramifar N, Gindl-Altmutter W, Bacher M, Edler M, Griesser T (2018) Surface chemical functionalization of cellulose nanocrystals by 3-aminopropyltriethoxysilane. Int J Biol Macromol 106:1288–1296. https://doi.org/10.1016/j.ijbiomac.2017.08.136

Kim J, Holing GJ, Somorjai GA (2011) Curing induced structural reorganization and enhanced reactivity of amion-terminated organic thin films on solid substrates: observations of two types of chemically and structurally unique amino groups on the surface. Langmuir 27:5171–5175. https://doi.org/10.1021/la2007205

Kontturi E, Laaksonen P, Linder MB, Nonappa GAH, Rojas OJ, Ikkala O (2018) Experimental evidence on medium driven cellulose surface adaptation demonstrated using nanofibrillated cellulose. Soft Matter 7:10917–10924. https://doi.org/10.1039/C1SM06073B

Li XM, Reinholdt D, Crego-Calama M (2007) What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces. Chem Soc Rev 36(8):1350–1368. https://doi.org/10.1039/b602486f

Li X, Hu Y (2019) Luminescent films functionalized with cellulose nanofibrils/CdTe quantum dots for anti-counterfeiting applications. Carbohydr Polym 203:167–175. https://doi.org/10.1016/j.carbpol.2018.09.028

Li X, Zou L, Wu G, Shen J (2014) Laser-induced damage on ordered and amorphous sol-gel silica coatings. Opt Mater Exp 4(12):2478–2484. https://doi.org/10.1364/ome.4.002478

Liang L, Qin X, Zheng K, Liu X (2019) Energy flux manipulation in upconversion nanosystems. Acc Chem Res 52(1):228–236. https://doi.org/10.1021/acs.accounts.8b00469

Lichtenstein K, Lavoine N (2017) Toward a deeper understanding of the thermal degradation mechanism of nanocellulose. Polym Degrad Stab 146:53–60. https://doi.org/10.1016/j.polymdegradstab.2017.09.018

Lizundia E, Puglia D, Nguyen T-D, Armentano I (2020) Nanocellulose nanocrystal based multifunctional nanohybrids. Prog Mater Sci 112:106668. https://doi.org/10.1016/j.pmatsci.2020.100668

Lyapin AA, Kuznetsov SV, Ryabochkina PA, Merculov AP, Chernov MV, Ermakova YA, Luginina AA, Fedorov PP (2017) Upconversion luminescence of Ca1−xHoxF2−y and Sr0.98-xErxHo0.02F2−y powders upon excitation by an infrared laser. Laser Phys Lett 14:076003. https://doi.org/10.1088/1612-202X/aa7418

Masmoudi M, Rahal C, Abdelmouleh M, Abdelhed R (2013) Hydrolysis process of γ-APS and characterization of silane film formed on copper in different conditions. Appl Surf Sci 286:71–77. https://doi.org/10.1016/j.apsusc.2013.09.018

Nguyen TD, Hamad WY, MacLachlan MJ (2017) Near-IR-sensitive upconverting nanostructured photonic cellulose films. Adv Opt Mater 5:1600514. https://doi.org/10.1002/adom.201600514

Okita Y, Saito T, Isogai A (2010) Entire surface oxidation of various cellulose microfibrils by TEMPO-mediated oxidation. Biomacromol 11(6):1696–1700. https://doi.org/10.1021/bm100214b

Orsolini P, Antonini C, Stojanovic A, Malfait JW, Caseri WR, Zimmermann T (2018) Superhydrophobicity of nanofibrillated cellulose materials through polysiloxane nanofilaments. Cellulose 25:1127–1146. https://doi.org/10.1007/s10570-017-1636-8

Ovsyankin VV, Feofilov PP (1966) Mechanism of summation of electronic excitations in activated crystals. JETP Lett 3:322–323

Pavia DL, Lampman GM, Kriz GS, Vvyyan JR (2009) Introduction to Spectroscopy. 4th edn. Belmont, USA

Peña-Alonso R, Rubio F, Rubio J (2005) The role of γ - Aminopropyltriethoxysilane (γ -APS) on thermal stability of TEOS-PDMS ormosils. J Sol-Gel Sci Technol 36:77–85. https://doi.org/10.1007/s10971-005-3408-4

Pereira ALS, Feitosa JPA, Morris JPS, Rosa MF (2020) Bacterial cellulose aerogels: influence of oxidation and silanization on mechanical and absorption properties. Carbohydr Polym 250:116927. https://doi.org/10.1016/j.carbpol.2020.116927

Peresin MS, Kammiovirta K, Heikkinen H, Johansson LS, Vartiainen J, Setälä H, Östberg M, Tammelin T (2017) Understanding the mechanisms of oxygen diffusion through surface functionalized nanocellulose films. Carbohydr Polym 174:309–317. https://doi.org/10.1016/j.carbpol.2017.09.018

Qiao B, Wang T-J, Gao H, Jin Y (2015) High density silanization of nano-silica particles using γ-amino propyltriethoxysilane (APTES). Appl Surf Sci 351:646–654. https://doi.org/10.1016/j.apsusc.2015.05.174

Qin X, Liu X, Huang W, Bettinelli M, Liu X (2017) Lanthanide activated phosphors based on 4f–5d optical transitions: theoretical and experimental aspects. Chem Rev 117:4488–4527. https://doi.org/10.1021/acs.chemrev.6b00691
