

Supporting information

Interfacial Nanoparticle Complexation of Oppositely Charged Nanocelluloses into Functional Filaments with Conductive, Drug Release or Antimicrobial Property

Kaitao Zhang¹, Sry D. Hujaya¹, Topias Järvinen², Panpan Li¹, Topias Kauhanen³, Mysore V. Tejesvi^{3,4}, Krisztian Kordas², Henrikki Liimatainen^{1*}

¹Fibre and Particle Engineering Research Unit, Faculty of Technology, University of Oulu, P.O. Box 4300, FI-90014, Finland

²Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu

³Department of Ecology and Genetics, PO Box 3000, University of Oulu

⁴Chain Antimicrobials Ltd, Teknologiantie 2, FI-90590, Oulu, Finland

AUTHOR INFORMATION

* Corresponding author: Henrikki Liimatainen

Email: Henrikki.Liimatainen@oulu.fi. Tel.: +358 8553 2416; Fax: +358 8553 2405.

EXPERIMENTAL SECTION

Preparation of 2,3-dialdehyde cellulose (DAC) by periodate oxidation. 15.0 g of bleached birch pulp was torn by hand into 1 cm × 1 cm pieces and stirred in 1500 ml deionized water in a beaker overnight. Then, 12.3 g of NaIO₄ and 27 g of LiCl were added into the suspension and reacted at 65°C for 3 h. After reaction, oxidized cellulose pulp was washed by filtration using 1000 ml of a 50:50 ethanol:water solution for three times and stored at 4 °C for further use. The aldehyde content of DAC was determined to be 3.79 mmol/g based on an oxime reaction between the aldehyde group and NH₂OH·HCl.

Preparation of cationic cellulose nanocrystals using aminoguanidine hydrochloride (AH-CNC). 75 g aminoguanidine hydrochloride (AH) and 125 g glycerol (AhG DES), i.e., in molar ratio 1:2, were mixed into a Scott-bottle. The mixture was preheated at 90 °C in an oil-bath to obtain a clear liquid, and then adjusted to 70 °C. After that, 10 g (abs.) DAC was added and stirred continuously by magnetic bar for 10 minutes. The reaction bottle was taken away from the oil-bath system and 250 ml of ethanol was added. The product suspension was filtrated and washed twice with 500 ml of ethanol. Cationic cellulose nanocrystals (AH-CNC) were produced via mechanical disintegration of 1 wt% cationized cellulose fiber water suspension by passing through a pair of chambers (400 and 200 μm) under a pressure of 1000 bars using a microfluidizer (Microfluidics M-110EH-30, USA) for two times. The concentration of obtained AH-CNC was 0.98 wt% (pH was adjusted to 4 using dilute HCl).

Preparation of anionic TEMPO-oxidized cellulose nanofibers (TO-CNF). TO-CNF was prepared according to a previously reported method. 1 g of bleached birch pulp was suspended in water (100 mL) containing TEMPO (0.016 g, 0.1 mmol) and sodium bromide (0.1 g, 1 mmol). 10.0 mmol of NaClO solution was added drop wise to the cellulose suspension, and the mixture was stirred at room temperature and kept at pH 10 for 5 h. The oxidation was stopped by adding 10 mL of ethanol, and oxidized fibers were completely washed by filtration with deionized water. The oxidized cellulose fiber suspension with a solid content of 0.6% w/w was sonicated for 1 h using an ultrasonic homogenizer (Heilscher UP 400s, power discharge 0.5 seconds and pause 0.5 seconds, 60 % amplitude and 22 mm probe tip diameter) to obtain TEMPO-oxidized cellulose nanofibers (pH 7.1).

Fabrications of different nanocellulose (NC) based INC fibers

Fabrication of pure nanocellulose based INC fiber

One droplet (100 μ L) of cationic AH-CNC suspension was placed on a polystyrene Petri dish and another droplet of 100 μ L anionic TO-CNF suspension was pipetted next to it without the two droplets coming into together. Subsequently, a pair of tweezers was plunged into the two droplets to make them into contact and then continuous filaments were drawn vertically from the formed interface film by a universal testing machine (Zwick D0724587, Switzerland) at a constant rate of 30 mm/min. Finally, the obtained wet nanocellulose based filaments were wrapped on the glass rod and dried at room temperature.

Fabrication of MWCNTs incorporated nanocellulose based (CMWCNTs/NC) INC fiber

Various amounts of carboxylated MWCNTs powder were mixed with 10 mL 0.5 wt% TO-CNF aqueous suspension and further sonicated for 10 min, resulting in 0.5 wt% TO-CNF suspension containing 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45% CNTs. The obtained suspension was used as negatively charged component to draw the filament with 0.5% cationic AH-CNC suspension. Because no black carbon solution was observed after drawing, we deduced that all CNTs were successfully incorporated into the filaments. The content of CNTs in the fabricated INC filaments was calculated by the following formula:

CNTs content (%) = $m_{\text{CNTs}} / (m_{\text{CNTs}} + m_{\text{AH-CNC}} + m_{\text{TO-CNF}} - m_{\text{left}}) \times 100\%$, where:

m_{CNTs} is the weight of CNTs for the filament drawing (g);

$m_{\text{AH-CNC}}$ is the weight of AH-CNC for the filament drawing;

$m_{\text{TO-CNF}}$ is the weight of TO-CNF for the filament drawing;

m_{left} is the dried weight of left nanocellulose after drawing.

Fabrications of DOX loaded or Ag NPs loaded nanocellulose based INC filament (DOX/NC or Ag NPs/NC INC filament)

10 mg/ml DOX was first prepared by dissolving DOX in deionized water, which was then added to 0.5 wt% AH-CNC dispersion resulting in a final concentration of 200 μ g/ml. The obtained suspension was used as the positively charged component to draw the filament with 0.5 wt% negatively charged T-CNF. All the left suspensions were collected and used to determine the remaining DOX after fiber drawing.

It showed that about 83% DOX was incorporated into filaments. The DOX loading efficiency into the INC filaments was calculated by the following formula:

DOX content (%) = $100\% \times (m_{\text{DOX}} - m_{\text{left}}) / m_{\text{DOX}}$, where:

m_{DOX} is the total amount of DOX used for thirty filament drawing (g);

m_{left} is the calculated by measuring the remaining amount of DOX in the collected suspensions via UV spectrophotometer after thirty drawing.

For Ag NPs-doped nanocellulose based filament, 0.4 wt% TO-CNF suspension with 0.005 mmol/mL Ag NPs was used to draw the fiber with 0.5 wt% AH-CNC.

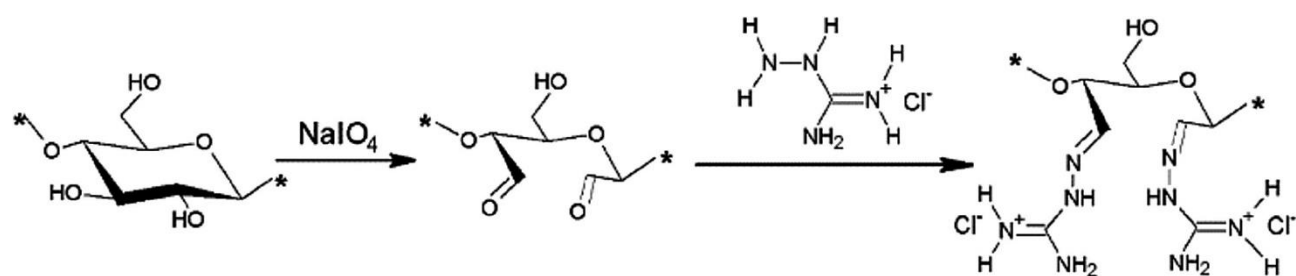


Figure S1. Reaction of cationization of cellulose using sequential periodate oxidation and imidization with aminoguanidine hydrochloride for AH-CNC preparation.

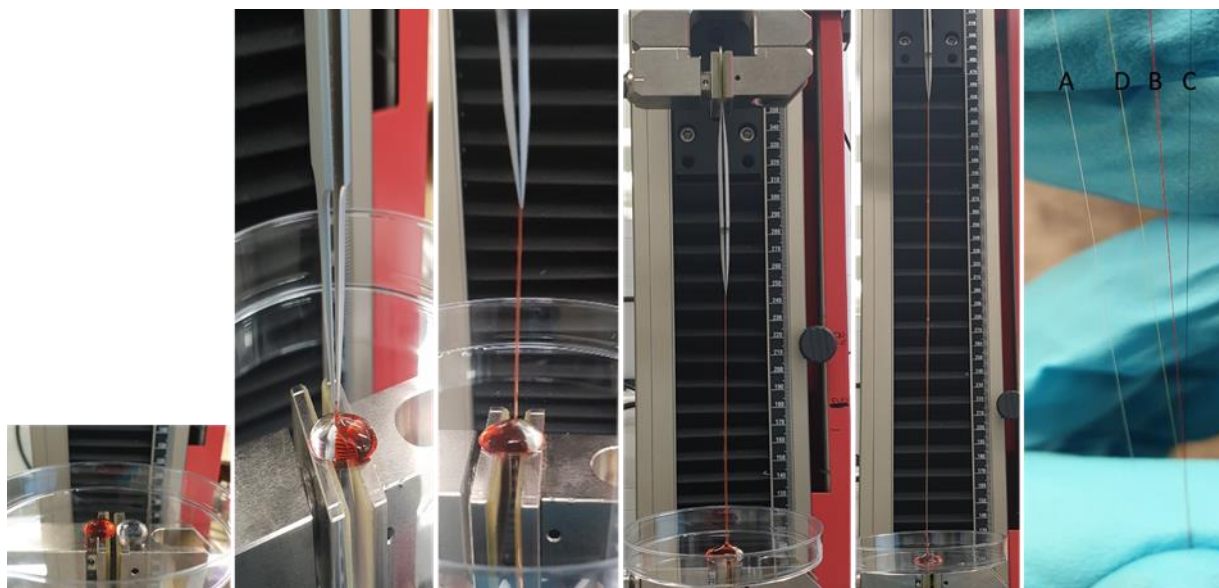


Figure S2. INC filament drawing using tensile test machine (DOX/NC based INC filament, red droplet is cationic AH-CNC with DOX and the transparent droplet is anionic TO-CNF). A. dried pure INC filament (white), B. dried DOX loaded INC filament (red), C. dried CNTs incorporated INC filament (black) and D. dried Ag NPs doped INC filament (yellow).

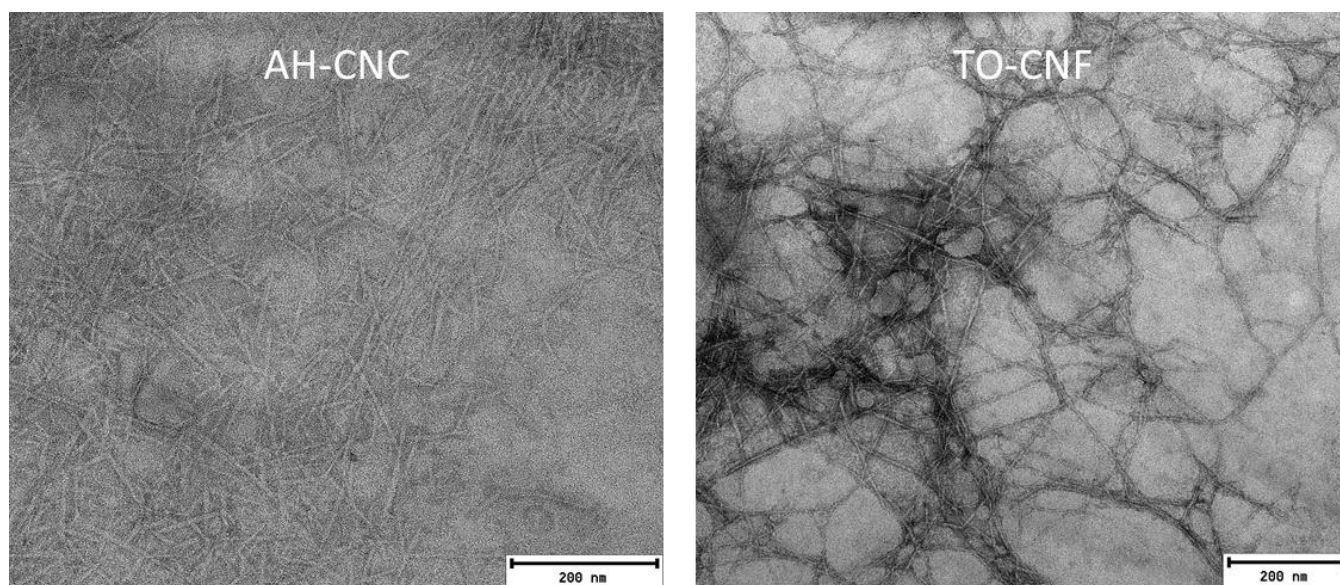


Figure S3. TEM images of positively charged AH-CNC and negatively charged TO-CNF.

Table S1. Feasibility of filament drawing from the interface between adjacent droplets of AH-CNC and TO-CNF at various combinations of concentrations.

	0.6% TO-CNF	0.5% TO-CNF	0.3% TO-CNF	0.1% TO-CNF
0.6% AH-CNC	Yes*	Yes*	Yes*	Yes
0.5% AH-CNC	Yes*	Yes*	Yes*	Yes
0.3% AH-CNC	Yes*	Yes*	Yes*	Yes
0.1% AH-CNC	Yes	Yes	Yes	Yes

* = The combination of concentrations marked with an asterisk were subjectively evaluated to be the most robust for drawing the filament

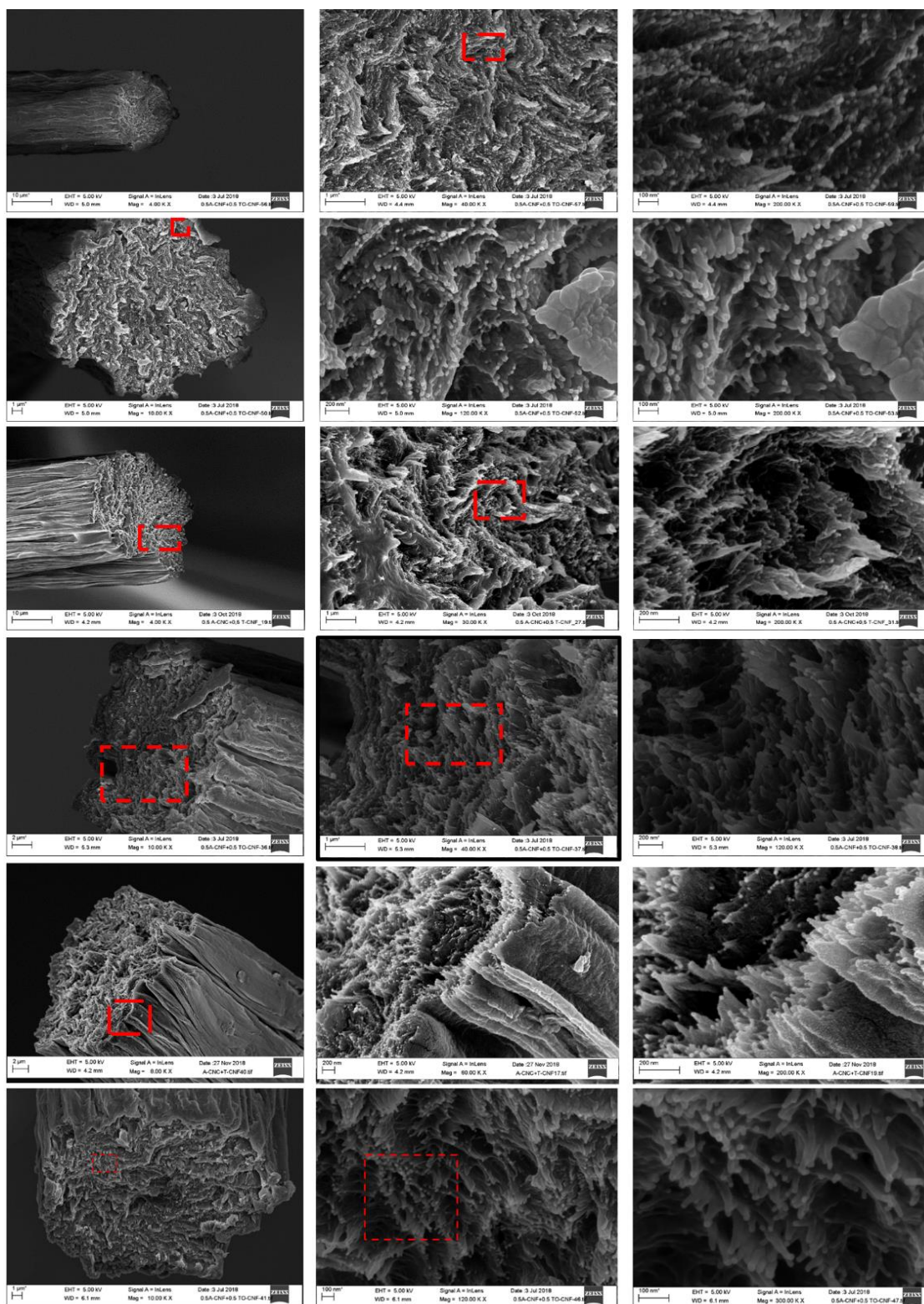


Figure S4. SEM images of cross-section areas of pure nanocellulose based INC filaments.

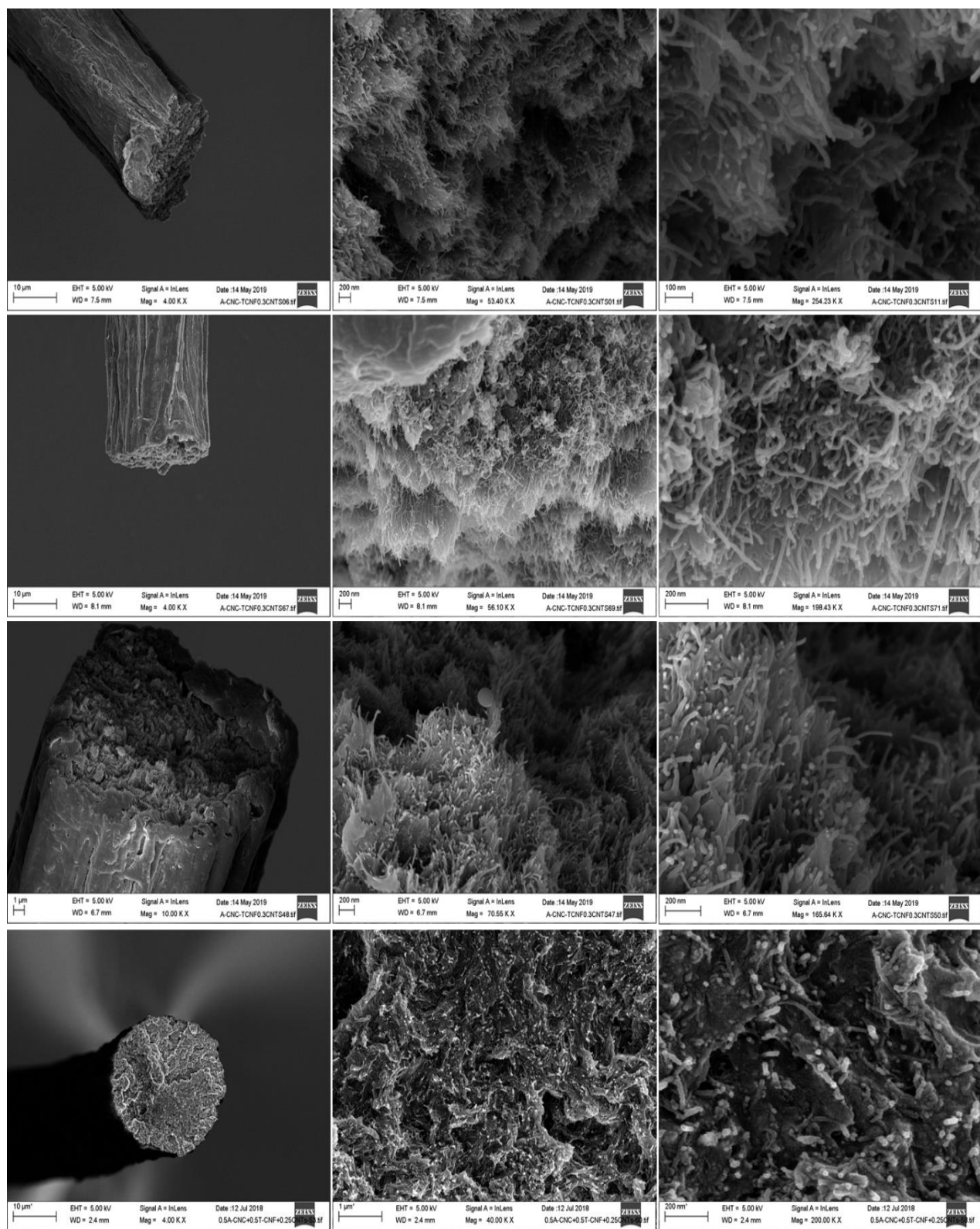


Figure S5. SEM images of cross-section area of CNTs/NC based INC filaments.

The cross-sectional swelling of the INC filaments in different solutions (PBS at pH 7.4 or ABS at pH 4). A minimum of ten dried filaments were placed on a microscope glass with 1 ~ 2 drops of selected swelling solutions. After 10 minutes, samples were covered with a glass cover and the filament diameter was measured by an optical microscope. The diameter of the dried filaments before the immersion were also measured.

Swelling ratio (%)

$$SD = \Delta D / D \times 100\%$$

Where, D = original diameter of filament, ΔD = increased diameter of swollen filament.

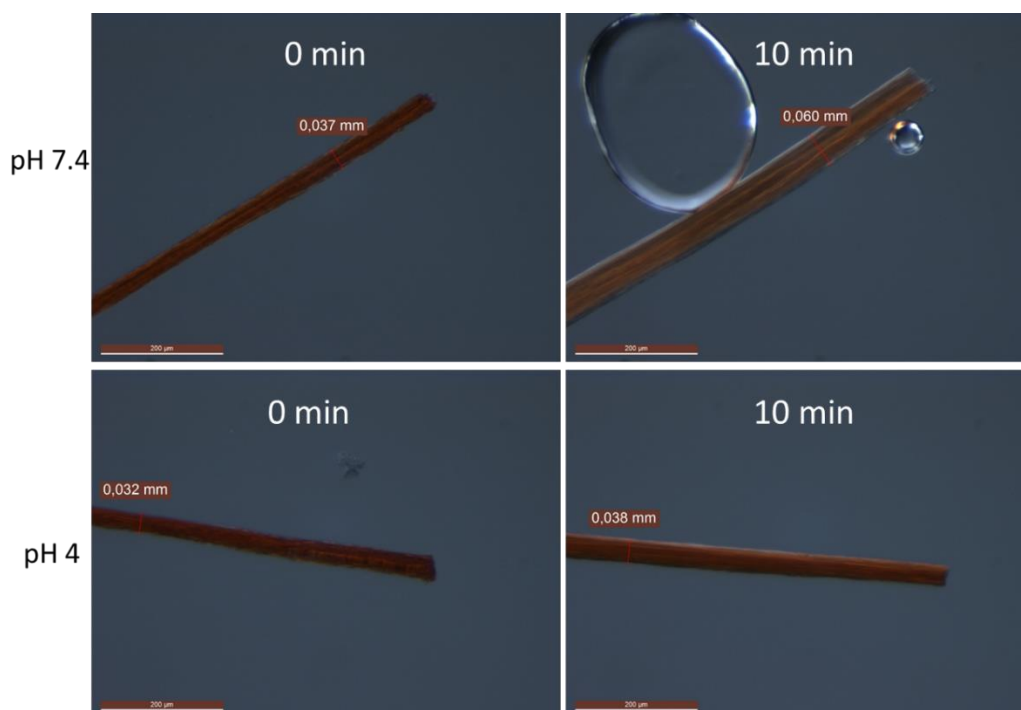


Figure S6. Water swelling of DOX/NC INC filaments in different pH for 10 min.



Figure S7. (A) Digital photo of DOX/NC INC filaments after immersing in different medium for more than one month. (B) Digital photo and (C) optical image of DOX/NC INC filaments after drug release in ABS for more than one month. The formed filament was insoluble and only swelling in these medium. The filaments could be re-obtained after drying.

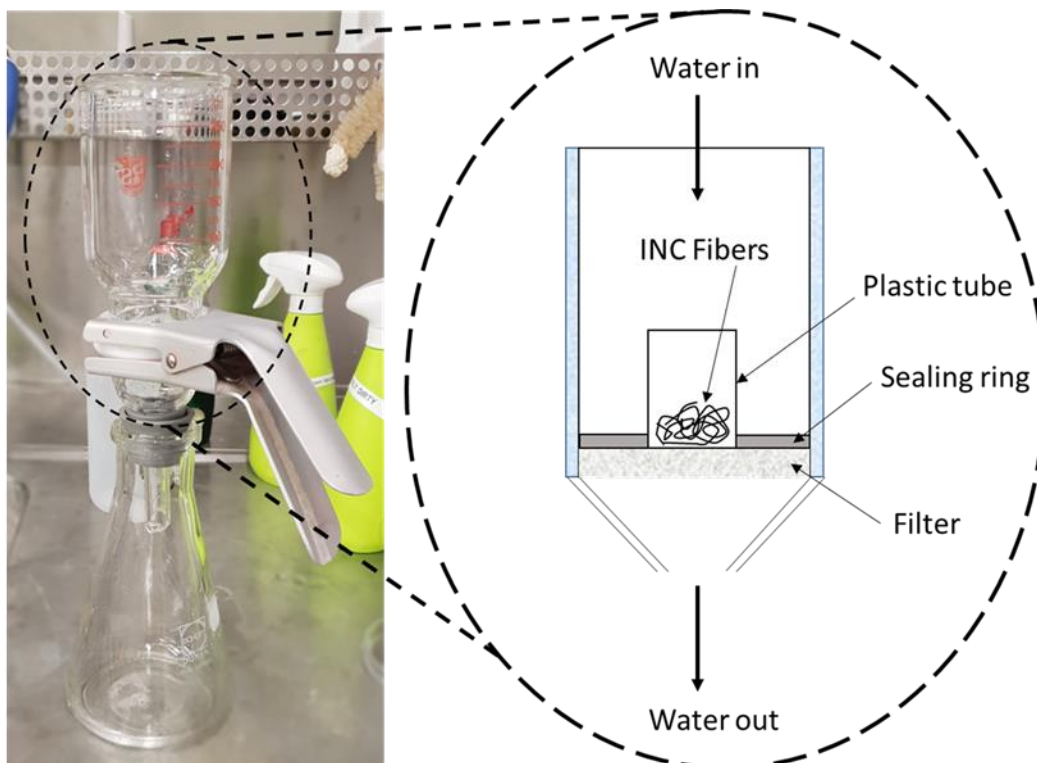


Figure S8. Schematic of the hydro-entanglement process

Six newly prepared nanocellulose based filaments with or without DOX were transferred into a plastic tube (6 mm in diameter). The plastic tube was placed through a sealing ring (a plastic mat perforated with openings of 6 mm in diameter). About 1 L of deionized water was continuously passed through the plastic tube by vacuum filtration for 1 min to entangle and compress the filaments. Entanglement of the filaments led to coherent scaffolds that retained good shape stability in water.

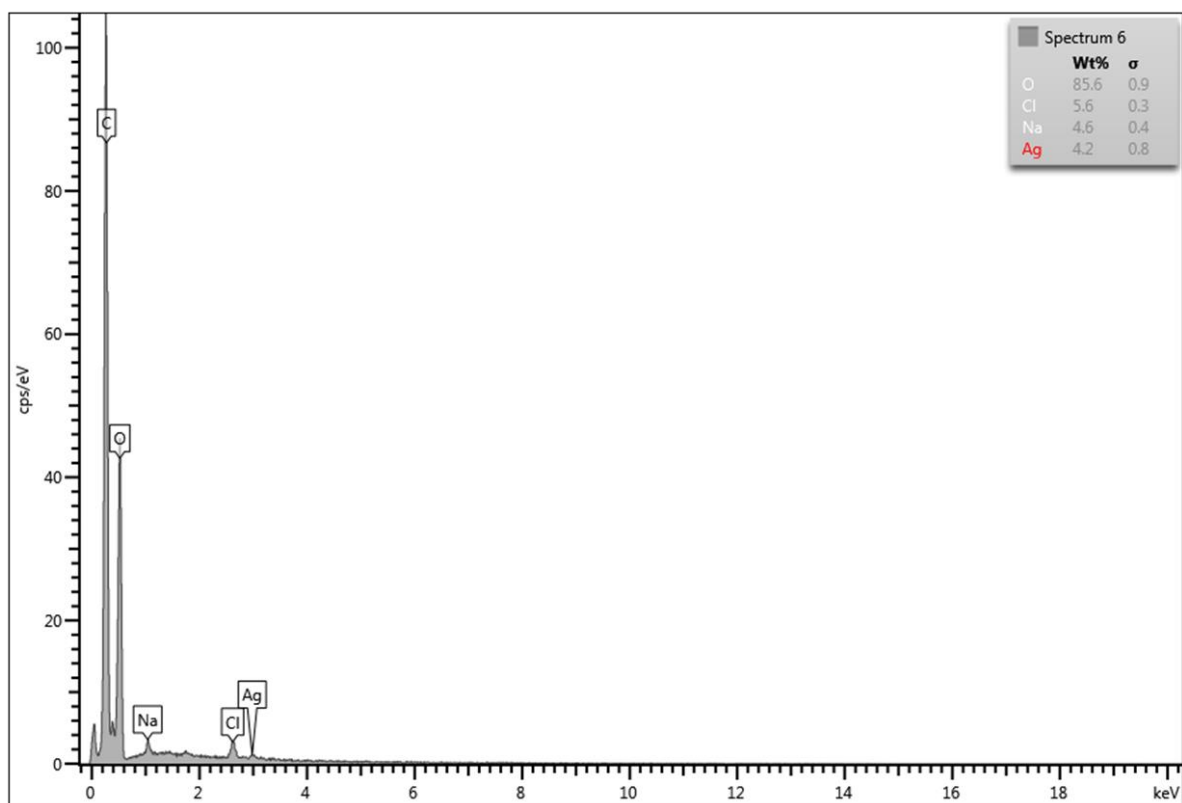


Figure. S9 Energy Dispersive X-ray Spectroscopy (EDS) spectra of Ag NPs/NC INC filament

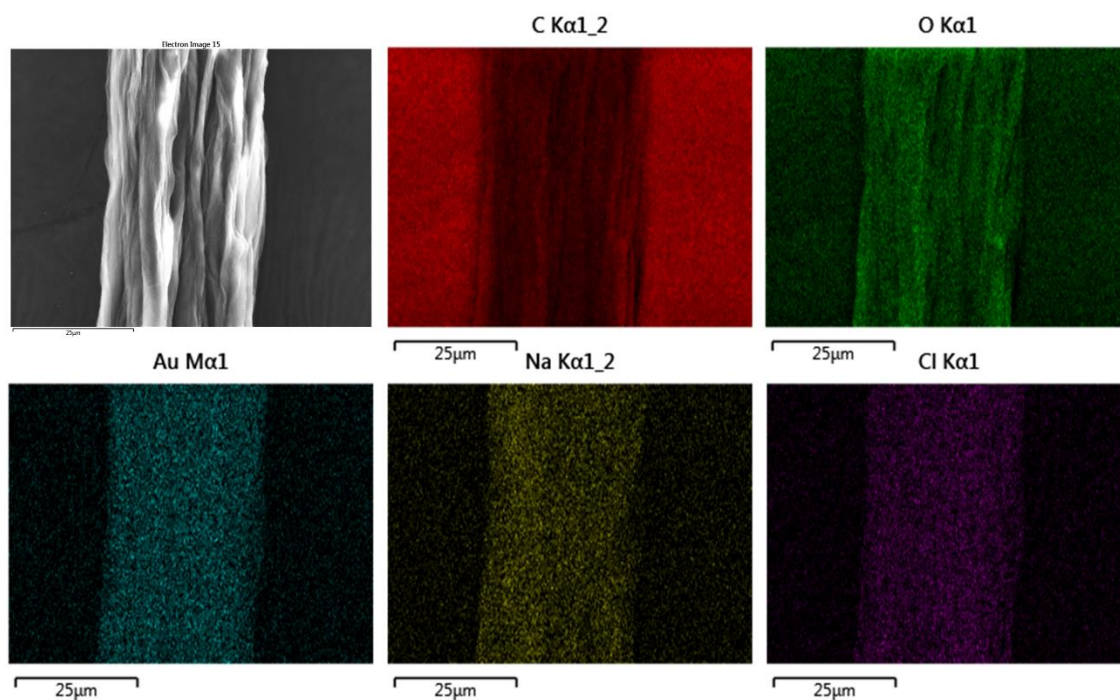


Figure S10. Energy dispersive spectroscopy (EDS) map of gold NPs doped INC filaments

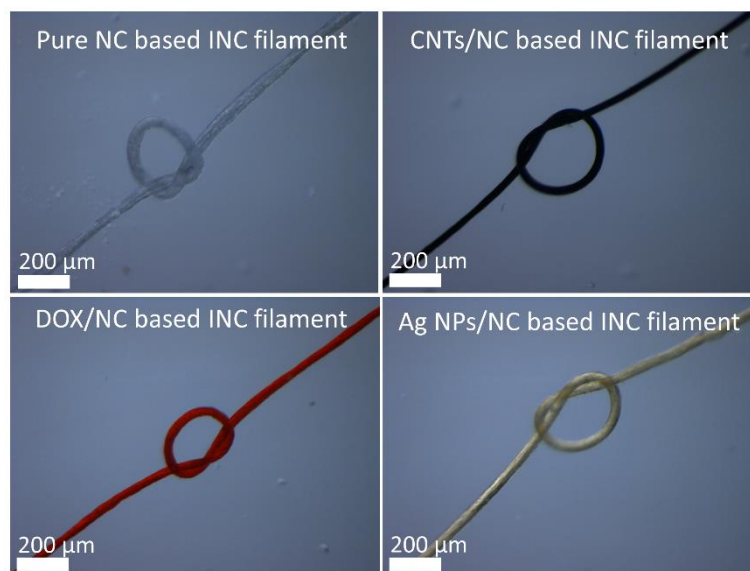


Figure S11. Optical images of various knotted NC based INC filaments

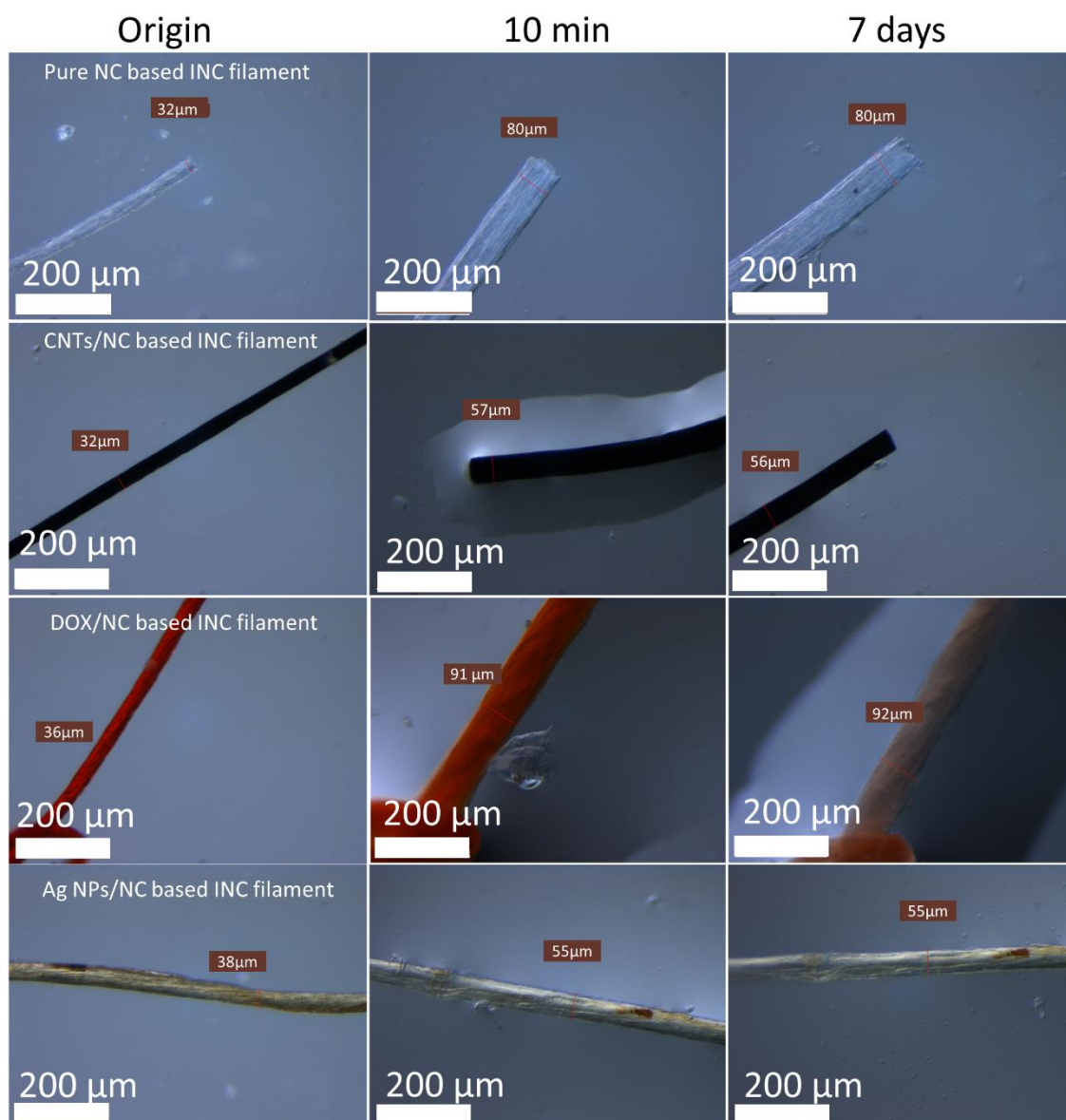


Figure S12. Optical images of different NC based INC filaments swelling in water for 10 min or 7 days.

The water resistance of different fabricated NC based INC filaments were primarily investigated by measuring the diameter after immersing these fibers into water. It was shown that these filaments swelled immediately once they were dipping in water but kept almost unchanged even after 7 days immersion.