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Fabrication and characterization of nanocellulose aerogel structures

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Abstract— **Nanocellulose is a promising new renewable and low-cost nanomaterial which has potential applications in many different fields from biomedical to electronic applications. Here, we report the fabricated aerogels from aqueous CNF and CNC dispersions using freeze-drying technique and analysis of their structural analysis using different microscopic techniques. Also, we report the development of dispenser for aqueous nanocellulose solutions to be installed into 3D-printer system.**

Keywords— **Nanocellulose, microscopy, aerogel, dispenser, 3D-printer.**

I. Introduction

Three dimensional (3D) printing has recently replaced many conventional microfabrication techniques such as lithography. 3D printing is advantageous especially in the case of special shapes and challenging materials, which conventional techniques cannot produce, e.g. cellulose based 3D objects [1].

Nanocellulose [2], e.g. cellulose nanofibril (CNF) and cellulose nanocrystal (CNC), is a promising strong, porous, lightweight, biocompatible, biodegradable and piezoelectric solution processable, low-cost biomaterial. We have recently demonstrated the suitability of nanocellulose for various electronic applications [3-6]. Also, nanocellulose has been shown to work as a stem cell culturing scaffold [7], giving a promise for the fabrication of bio-implants to replace lost or damaged organs of humans or animals.

In this paper, we (1) report the microscopic structures of nanocellulose aerogels fabricated from CNF and CNC suspensions using freeze-drying method, and (2) report the development of dispenser system to be embedded onto a commercial 3D printer to make it suitable for printing aqueous nanocellulose dispersions.

II. Preparation of Nanocellulose Aerogels

We have fabricated CNF and CNC aerogels free-drying method, where the aqueous nanocellulose dispersion was frozen and subsequently dried in vacuum by sublimation, leaving a highly porous cellulose matrix, suitable for example for biomedical or electronic applications. Aqueous dispersions of CNF (1.35 w-%) and CNC (1.39 w-%) were obtained from Aalto University. The CNF was obtained from a bleached birch cellulose mass which underwent 6 passes in microfibrillator equipment resulting a viscous CNF gel. The CNC was fabricated from CNF gel using a strong acid hydrolysis, which removed the amorphous parts of the CNF.

Prior to being placed to a freezer, a certain volume of CNF gel was deposited on a glass substrate, whereas CNC solution was dispensed on the petri dish due to being less viscous that CNF. After keeping a few hours in the freezer, the samples where placed into the vacuum chamber and let dry about 24 hours. After removal from the vacuum chamber the samples appeared as white, porous aerogel structures (see Fig. 1a-b).

The CNF gel was found very robust, but it was noticed that the CNC aerogel is very fragile as such an it cannot be easily handled as free-standing structure without a support.

III. Microscopic Analysis of Aerogels

Several different microscopy techniques to try to distinquish different characteristics and also to study suitability of the certain microscopy technique for this type of new material. The scanning electron microscopy (SEM), µCT (X-ray micro–computed tomography) microscopy, and scanning helium ion microscope (HIM) were used in the CNF and CNC aerogel characterization.

The SEM images are shown in the Fig. 1c-f. In addition to nanofibrils observed in Fig. 1e, the CNF gel starting material contain also larger fibrils (see Fig 1c) as residues from the fibrillation process. In comparison, it can be observed from the Fig. 1d and 1f that the surface of CNC aerogel contains no large fibrils but only about 200 nm long nanocrystals.

The µCT images in Fig. 1g-h show the 3D tomography of the aerogels. Fig 1g shows that CNF fibrils have formed type of parallel surfaces while forming the aerogel structure. On the other hand, the CNC aerogel is composed of randomly aligned needles.

The HIM images are shown in Fig. 2. It can be observed from the images that HIM technique gives quite good depth-view, giving a 3D-vision to the material. It has to be noted that HIM technique does not require a conducting samples as is the case in SEM technique. One can see that both HIM and µCT images show similar features for CNF and CNC aerogels. As in observed from Fig. 1g, also Fig. 2a-b show that CNF fibrils are oriented as surface like structures. On the other hand, as seen in Fig. 1h, also Fig. 2 c-d show that CNC crystals in an aerogel orient a tree like formation made of CNC needles.

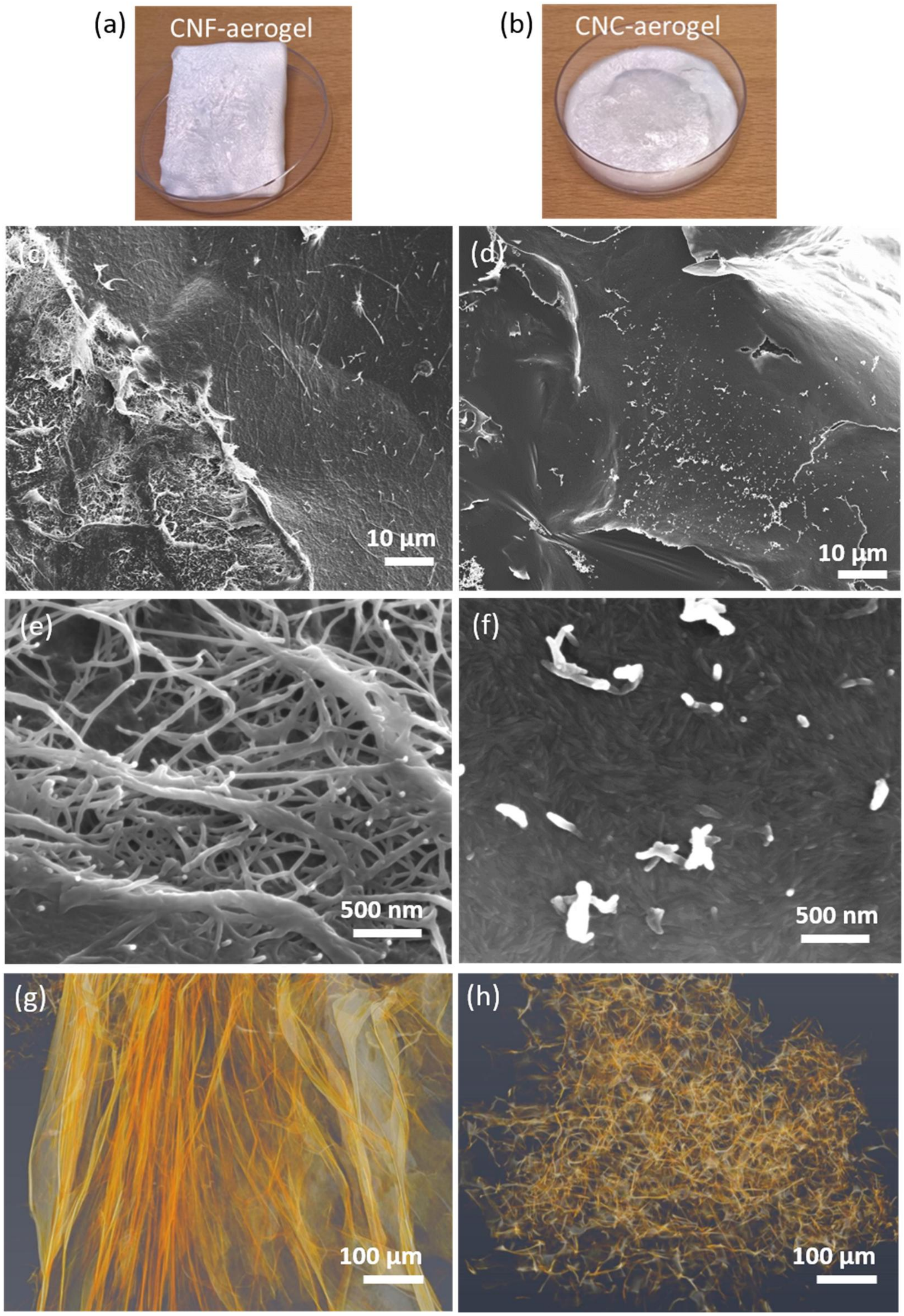

Fig. 1. Photographs of (a) CNF and (b) CNC aerogels. Scanning electron microscope (SEM) images of the (c, e) CNF and (d, f) CNC aerogels surfaces. µCT (X-ray micro–computed tomography) images of (g) CNF and (h) CNC aerogels.

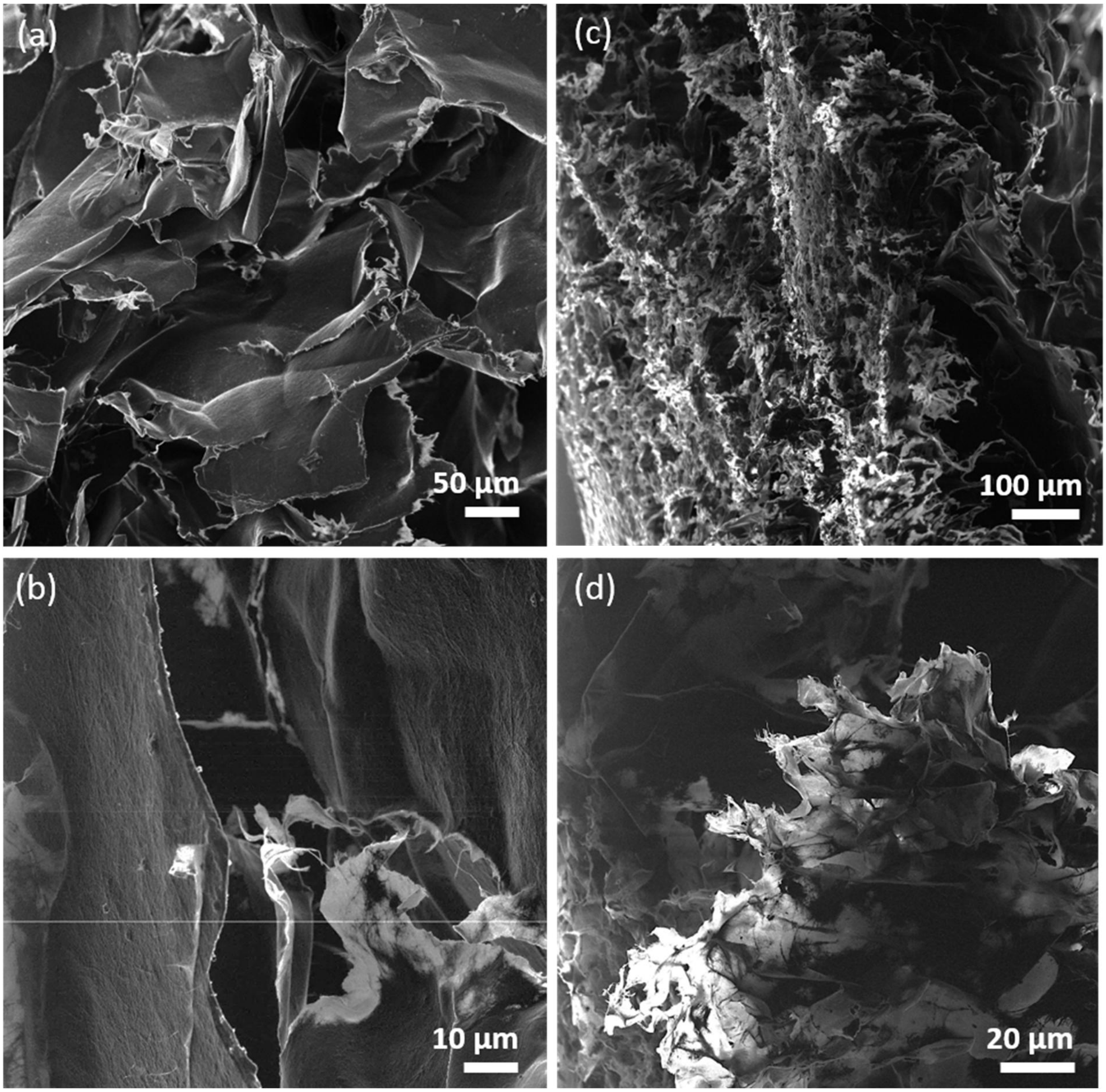

Fig. 2. Scanning helium ion microscope (HIM) images of (a-b) CNF and (c-d) CNC aerogels.

IV. DISPENSER FOR NANOCELLULOSE PRINTING

We developed a dispenser system dedicated for printing of aqueous CNF or CNC suspensions. The development of the dispenser system is reported in more details elsewhere [8].

The dispenser system is composed of a 10ml plastic syringe and a 3D-printer step motor for moving the syringe piston through the threaded roc (see Fig. 3). A simple Labview software was programmed for driving the stepper motor via Arduino Uno microcontroller board.

Fig. 3c shows the accumulation of CNF dispersion volume during continuous dosing with different dosing rates. The average dosing accuracy of the dispenser system seems relatively high and is considered to be on acceptable level for 3D-printing of CNF dispersion.

Fig. 3d shows an example of CNF structure semi-manually printed on a petri dish and stored in the freezer for a few weeks. The image shows that CNF gel has turned to white, whereas the CNF gel in liquid for is almost transparent. This indicates that the CNF structure has undergone freeze-drying during its storage in the freezer. However, the normal kitchen freezer used here is not optimal for obtaining thorough freeze-drying which ultimately should maintain the initial 3D structure of the CNF object even when dried.

In the following work, the in-house made dispenser system will be fully integrated into a commercial 3D-printer system (Prusa i3). Also, freeze-drying method will be further developed to obtain better quality 3D nanocellulose objects.

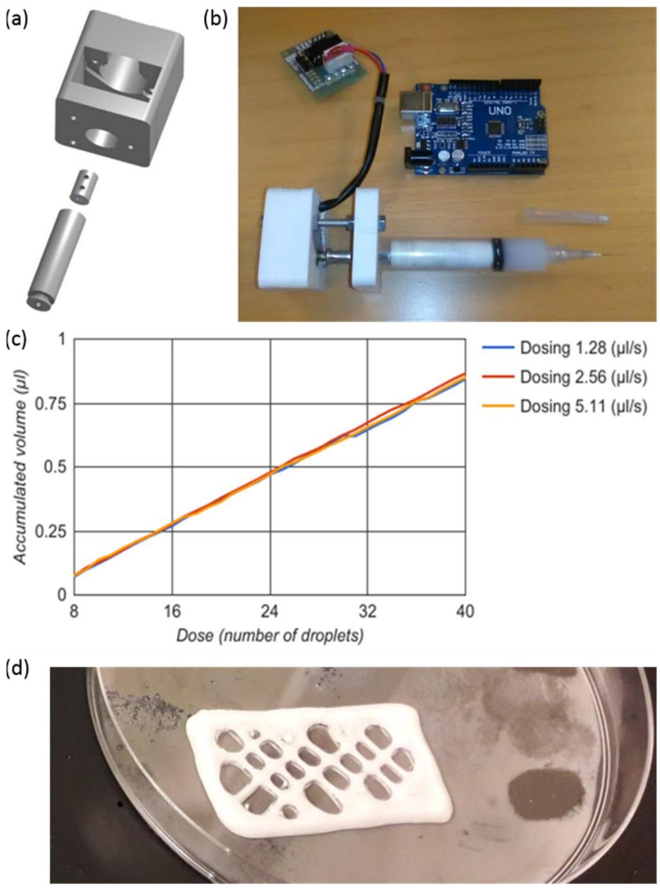

Fig. 3. (a) CAD drawing of dispenser building blocks, and (b) photograph of the nanocellulose filled syringe assembled into the dispenser system. (c) Accumulated volumes of CNF dispersion using volume of 25ul with different dosing rates. (d) An example of 3D-printed CNF-gel structure.

V. CONCLUSIONS

Here, we proved that the freeze-drying technique is suitable for fabrication of porous, lightweight aerogel from aqueous CNF and CNC dispersions. As a conclusion from the microscopic analysis, both CNF and CNC aerogels look highly porous as expected, but CNF aerogel shown some long-range arrangement to wall like structures, whereas CNC aerogel is quite homogeneous.

The aerogel structures studied by microscopy were not patterned and there was no overall control of the outer dimensions of the aerogel structures. In the future, however, 3D-printing system with in-house built dispenser will be used for the aerogel object definition.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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