HIGHLY TRANSPARENT CELLULOSE SUBSTRATE FOR DYE SENSITIZED SOLAR CELLS

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ABSTRACT: Current electronic devices are fabricated mostly on glass or plastic films which are often hard to recycle. In this study, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidized nano-cellulose (TOCN) film was explored as a green substrate candidate for next-generation electronic applications and its optical, surface and mechanical properties are presented in this report. Its prospective integration in the future dye-sensitized solar cells (DSSCs) was investigated by testing as one of the electrodes in a counter electrode-counter electrode configuration (CE-CE). The TOCN film was able to undergo the device sealing process at 220°C and 140 °C without any change in its color or dimension. The results highlight the potential of environmentally friendly and room temperature processed nano-fiber based films as an alternative substrate for bifacial devices.

Keywords: Substrates, optical properties, TEMPO oxidized cellulose, dye-sensitized solar cells

1 INTRODUCTION

Cellulosic materials are abundant, strong and light-weight. These have recently been received much attention as a substrate in electronic applications [1-2]. Conventional cellulose based products, mostly consisting of 20–50 µm (diameter) size fibers, are opaque, permeable to solvents and have a rough surface contour with low thermal stability. Therefore, their integration in electronic and electrochemical devices has been a challenge particularly in solvent based devices manufactured at high temperatures [3].

The various cellulose processing techniques provide an opportunity to improve its optical, surface and mechanical properties and pave the way to more sustainable and biodegradable products. For example, the nano-fibrillated cellulose (NFC) production [4] and its surface modification with selective 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) treatment exchanging the hydroxyl group of the cellulose to carboxyl based group [5] were two breakthroughs in forest products technology. Due to the better dispersion achieved by nano-fibril production and functional group alteration, the film formation was improved and high transparency values, up to 90% transmittance of the incident light for 20 µm films, with acceptable strength values (Young's Modulus value of close to 7 GPa) were reported [6]. Recently numerous electronic devices were successfully integrated on the transparent nano-fiber based films such as, transistors [7], antennas [8] and organic solar cells [9] however, the solvent permeation has remained as the key challenge in the application of TEMPO-oxidized nano-cellulose (TOCN) films to the devices which include liquid components.

We present here cellulose substrates (TOCN films) with high bendability, light transmittance and strength along with low roughness. Slow drying process with two level humidity conditions improved the properties of the TOCN films owing to the better film formation. The physical and chemical properties of this substrate are first investigated through different characterization techniques, discussed in the later sections of this report. The integration in dye-sensitized solar cells (DSSCs) [10] as a counter electrode (CE) was tested by fabricating CE-CE electrochemical cells which exhibited favorable properties such as low charge transfer resistance (R_{CT}) essentially required to produce high performance DSSCs.

2 EXPERIMENTAL SECTION

2.1 Materials

All reagents were purchased from Sigma-Aldrich and used without further purification. EL-HSE high stability electrolyte was obtained from Dyesol.

2.2 Preparation of cellulose films

Hydroxyl groups of nanofibrillated cellulose from birch kraft fibers were selectively exchanged with carboxylate groups by TEMPO catalyst at room temperature and pH 10 [11]. After the mechanical disintegration in a micro fluidizer (Microfluidics M-110EH-30, Microfluidics Int., USA), 0.4 wt % aqueous dispersion was obtained after 24 h of magnetic stirring followed by a mild centrifuge at 4000g for 10 min in order to obtain homogenous dispersion without any aggregates. Casting solution was dispensed onto poly (styrene) Petri dishes and the water was evaporated in 2 steps, i.e. first at ordinary room condition (23°C-35% RH) until the cast solution lost half of its water content and then in a climate room (23 °C-66% RH). A post-heating treatment was carried out at 35 °C for 5 min in order to detach the TOCN film without any damage. The TOCN films were initially sputtered with 300 nm ITO layer (ITOCN film) and then 10 nm platinum layer (PITOCN film).

2.3 Cell Preparation

Conventional CEs were prepared by sputtering 10 nm platinum on FTO-coated glass. The platinized FTO-coated glass-platinized FTO-coated glass (G_{Pt}-G_{Pt}), and the platinized FTO-coated glass-PITOCN (G_{Pt}-PITOCN) CEs were sealed with 25 µm thick thermoplastic foil (Surlyn) on a hot plate at 140°C. The electrolyte was then

injected via drilled holes. 25 µm thick cover foil (Surlyn) and thin glass cover were used to seal both type of devices by using hot press at 220°C.

2.4 Measurements

An optical goniometer (CAM 200 from KSV instruments), which was equipped with a camera and dispenser system, was used to capture a sessile drop behavior on TOCN and ITOCN surfaces and the records were analyzed by using a built-in image analysis software to determine the contact angle of the drop based on Young and Laplace equation. Perkin Elmer lambda 950 UV-Vis spectrophotometer was utilized to measure the transmittance of FTO-coated commercial glass, TOCN and ITOCN films. Electrochemical impedance spectroscopy (EIS) data was recorded at open circuit voltage conditions using Zahner-Elektrik IM6 potentiostat and the data was fitted by Zview2 software. The measurement frequency range was from 100 mHz to 100 KHz. The surface properties of flexible films were observed with a scanning electron microscope (Zeiss Sigma VP scanning electron microscope) at 1 kV acceleration voltage, and with a Multimode 8 atomic force microscope (AFM) equipped with a NanoScope V controller (Bruker Corporation, Billerica, MA), operating in tapping mode. The obtained images from AFM were processed by utilizing NanoScope 8.15 software (Bruker). No image correction (except flattening) was employed. The mechanical tests were carried out using a vertical tensile tester, MTS 400/M (MTS Systems, USA), in accordance with ISO 527-3 (Specimen type 5) loading 50 N at 1 mm/min cross-head speed.

3 RESULTS AND DISCUSSION

3.1 Surface Properties

A well-dispersed nano-fiber network along with a smooth surface promote the applicability of the coatings [6]. Investigated with AFM and SEM, TOCN (Figure 1 a) and ITOCN substrates exhibited homogenous topology with the surface RMS roughness values of 8.8±1 nm and 20±1 nm, respectively (Figure 1 b-d and Figure 2). The high water contact angle of 118° (Figure 1 a inset) was measured on the TOCN film which has even surface with low roughness facilitating the even distribution of ITO conductive coating on TOCN surface.

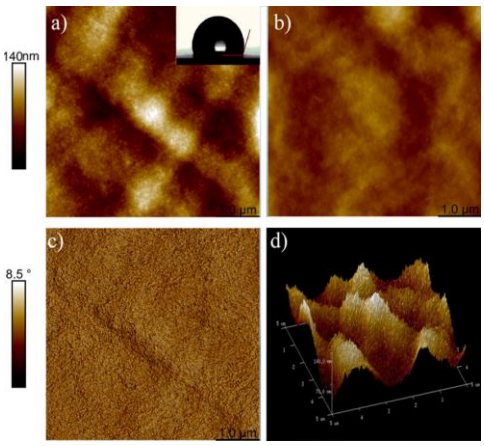

Figure 1: AFM images of a) TOCN film (inset: water contact angle on TOCN), b-d) ITOCN film (height, phase and 3D modes, respectively).

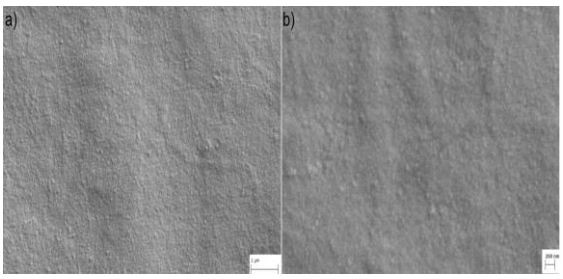

Figure 2: Top view SEM image of ITOCN film a) lower magnification (Scale bar: 1µm), b) higher magnification (Scale bar: 200nm).

The electrolyte absorbance resistance of the substrates was tested with a modified Cobb test in accordance with the ISO 535 and EN 20535 standards as explained in our previous study [13]. Five identical TOCN substrates were exposed to the 3-methoxypropionitrile solvent-based electrolyte for 20 minutes. No alteration in the weight of the TOCN films was detected. The 4 µL electrolyte sessile drop on TOCN surface was monitored in order to further elucidate the interaction of the TOCN surface and the electrolyte. The drop exhibited a stable contact angle (30°) without any difference in its height and base line during the goniometric measurements.

3.2 Transparency

The key requirement for the optical and/or bifacial electronic devices is enhancing the transmittance of the incident light to the photoactive layers, therefore, transparent FTO-coated commercial glass has been widely used in research labs [12]. The TOCN film and ITOCN film with 300 nm ITO coating (Figure 3 a-c) exhibited transmittance values of 86% and 76%, respectively, while FTO-coated glass transmitted 82% of the incident light at 550 nm (Figure 3 d). The transmittance of TOCN film was superior to FTO-coated glass between 570 and 660 nm wavelength values in the optical spectra reaching 85% transmittance at 600 nm whereas the FTO-coated glass had a transmittance value of 80-81% in this region.

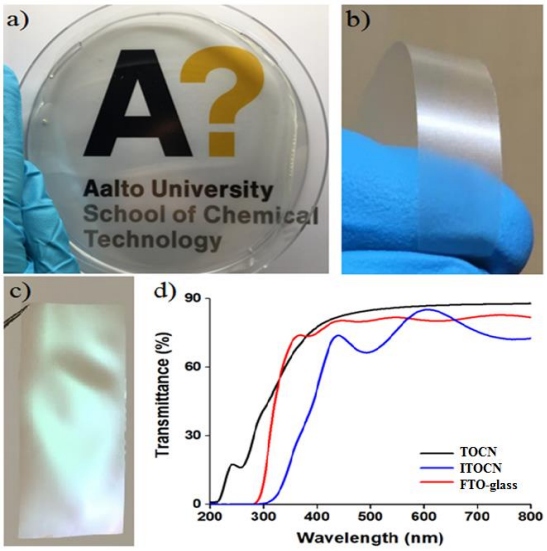

Figure 3: a) TOCN film on Petri dish, b) TOCN stripe, c) ITOCN stripe, d) transmittance of FTO-coated glass and TOCN and ITOCN films.

3.3 Mechanical Properties

The film-forming properties and the durability of TOCN films were characterized by the mechanical parameters recorded during the tensile tests and the bending tests. The average Young's modulus of 8 dog-bone-shaped specimens consisting of 70 g/m^2 grammage was recorded as 9.5±1 GPa and after several bending cycles (2 cm bending radius), no specimen deformation was observed. The physical properties of the TOCN films prepared in this study and the previously reported TEMPO oxidized nano-cellulose films are presented in Table I.

Table I: Physical properties of the TOCN films prepared for this study and reported TOCN films in literature

	TOCN	Reported TOCN
Young's modulus (GPa)	9.5±1	6-15 [14, 15]
Density (g/cm^3)	1.6	0.5-1.4 [16, 14]
Thickness (µm)	44±1	20-50 [6, 17]

3.4 Electrical Impedance Spectra (EIS)

The characteristics of the cellulose substrate presented in earlier sections motivated us to test its integration in the future dye-sensitized solar cells. Before that we fabricated CE-CE cells and investigated the electrochemical impedance characteristics of both types of CE-CE cells (Figure 4). Figure 4 a represents the impedance spectrum of a CE-CE symmetrical cell that was constructed by platinizing two identical FTO-glass substrates whereas in case of Figure 4 b, FTO Glass CE was replaced with the ITO and Pt coated cellulose substrate (PITOCN) and then its electrochemical impedance spectrum was measured. The case for FTO platinized CEs was straight-forward as expected, the CE-CE cells exhibited two semicircles in the Nyquist plot: one appeared at high frequency (1-10 kHz) which corresponds to charge transfer resistance (R_{CT} = 1.9 Ω) whereas the second semicircle appeared at low frequency (1-10 Hz) and relates to the diffusion resistance (R_D = 0.7 Ω) (Table II) [18].

Replacing one platinized FTO with PITOCN substrate did not change any peak position due to the same Pt catalyst layer which was an expected result. The higher series resistance (R_S = 21.8 Ω) was also expected due to higher sheet resistance of PITOCN (R_{SH} = 60 Ω/Sq) which was effectively suppressed after the platinization.

Although the R_{CT} was deduced from the impedance spectra of each type of CE-CE cells, a simpler method can also be applied to calculate the more accurate value. It is to simply subtract the R_{CT} value of the platinized FTO-glass substrate based CE-CE cell since the same platinized FTO-glass substrate was used in platinized FTO-glass and PITOCN based CE-CE cells. Hence with this assumption, we calculated R_{CT} = 3.5 Ω for PITOCN substrate which is comparable to FTO-Pt CE.

These results suggest that the cellulose substrate presented in this report can be potentially integrated as a counter electrode in DSSC. Hence we aim to fabricate DSSCs with this interesting candidate substrate in our future work.

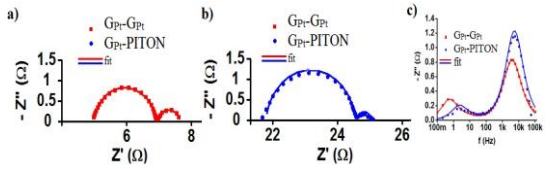

Figure 4: EIS platinized glass- platinized glass (G_{Pt}-G_{Pt}) and platinized glass-PITOCN (G_{Pt}-PITOCN) cells. a) Nyquist plot, b) imaginary impedance (Z'') of both cells as a function of frequency.

Table II: EIS parameter of CE-CE cells. The values are calculated for single electrode.

Cell	R_S (Ω)	R_{CT} (Ω)	R_D (Ω)
G_{Pt}-PITOCN	21.8	2.7	0.5
G_{Pt}-G_{Pt}	4.9	1.9	0.7

4 CONCLUSIONS

Flexible, transparent, strong and thermally stable cellulose film with homogenous topology was presented as a potential substrate for electronic applications. Its future integration in the DSSCs was tested by fabricating CE-CE cells which showed comparable R_{CT} to traditional platinized FTO-glass CE. These results highlight the potential application of environmentally friendly and room temperature processed nano-fiber based films as an alternative substrate for DSSC devices.

5 ACKNOWLEDGEMENTS

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Highly transparent cellulose substrate for dye sensitized solar cells

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Motivation

- Cellulose is mechanically robust and light-weight and it's innovative processing techniques provides an opportunity to produce a natural fiber based substrates for electronic and light to energy conversion applications.
- As usually a costly component in photovoltaic devices the conventional fragile substrate, FTO glass, needs to be replaced to produce cost efficient solar cells.
- We present here a cellulose substrate with high bendability, light transmittance and strength along with low roughness and present its possible futuristic integration in dye-sensitized solar cells (DSSCs). These substrates were tested by fabricating counter electrode-counter electrode (CE-CE) electrochemical cells. The substrates were coated with indium tin oxide (ITO) to serve as a conducting layer and platinum as the catalyst layer. Their electrical performance was evaluated by electrochemical impedance spectroscopy (EIS).

Materials and Methods

2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidized nano-cellulose films (TONs) were prepared at room temperature and pH 10 from never dried birch kraft fibers. Followed by mechanical disintegration, magnetic stirring and mild centrifuge, 0.4 wt % aqueous dispersion was cast in a Petri dish and left for water evaporation at 23°C for several days. TONs were initially coated with 300 nm ITO layer (ITON) and then10 nm platinum (PITON).

CEs were prepared by sputtering platinum on FTO-coated glass and PITON substrates at room temperature. Platinized glass-platinized glass (G_{Pt}-G_{Pt}) and platinized glass-PITON (G_{Pt}-PITON) CEs were sealed with 25 µm thick thermoplastic foil on a hot plate at 140°C in 2-3 min. The electrolyte was injected via drilled holes. 20 µm thick foil and thin glass cover were used to seal the device by using hot press at 220°C.

Results and Discussion

TON, ITON and PITON were tested in order to gain more in-depth understanding about the potential as novel transparent substrates for electronic devices containing liquid electrolytes.

Transparency

86% and 76% transmittance values were achieved for TON and ITON, respectively while, FTO-coated glass transmitted 82% of the incident light at 550 nm (Figure 1).

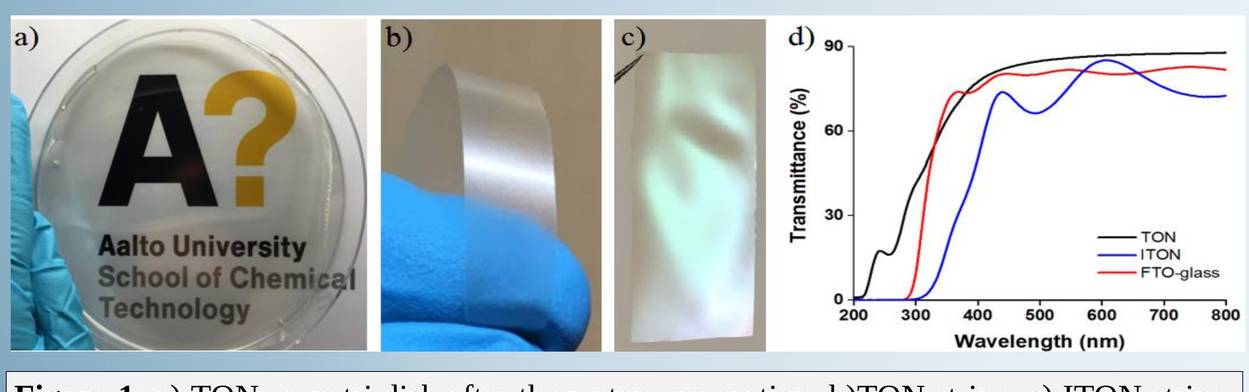

Figure 1: a) TON on petri dish after the water evaporation, b)TON stripe, c) ITON stripe, c) transmittance of TON, ITON and FTO-coated glass.

Surface Properties

Investigated with AFM and SEM (Figure 2 and 3), TON and ITON exhibited homogenous topology with the surface roughness of 8.8±1 nm and 20±1 nm, respectively. The high water contact angle on TON (118°) confirms the neat surface facilitating the even distribution of ITO on TON surface.

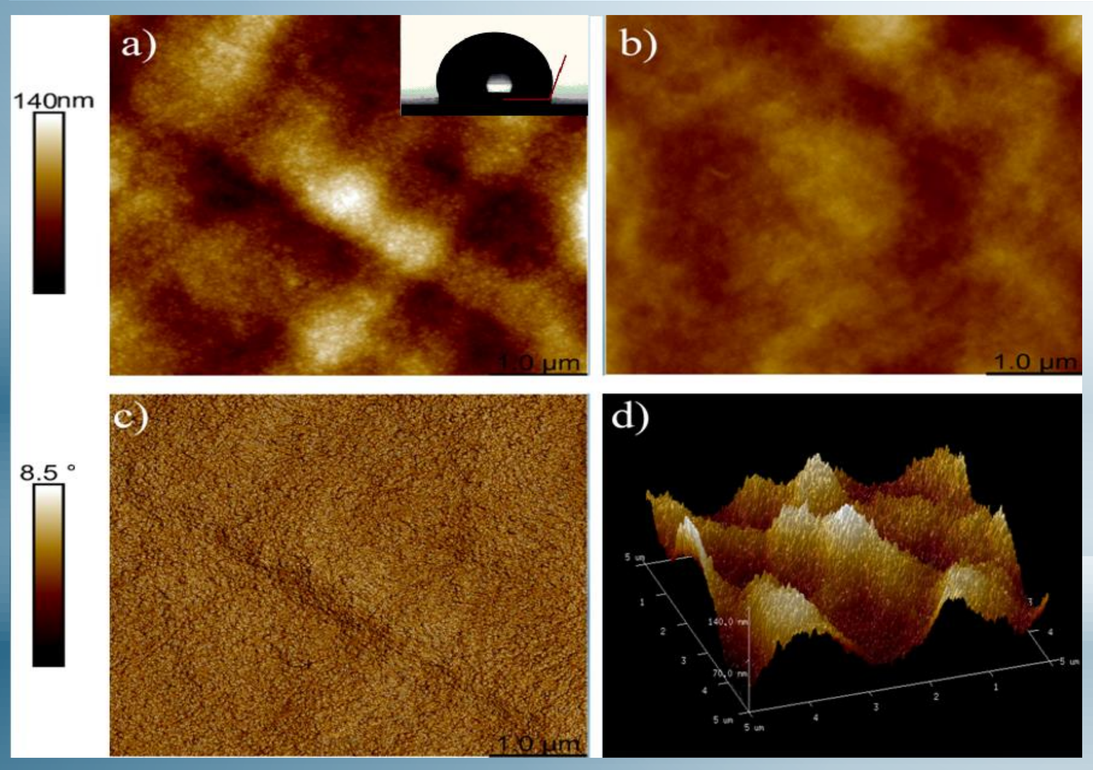

Figure 2: AFM images of a) TON (inset: water contact angle on TON) b-d) ITON (height, phase and 3D modes, respectively).

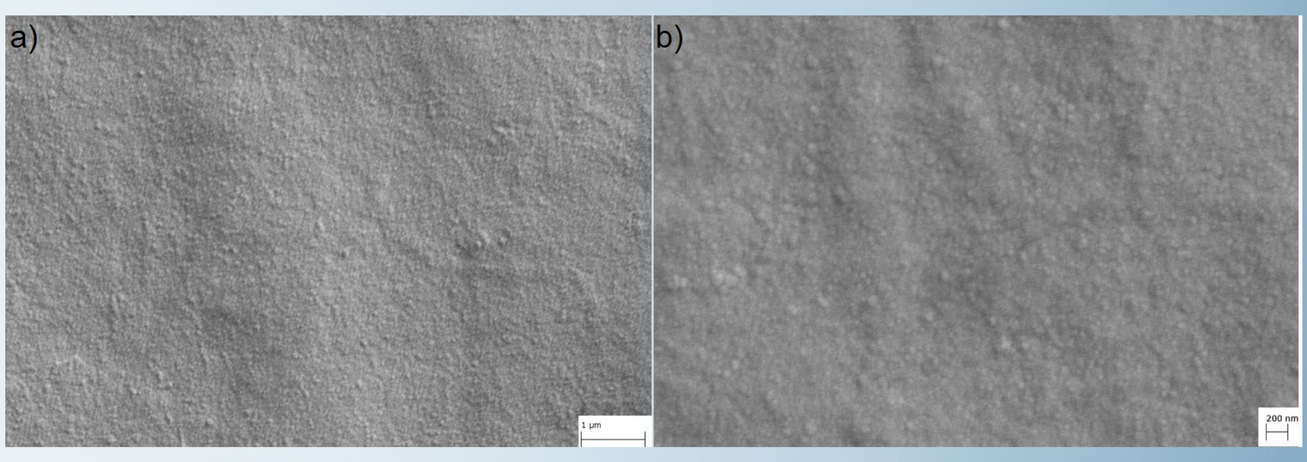

Figure 3: Top view SEM of ITON a) lower magnification, b) higher magnification.

Mechanical Properties

Young's modulus was recorded as 9.5±0.9 GPa from 8 dog-bone-shaped specimens consisting of 70 g/m^2 grammage. The stress–strain curve of the sample with highest Young's modulus is shown in Figure 4. A strain of up to 1.4% with 1 mm break elongation was measured. After several bending cycles (2 cm bending radius), no specimen deformation was observed.

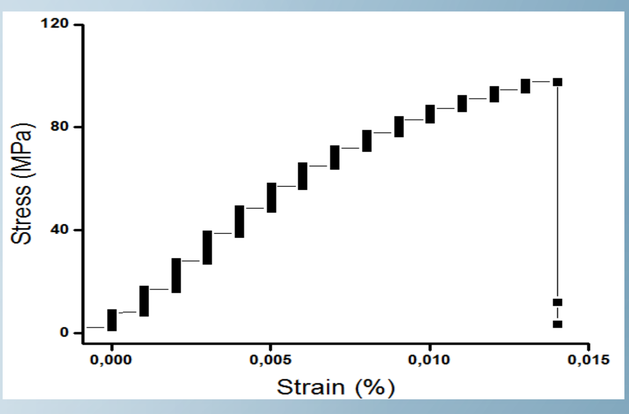

Figure 4: Stress–strain curve for PITON

Electrical Impedance Spectra (EIS)

EIS and resistance values extracted from EIS are presented in Figure 5 and Table 1, respectively.

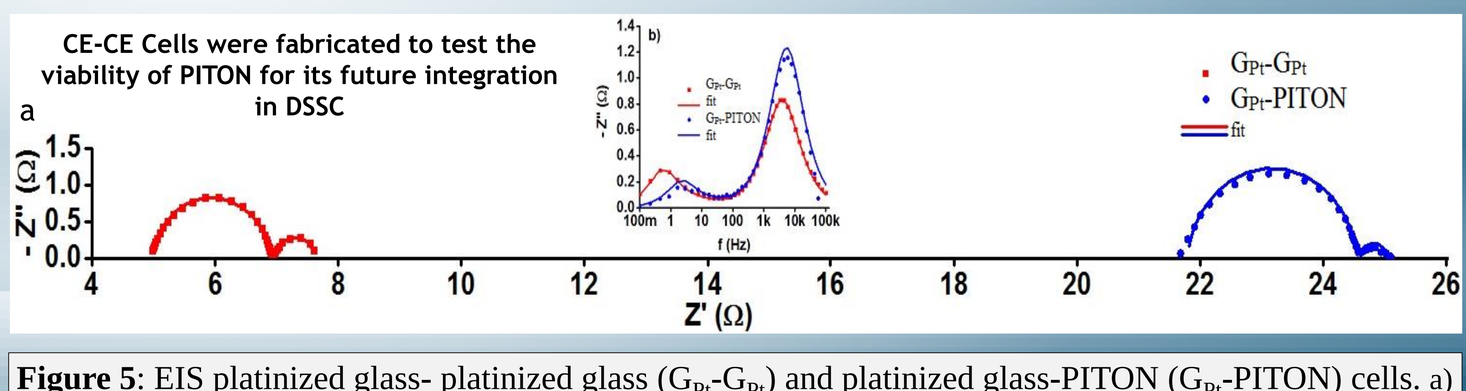

Figure 5: EIS platinized glass- platinized glass (G_{Pt}-G_{Pt}) and platinized glass-PITON (G_{Pt}-PITON) cells. a) Nyquist plot, b) imaginary impedance Z'' as a function of frequency.

Table 1: EIS parameters of CE-CE cells. The values are calculated for single electrode.

Cell	R_S (Ω)	R_{CT} (Ω)	R_D (Ω)
G_{Pt}-PITON	21.8	2.7	0.5
G_{Pt}-G_{Pt}	4.9	1.9	0.7

Conclusions

Flexible, transparent, strong and thermally-stable cellulose film with homogenous topology was presented as a potential substrate for electronic applications. Its prospective integration in the futuristic DSSCs was investigated by testing one of the electrodes in CE-CE cells. The results highlight the potential of environmentally-friendly and room temperature processed fiber based films as an alternative substrate for bifacial devices.

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Acknowledgements

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