

Nanocellulose as sustainable replacement for plastic substrates in printed electronics applications

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Abstract—The concepts of IoT, AI, I4.0, and 6G provide amazing opportunities for improving our quality of living, but also require tremendous amounts of data to operate as envisioned. To fulfil this demand for information, a large number of sensors and sensing devices is needed. Evolving sensing capabilities are associated with an increasing amount of electronic and plastic waste, which is rapidly becoming one of the major problems of our society. This research utilizes printed electronics as a method that is capable of fabricating high volumes of sensors to fulfil the requirements of emerging technologies. This study introduces printed environmentally friendly (carbon and water-based inks) conductive electrodes that could serve as vital signals’ sensors. Our results indicate that replacement of PET substrates with biodegradable nanocellulose increases the reliability of the printed electrodes, thanks to ink penetration into the nanocellulose structure. Successful utilization of biodegradable materials and printed electronics provides another example that positions printing technologies as one of the sustainable fabrication methods of the future.

Keywords—printed electronics, printing, nanocellulose, sustainable fabrication, conductive electrodes, screen-printing.

I. INTRODUCTION

As a consequence of the rapid development of IoT and ubiquitous technologies, our proximity is rapidly accommodating an overwhelming amount of sensors/sensing devices that ultimately contribute to an ever-increasing amount of electronic waste [1]. In addition, plastic waste is becoming one of the major environmental problems of our society. According to World Economic Forum reports, by 2050 the amount of plastic production will increase threefold, while the amount of micro/nano plastics in the oceans will be comparable to the amount of fish [2]. Although these are just projections, they illustrate the scale of the problem. Hence, there is a growing demand for capable and sustainable fabrication methods.

Printed electronics is one of the fabrication technologies that can fulfil the needs of IoT by providing production capacity to deliver billions of sensing elements and systems at nominal costs [3,4]. In principle, printed electronics is a set of various printing methods that use functionalized inks and controlled material deposition to create electronic devices [5].

In addition to flexibility, selectivity and biocompatibility, this is a unique fabrication method that generates a negligible amount of material waste, making it a well-suited candidate for becoming one of the future’s sustainable fabrication technologies.

However, printed electronics faces several challenges. Among them, the following three are considered major obstructions:

- Wide usage of plastic substrates due to their favourable properties, such as mechanical strength, smoothness, flexibility, low permeability, transparency, etc. Recent research has focused on replacing plastics with more environmentally friendly materials, like stone paper, wood derivatives, nanocellulose, or more unorthodox solutions, including corn starch, palm leaves, or seaweed [6]. Although the preliminary results are promising, current state-of-the-art replacements are not fully biodegradable, or the properties of the final products do not fulfil the functionality requirements [7]. Some of the efforts related to the development of nanocellulose provide a promising set of data necessary to create a material that fulfils the requirements of printed electronics [8-10].
- Usage of depleting rare-earth and toxic materials during the fabrication process. A number of recent studies have concentrated on the implementation and development of novel biodegradable functional 0D, 1D, and 2D materials compatible with non-toxic solvents, i.e., carbon-based or MXenes [11-13].
- Reduced performance of flexible printed components compared to their rigid counterparts. Fundamentally, flexible printed components are not intended to compete with their rigid conventional counterparts. While they can be produced with relatively inexpensive equipment in large scale at a minimal cost, flexible printed components have limited performance [14]. Moreover, the performance and reliability requirements of printed sensors strongly depend on their application. For instance, our previous research related to R2R-printed stretchable sensors indicated several critical

aspects, including shape of the features, nanoparticle dimensions, ink formulation, interfacial interactions, and protective layers that directly affect the reliability and performance of printed sensors, and need further intensive research [15,16].

Although the advancements achieved by the previous research partially resolve some of the challenges related to printed electronics, a more holistic approach and comprehensive solutions are needed in order to position printed electronics as a reliable and sustainable fabricating method for sensing applications [17].

This research focuses on developing a comprehensive printing framework that addresses all three abovementioned challenges. To resolve the problem of plastic waste, the PET substrate has been replaced with a nanocellulose substitute (Figure 1a). The problem of rare materials and solvents toxicity has been resolved by introducing water-based carbon inks. These inks were utilized to screen-print horseshoe pattern electrodes (Figure 1b). The horseshoe pattern was selected because it helps in distributing the mechanical stress introduced by the bending process.

Finally, the reliability analysis provides evidence regarding the behaviour of the printed structures under stress. Importantly, the behaviour of the patterns printed on the nanocellulose substrates is compared with their PET equivalent (Figure 1c).

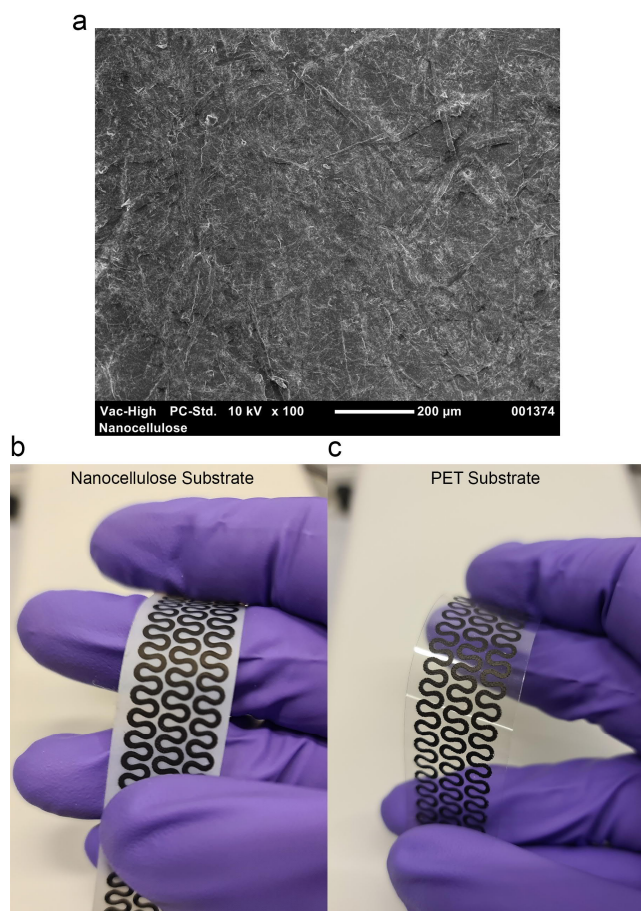


Fig. 1. Printed water-based carbon electrodes on nanocellulose substrate. a) SEM image of the nanocellulose surface. b) Horseshoe electrode pattern printed on nanocellulose substrate. c) Horseshoe electrode pattern printed on PET substrate.

II. METHODS

To achieve flexible nanocellulose films, 4 g of birch Kraft pulp was treated with a DES system (Deep Eutectic Solvents) and nanofibrillated. Firstly, 400 g of DES system was synthesized by adding ammonium thiocyanate and urea (with 1:2 molar ratio) in a beaker and heated up to 100 °C, to produce fluidic transparent solvent. Consequently, the pulp was added to DES and mixed at 100 °C for 2 hours. The DES-treated cellulose was vacuum filtered and washed three times with 1000 ml of D.I. water.

Before nanofibrillation, cellulose pulp was diluted into aqueous 0.3 % suspension and dispersed with an ultra Turrax (at 10.000 rpm), for 30 seconds. The nanocellulose hydrogel was prepared by passing the pulp mixture through a microfluidizer (M-110EH-30), three times at a pressure of 1300 bar (400 μm and 200 μm chambers) and two times at a pressure of 2000 bar (400 μm and 100 μm chambers). The produced mixture was degassed under vacuum and then films prepared using the vacuum filtration technique (57.17 g·m⁻²).

The horseshoe pattern electrodes were printed by using EKRA E2 screen printer and VA 165-0.050W-Øx22.5° mesh. The water-based carbon conductive ink (Bare Conductive) has a sheet resistance of 55Ω/sq at 50 micron film thickness. To increase the printability, prior the printing, both substrates were plasma-treated for 1 min [18]. Consequently, the layers were dried in the oven at 50 °C, for 15 min. SEM image of the nanocellulose surface was acquired using SEM NeoScope JCM-5000 at x100 magnification. The microscope images were acquired by using Nikon Eclipse LV150N optical microscope.

The resistance during the bending was measured using the four-probe measurement setup. 20,000 cycles of bending on a rod of 15 mm radius at a frequency of 0.5 Hz were applied to the samples. The system used an Agilent 34401A multimeter (30 Hz sampling rate) connected to the computer with LabView software used for management and data acquisition.

III. RESULTS

The resistance of the conductive lines was used to assess the quality of the electrodes and their performance during bending cycles. As presented in Figure 2a, the single bending cycle is composed of two phases: bending – the electrode is under stress and the resistance increases; relaxation – where the electrode returns to its initial state and the resistance decreases. For the nanocellulose substrate (Figure 2b), the “bent” and “relaxation” resistances remain stable throughout the whole cycling period. While for the PET substrate (Figure 2c), the “bent” resistance of the electrodes continuously increases. In addition, three step surges of resistance are noticeable at 2,500, 6,000, and 9,000 cycles. At the same time, the “relaxation” resistance of the electrodes increases insignificantly, regardless of the substrate. Noteworthy, for both substrate materials, at the first stage of cycling, the resistance decreases. According to Yamaguchi et al., this phenomenon can be attributed to “a net reduction in the distance between the aggregates, particularly in the direction at a right angle to the stretch. This could result in the creation of convoluted but additional conduction paths, which would result in a reduction in the measured electrical resistance.” [19].

The following continuous trend of the increasing resistance and its causes have been explained in previous research by Liang et al. [20]. Although the electrodes were printed under the same conditions, there is a significant difference in the initial electrode resistances – 1120 Ω and 4900 Ω for Nanocellulose and PET substrates, respectively.

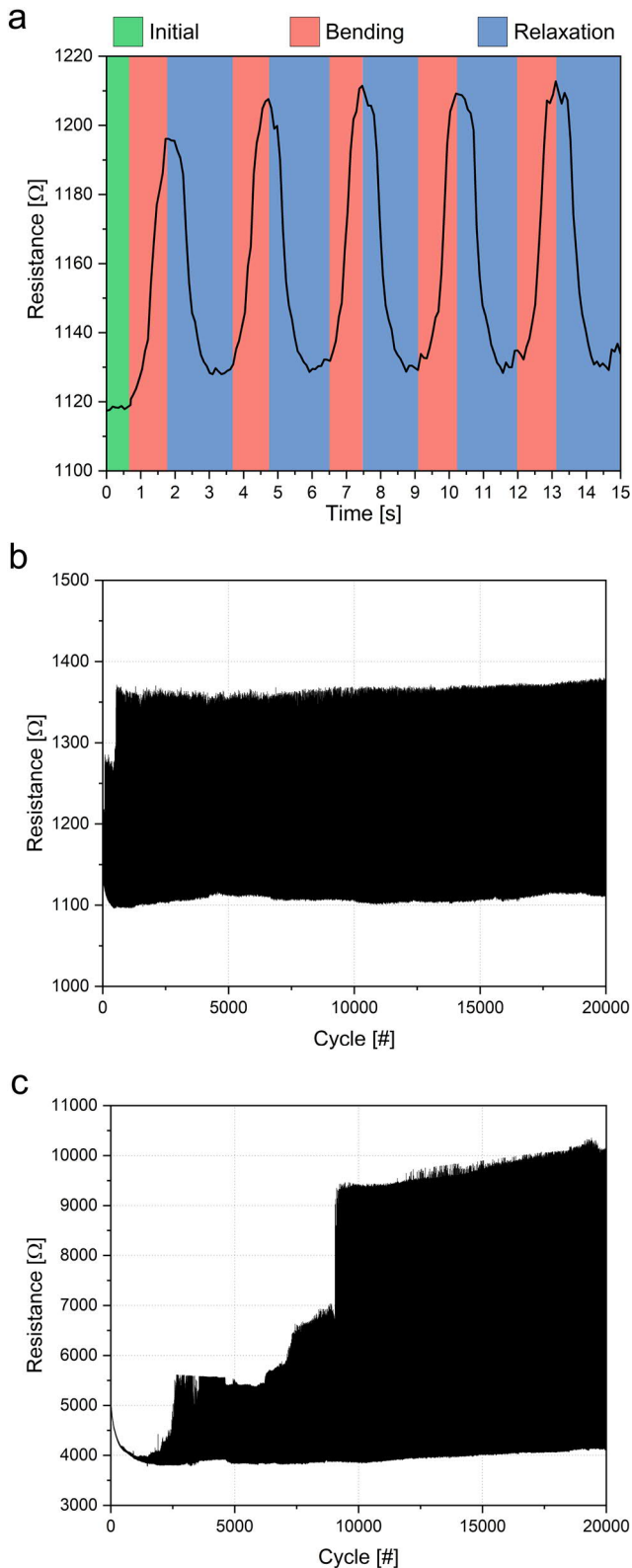


Fig. 2. Reliability cycling of the electrodes. a) Initial 15 seconds of the cycling process indicates the division of the cycling process into bending and relaxation phases. b) Resistance change for the full cycling of the electrodes printed on the nanocellulose substrate. c) Resistance change for the full cycling of the electrodes printed on the PET substrate.

In order to better understand the behaviour of the electrodes, cross-sectional optical microscopy was performed. The comparison of printed electrodes on the PET and Nanocellulose substrates is demonstrated in Figure 3. The figure clearly shows different behaviours of the ink on the substrate. For the PET substrate, all ink remains on the surface. For the Nanocellulose substrate, the ink partially penetrates the structure of the substrate.

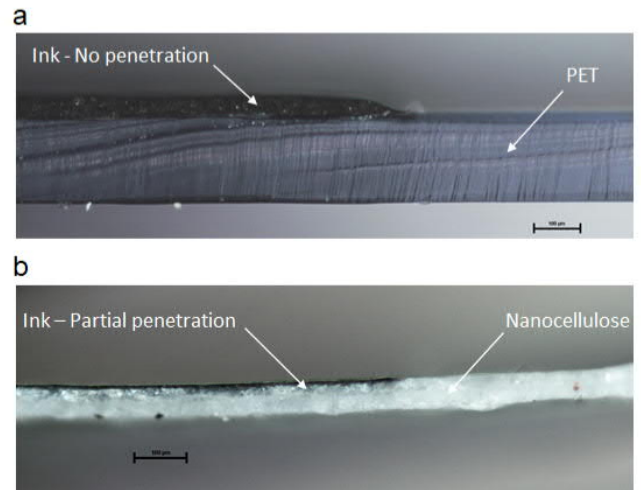


Fig. 3. Cross-sectional image of carbon inks. a) Dried ink on the surface of PET substrate. b) Carbon ink that partially penetrates the surface of the nanocellulose substrate.

After completing the cycling, the SEM analysis of the electrode structures was performed and depicted in Figure 4. The evident cracks are the main contributor to the increasing resistance and the images show the difference between the cracking mechanism for different substrates. For the PET substrate, large cracks occur on the surface, affecting the integrity of the electrodes. For the Nanocellulose substrate, a high number of very small cracks occurs on the surface. However, the integrity of the electrodes remains intact. These results are in agreement with the resistance records.

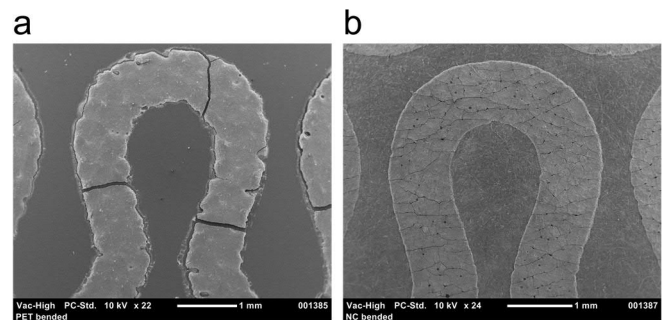


Fig. 4. SEM images after 20,000 bending cycles. a) Electrodes printed on the PET substrate. Large cracks are clearly visible. b) Electrodes printed on the Nanocellulose substrate. Many small cracks occur on the surface of the electrode.

After the cycling process, the electrodes printed on the PET substrate become very fragile and start peeling off from the PET surface (Figure 5). Importantly, the delamination process does not occur for the Nanocellulose substrates.

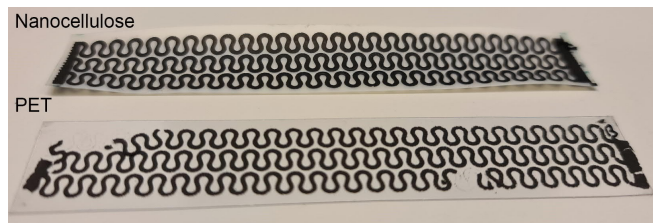


Fig. 5. Post-cycling comparison of the electrodes printed on the PET and nanocellulose substrates. Evident delamination of the electrodes from the PET substrates is one of the main reasons for poor performance.

IV. DISCUSSION AND CONCLUSIONS

This research provides interesting insights into the behaviour of water-based carbon inks on various substrates. The results indicate that the nanocellulose provides better support for the conductive inks and allows penetration of the inks into the structure of the substrate. Although the surface of the cycled electrodes on the nanocellulose substrate is cracked, it does not have a significant influence on the electrode performance. On the other hand, PET substrates do not allow penetration of the water-based inks into their structures. Thus, all the ink material remains on the surface of the substrate without any support and prone to stress and delamination. Although the promising results indicate the potential of the proposed method, there is a need for further study related to control of ink penetration and interactions between various solvents, conductive materials and nanocellulose substrates. To conclude, this research provides evidence that a combination of nanocellulose and printed electronics enables fabrication of fully sustainable sensing systems.

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