Sensor phenomena

Sustainable Printed Chitosan-Based Humidity Sensor on Flexible Biocompatible Polymer Substrate

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Abstract—Humidity is one of the most relevant physical parameters to sense and control for a wide range of commercial and industrial applications. Consequently, there is continuing demand for the development of innovative and sustainable humidity sensor solutions. Here, the development and characterization of fully additively manufactured, highly sensitive, resistive Chitosan-based humidity sensors on flexible thermoplastic polyurethane (TPU) foil, as well as on a glass carrier substrate are presented. The sensors unite aspects of sustainability and high performance in a broad humidity range (20–90%rH). The humidity response follows an exponential curve progression with relative changes in the resistance per %rH of 6.9% and 5.7% for the glass carrier sensor and the TPU sensor, respectively. In absolute values, this means that the Chitosan-based sensors are particularly sensitive in the low humidity range with a vast dynamic range (ten times larger compared to commonly used capacitive humidity sensors). The flexible sensor on the TPU substrate shows great stability even after repeated bending. In addition, the combination of flexible and biocompatible materials (TPU and Chitosan) with additive manufacturing technologies makes the sensor particularly sustainable while having great potential for a plethora of biomedical applications.

Index Terms—Sensor phenomena, sensors, additive manufacturing, Chitosan, flexible electronics, humidity sensor, sustainable sensors.

I. INTRODUCTION

Social and ecological challenges of the 21st century urge for innovative solutions for future efficient use of resources together with an increased use of renewable raw materials, which impact all aspects of our daily lives. While the electronics industry has been a pacesetter for digitalization and technologization, decisively contributing to the amenities and comfort of today's living standards, the impact on the environment must not be disregarded. Globally, the fastest growing waste stream is the electronic waste with each human being generating, on average, 7.3 kg of e-waste per year, an alarmingly large amount, which is expected to further rise to 9 kg per capita by the year 2030 [1]. Simultaneously, the number of sensors deployed increases at a high pace, due to the exploding rise of smart products, facilitating ubiquitous sensing [2].

While recycling is a well-intentioned strategy to reduce the amount of electronic waste, the reality is that this issue needs to be addressed earlier in the design and development phase by employing ecological, biosourced raw materials and efficient manufacturing technologies while minimizing material consumption and waste products. Additive manufacturing, and in particular digital printing, offers many advantages over conventional electronics fabrication techniques in terms of lower environmental impact, due to reduced consumption of materials as well as high flexibility in terms of design and a low-cost fabrication, even at small batch sizes [3], [4]. Consequently, more and more additively manufactured and fully printed sensors have been reported in the literature [5], [6].

Humidity is one of the most relevant physical parameters to sense and control for a wide range of commercial and industrial applications, such as building ventilation control, cleanrooms in the semiconductor and automotive industries, industrial drying, agriculture, weather monitoring, structural health monitoring, and process monitoring in the chemical, electronics, food/beverage, pharmaceutical, cosmetics, and biomedical analysis industries [7]. A common approach for printed humidity sensing is the realization as interdigitated capacitive structure, where the measured capacitance is dependent on the permittivity which changes with different humidity levels [8], [9].

Such sensors can be realized on numerous sustainable and even biodegradable substrates [10]. The relationship between humidity-dependent permittivity and capacitance is commonly modeled by a second-order polynomial growth, which makes these types of sensors rather sensitive in a higher humidity range [11]. As an example, Rauter et al. [12] presented a fully printed wireless and battery-free humidity sensor on an uncoated paper substrate for integration in composite lightweight parts. While the simplicity of the design and realization are strong arguments in favor of the interdigitated humidity sensor concept, there are some hurdles in its way for practical application. On the one hand, such sensors typically have a small capacitance in the range of a few pF and, consequently, small changes in capacitance due to changing humidity levels are difficult to read out without highly sensitive and dedicated laboratory measurement equipment. On the other hand, without proper shielding, the measurement results can be influenced by nearby objects, due to fringing field manipulation [13].

One alternative to the capacitive sensing approach would be resistive humidity sensing, which can be realized using Chitosan as active

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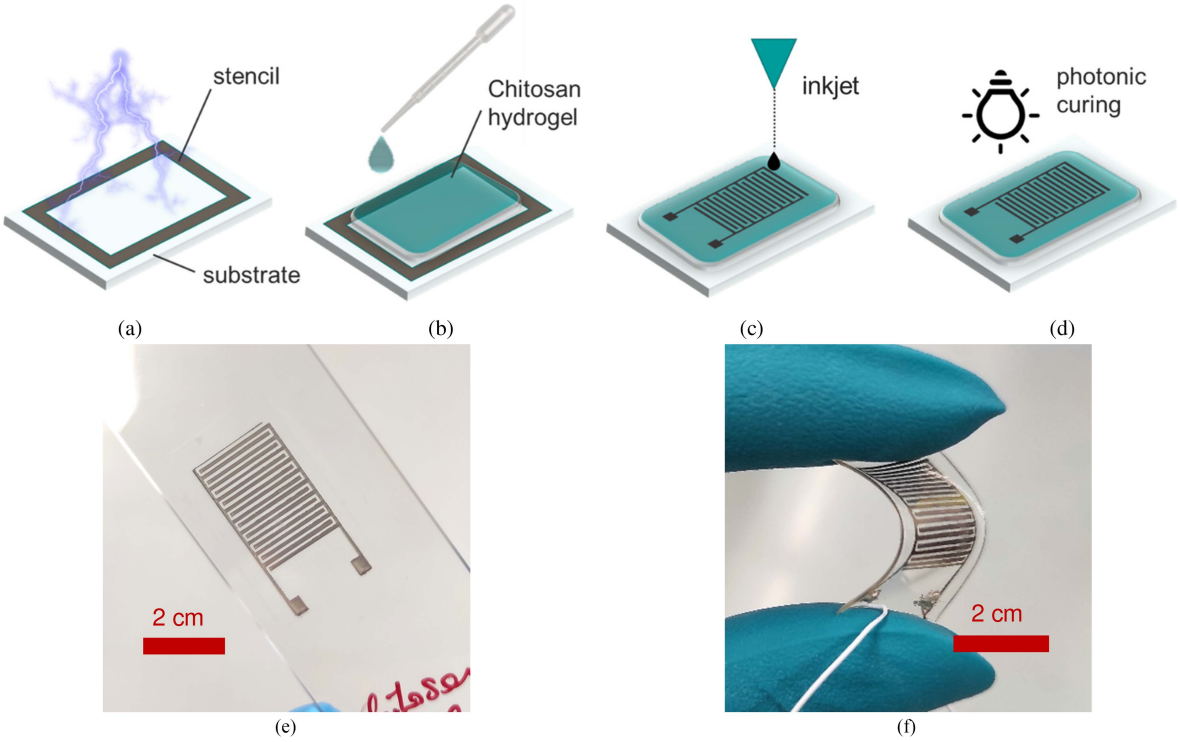

Fig. 1. Fabrication of Chitosan-based humidity sensor on thermoplastic polyurethane substrate. (a) Surface activation of the substrate with plasma treatment. (b) Drop-casting of Chitosan hydrogel which spreads evenly within the boundaries of the self-adhesive polymeric stencil (c) after drying and removing the stencil Ag electrodes are inkjet-printed onto the Chitosan layer. (d) Photonic curing of the inkjet-printed layer. Finalized functional Chitosan humidity sensor on (e) glass and (f) flexible thermoplastic polyurethane substrate.

sensing material [14]. Chitosan is a well-studied natural conductive biopolymer synthesized from chitin and hence edible, renewable, environmentally friendly, low-cost, biocompatible, and biodegradable [15], [16]. The electrical resistance of Chitosan is very much influenced by the chemisorption of Oxygen species on the sensor surface. As soon as a constant voltage is applied, electrons are transferred from the valence band to the conduction band forming ionic species (O_2^-, O^-) and reducing the number of free electrons which increases the electrical resistance (R). In the presence of water, however, O_2 is formed and electrons are released in the process which in turn enhances conductivity [17]. This effect could be exploited for the realization of humidity sensors as reported by Nasution et al. [14], [17], who noticed an increase in the output voltage of a Chitosan-film with rising ambient humidity levels. Other previously published work in this field has not yet applied this effect and either utilizes Chitosan's swelling behavior to enhance the sensitivity of the sensor material composite [18], or for the realization of a tunable Fabry–Pérot resonator [19]. Here, we present the first fully additively manufactured, highly sensitive, resistive, Chitosan-based humidity sensor utilizing the sensing principle described in [14]. It combines aspects of sustainability in materials and production technique with high performance.

II. METHODS

A. Sensor Fabrication

Two different types of Chitosan-based humidity sensors were fabricated, one on a glass carrier substrate and the other one on a transparent, flexible, biocompatible thermoplastic polyurethane (TPU) foil (Expafol, Spain) with a thickness of 300 μm.

Chitosan powder was purchased from Sigma Aldrich (448 877, medium molecular weight) and a water-based Chitosan solution with a concentration of 10 g/L was prepared according to the process described by Zangmeister et al. [20]. Since Chitosan is only soluble in a slightly acidic solution, 2 M HCl were added drop by drop during stirring to lower the pH value of the solution to pH $<$ 6. The solution was then stirred for $\sim$2 hours using a magnetic stirrer while adding small amounts of HCl until the Chitosan powder was fully dissolved resulting in a rather viscous solution (hydrogel). The solution was then filtered using a glass fiber filter with grade GF/F (0.7 μm).

The fabrication of the sensor comprises four major steps, as illustrated in Fig. 1(a)–(d). As the TPU has hydrophilic properties, the surface was first plasma treated to ensure proper wetting of the Chitosan hydrogel [see Fig. 1(a)]. For the fabrication of the sensor on a glass carrier substrate, no such surface activation was necessary. Then, around 1 mL of the Chitosan hydrogel was drop-casted on the activated TPU substrate on an area of 2.5 x 4 cm^2, which was confined by a self-adhesive polymer foil functioning as a stencil [see Fig. 1(b)]. After the drop-casting process, the Chitosan hydrogel layers were dried for 24 hours at room conditions ($\sim$ 23 °vvC, $\sim$ 30% rH). Subsequently, the electrodes were manufactured using inkjet-printing of Ag-nanoparticle ink (Sicrys^{TM}I50TM-115, PV-Nanocell, Israel) on top of the dried Chitosan layer, as illustrated in Fig. 1(c). A PIXDRO LP50 (Süss Microtec SE, Germany) inkjet-printing system equipped with a Spectra SE-128 AA 128 (Fujifilm Dimatix Inc., USA) 30 pL print head assembly at a resolution of 400 x 400 dpi was used. After drying in ambient conditions ($\sim$ 23 °C, 30% rH), the printed electrodes on the thermally sensitive substrate were sintered using photonic curing (Pulse Forge 1200, Novacetrix, USA, overall energy of 960 mJ/cm^2).

B. Characterization

The sensors were physically contacted with cables and exposed to a relative humidity from 20 to 90% in steps of 10% at 20 °C, in an environmental testing chamber (Voetsch VC^3 4018, Germany). The

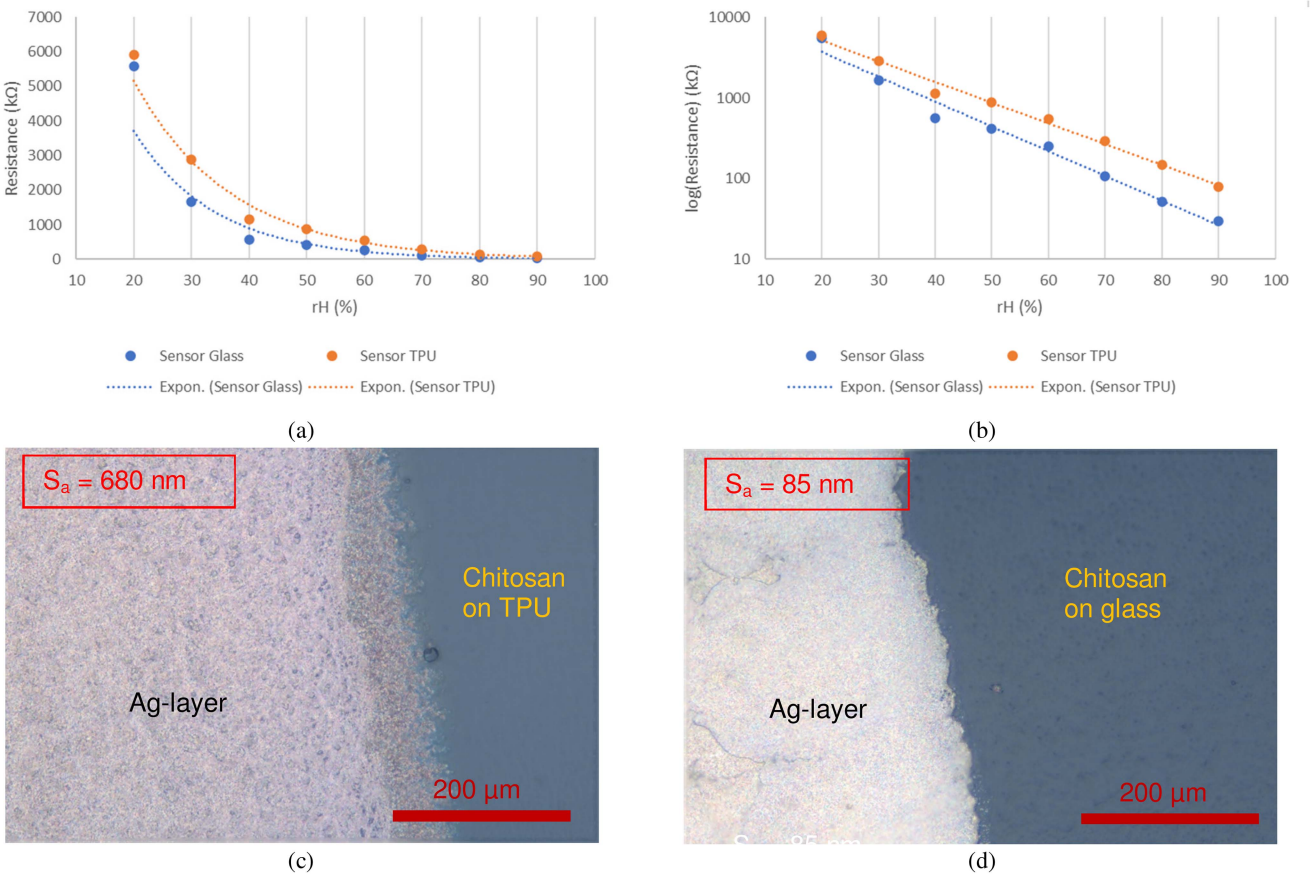

Fig. 2. (a) Response of the Chitosan-based humidity sensors on glass and thermoplastic polyurethane substrate. (b) Response of the Chitosan-based humidity sensors on glass and thermoplastic polyurethane substrate with logarithmic vertical axis; optical microscopy images of inkjet-printed Ag layer and Chitosan on (c) TPU and (d) glass carrier substrate.

change in resistance was measured using a Keithley digital multimeter (Keithley 2700, Tektronix, Inc., USA). The quality and topology of the Chitosan and Ag-printed layers were studied using optical microscopy and white light interferometry. In addition, to study the stability of the flexible sensor on the TPU substrate, 100 bending cycles (angle of 150°) at room conditions (~ 23 °C, ~ 30% rH) have been performed and the electrical resistance was measured before and after the bending test.

III. RESULTS AND DISCUSSION

As Chitosan is highly hydrophobic the humidity range for sensor characterization was limited to a maximum level of 90% rH. Above that level, the Chitosan layer absorbs the humidity which leads to swelling and hydrogel formation destroying the printed electrodes. Fig. 2(a) shows the humidity response of the Chitosan-based sensors on glass and TPU substrate. For interdigitated sensors, the relationship between humidity and capacitance is commonly modeled by a quadratic function [11]. In the case of the presented resistive Chitosan-based sensors, though, the measurement data can be better approximated exponentially with a negative exponential coefficient (1). This means that the resistance decreases with increasing humidity and the sensors have a much higher sensitivity in the lower humidity range in terms of absolute values. More specifically, the humidity-dependent sensor resistance R(H) can be modeled as

$$R\ (H) = R_0 \cdot e^{-\lambda H} \tag{1}$$

where R_0 corresponds to the theoretical electrical resistance at 0% rH and H is the relative humidity in %. The exponential coefficient λ is a sensor-specific unitless constant and equals to 0.071 and 0.059 for the glass and the TPU sensor, respectively. Consequently, the sensitivity as the relative change in resistance per %rH can be calculated and amounts to 6.9 and 5.7% for the glass reference sensor and the TPU sensor, respectively. The dynamic range of the sensors reveals a 75-fold (TPU) as well as a 185-fold (glass) change in resistance between 20% and 90%rH, which is more than ten times larger than reported in the literature for customary interdigitated capacitive humidity sensors [10]. In Fig. 2(b), the same humidity response is plotted with a logarithmic vertical axis. From the linearized data the coefficient of determination (R^2) can be calculated as a measure for the goodness of fit. For both sensors, a high level of correlation with the proposed exponential approximation can be observed with $R^2 = 0.954$ and $R^2 = 0.985$ for the glass reference sensor and the TPU sensor, respectively. Fig. 2(c) and (d) shows optical microscopy images of the printed Ag-layer and Chitosan on both substrates. Using white light interferometry, the surface roughness of the printed and cured Ag-layers could be quantified. The arithmetic average of profile height equals to $S_a = 680$ nm and $S_a = 85$ nm for the TPU and the glass carrier substrate, respectively. The higher surface roughness on the TPU substrate can be explained by the plasma surface activation of the TPU altering the wetting behavior of the Chitosan hydrogel during drop casting. This also increases the resistance of the printed layers due to an elongation of the conductive pathway, as exemplarily studied by Siegel et al. [21] for rough paper surfaces. The bending

test of the flexible sensor on TPU substrate led to a decrease in the resistance of 1.2% after 100 cycles within 5 min. This minor change could as well be attributed to small variations in the ambient humidity during the test and is negligible compared to the humidity sensing response of 5.7% per % rH. This indicates excellent stability of the flexible sensor even after repeated bending. Together with the biocompatibility of the used materials, its stability toward bending makes the presented sensor potentially useful for wearables and biomedical applications.

IV. CONCLUSION

The development of a fully additively manufactured, highly sensitive, Chitosan-based humidity sensor that unites aspects of sustainability and high performance in a broad humidity range is presented. The combination of flexible and biocompatible materials (TPU and Chitosan) with additive manufacturing technologies makes the sensor highly sustainable while being well-suited for all sorts of biomedical applications. The humidity response follows an exponential decay curve with relative changes in the resistance per % rH of 6.9% and 5.7% for the glass carrier sensor and the TPU sensor, respectively. In absolute values, this means that the presented Chitosan-based sensors are particularly sensitive in the low humidity range. Furthermore, the dynamic range is larger by a factor of ten compared to commonly used capacitive humidity sensors [10].

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