A Cellulose Nanofiber Capacitive Humidity Sensor with High Sensitivity and Fast Recovery Characteristics

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Abstract: Humidity sensors with high sensitivity and fast response characteristics are of great interest for researchers. In this work, capacitive humidity sensors were fabricated using ionic liquid/cellulose nanofibers (CNFs) as the composited sensing film. The porous CNFs are beneficial for preparing sensing films via a solution process, and the ionic liquid could be uniformly dispersed in the films. The humidity-sensing performance of the as-prepared sensors was investigated. The optimized sensor showed a high response (27.95 pF/% RH) in a wide humidity range (11–95% RH) and a fast response speed in the adsorption process (the recovery time was only ~1 s). The high response of the sensors was attributed to the polarization at the interface between the electrolyte and the metal electrode, while the fast recovery was due to the rapid desorption of water molecules on the sensing films. Finally, the application of the obtained sensors in human breath monitoring was explored.

Keywords: humidity sensor; high sensitivity; fast recovery; breath monitoring

1. Introduction

Humidity is an indispensable part of human life, and plays an increasingly important role in agriculture, military, medical, machinery and other fields [1–3]. It is worth noting that in recent years, an increasing amount of research has been conducted to reflect the state of human breathing through humidity detection. Especially since the outbreak of COVID-19, many related industries have paid attention to the monitoring of human breathing status and breathing rate, aiming to develop high-quality breath monitors to deal with various related problems [4]. In this case, humidity sensors and non-contact sensors have attracted the extensive attention of researchers [5–7].

Different kinds of materials have been used to fabricate humidity sensors, such as polymers, metal oxides, electrolytes and so on [8–10]. The huge increase in the variety of materials means the generation of electronic waste (e-waste) [11]. E-waste will directly affect human life and even the entire ecosystem; it is therefore crucial to prepare bio-friendly sensors. As a biodegradable polymer, cellulose owns a natural hydrophilic skeleton and a large specific surface area, which can not only effectively avoid the generation of e-waste, but also facilitate the adsorption of water molecules [12–14]. However, humidity sensors based on pure cellulose show poor sensitivity due to the limited hydrophilicity and non-adjustable structure of cellulose [15]. The construction of composited materials is an effective method of improving the sensing performance of cellulose humidity sensors. For example, KOH was introduced into regenerated cellulose as a humidity-sensing electrolyte to improve the sensitivity of cellulose sensors [16]. A porous conductive film was prepared by adding carbon black to cellulose nanofibers (CNFs), and the response and recovery times of the corresponding humidity sensors were shortened to 10 s and 6 s, respectively [17].

In this work, an ionic liquid was introduced to CNFs for preparing sensing films. The sensitivity of the cellulose-based humidity sensor was greatly improved by the polarization at the interface between the electrolyte and the metal electrode. The sensor could be used for...
human breathing detection, fingertip humidity detection, etc., and could transmit electrical signals stably, indicating its application potential in medical care and other fields.

2. Experimental Section
2.1. Materials

1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. Cellulose nanofibers (CNFs) solution was purchased from ScienceK Co., Ltd., Huzhou, China. All chemicals were used as received without further purification. The water was purified through a Millipore system, which was used throughout all the experiments.

2.2. Preparation of Humidity Sensors

([BMIM]Cl was dissolved in deionized (DI) water at a concentration of 10 mg/mL. Subsequently, ionic liquid aqueous solution was mixed with CNFs solution to prepare ionic liquid/cellulose-composited sensing film. Cellulose-based humidity sensors with different contents of the ionic liquid were prepared. The mass fractions of ionic liquid were 0 wt%, 2 wt%, 5 wt%, 10 wt% and 15 wt%, respectively, and the corresponding humidity sensors were named as blank CNFs, CIL@Cl-1, CIL@Cl-2, CIL@Cl-3 and CIL@Cl-4. Furthermore, another ionic liquid, 1-butyl-3-methylimidazolium bromide ([BMIM]Br), was used for comparison. Under the premise of ensuring that other conditions remained unchanged, the same molar amount of ([BMIM]Br as CIL@Cl-2 was introduced to CNFs, and the prepared sensor was named as CIL@Br-2.

Carrier sheet glasses were used as the substrate of the humidity sensors. The complete component fabrication process is shown in Figure 1. The interdigitated electrodes (IDEs) were screen-printed with silver paste on the glass substrate. In order to make the electrodes more stable, the glass substrate with the electrodes was heated and cured in an oven at 90 °C for 30 min. Then, 10 µL of the prepared solution was dripped onto the treated glass substrate via a pipette gun. Finally, humidity sensors were obtained by natural drying at room temperature in an atmospheric environment.

![Figure 1](image-url). (a) Fabrication schematic of cellulose-based humidity sensors. (b) The photo of CIL@Cl-2 sensor.

2.3. Preparation of QCM Sensors

A portion of the above prepared 5 wt% ([BMIM]Cl/cellulose solution was taken and diluted 15 times in DI water. The sensor prepared by dropping 2 µL of the solution on the quartz crystal microbalance (QCM) chip with a micro-injector was named QCM-5. At the same time, in order to compare it with the blank cellulose QCM sensor, we also performed the same treatment on the blank cellulose solution, and the obtained sensor was named QCM-0.

2.4. Measurements

Different relative humidity (RH) atmospheres were provided with saturated salt solutions (LiCl for 11% RH, MgCl₂ for 33% RH, Mg(NO₃)₂ for 54% RH, NaCl for 75% RH, KCl for 85% RH, KNO₃ for 95% RH). The humidity-sensing properties of the sensors were measured with a Keysight E4990A impedance analyzer. The QCM test system (Figure S1a) consisted of an oscillator circuit, a frequency meter (Keysight 53220A impedance analyzer) and a computer. The scanning electron microscopy (SEM) images were taken by a JSM-
6700F electron microscope (JEOL, Japan). The energy dispersive X-ray (EDX) analyses of the papers were characterized during field emission scanning electron microscopy (FESEM) measurements. Response time is defined as the point at which the response value reaches 90% of the stable value when the humidity increases and the recovery time is the time when the humidity decreases. Additionally, in the measurements of humidity characteristics, three sensors of each type were chosen to represent the experimental error of parallel samples. The test process was carried out with a sinusoidal voltage of 1 V in an environment of ca. 20 °C.

3. Results and Discussion

3.1. Materials Characterization

Figure 2 shows SEM images and EDX element mapping images of blank CNFs and CIL@Cl-1–4. At low magnification, the surface of CNFs exhibited a dense film, as shown in Figure 2a. At a high magnification, the morphological characterization results of CIL@Cl-1–4 and blank CNFs were similar. As shown in Figure 2b–f, the nanofibers intertwined with each other to form cross-linking networks with micro-pores, which may be conducive to adsorbing water molecules. To verify the distribution of (BMIM)Cl in CNFs, EDX tests were also performed on blank CNFs and CIL@Cl-2 (Figure 2g,h). As a characteristic element of (BMIM)Cl, the Cl element was uniformly distributed in CIL@Cl-2, while there was almost no distribution of the Cl element in blank CNFs.

![Figure 2](image)

**Figure 2.** SEM images of (a) blank CNFs and high magnification SEM images of (b) blank CNFs, (c) CIL@Cl-1, (d) CIL@Cl-2, (e) CIL@Cl-3, (f) CIL@Cl-4. EDX element mapping images of (g) blank CNFs and (h) CIL@Cl-2.

3.2. Humidity-Sensing Properties

The humidity-sensing properties of the prepared sensors were measured on an impedance analyzer. The responses of CIL@Cl-1–4 sensors to humidity at different frequencies are shown in Figure S2. The sensitivities of all the sensors increased with decreasing frequency. Figure 3a shows the capacitance response curves of all prepared sensors in different humidities at 500 Hz. The blank CNFs sensor had a significant response at a higher humidity, but the capacitance change was not obvious in a lower humidity. After the addition of ionic liquid (BMIM)Cl, the sensors showed an obvious response in the whole humidity range. The response of the sensors in different humidities increased with the
ionic liquid content. For the CIL@Cl-2 sensor, the capacitance at 11% RH and 95% RH was 2.2 pF and 2350 pF, respectively.

![Graph showing capacitance-RH curves for blank CNFs and CIL@Cl-1-4 sensors. Adsorption and desorption curves for CIL@Cl-1, CIL@Cl-2, CIL@Cl-3, and CIL@Cl-4 are shown.](image)

Figure 3. (a) Capacitance–RH curves of blank CNFs and CIL@Cl-1–4 sensors. Adsorption and desorption curves of (b) CIL@Cl-1, (c) CIL@Cl-2, (d) CIL@Cl-3 and (e) CIL@Cl-4.

The sensitivity of a humidity sensor can be defined by the following formula [18]:

$$S = \frac{C_2 - C_1}{RH_2 - RH_1}$$  \hspace{1cm} (1)

where $C_1$ represents the capacitance value measured at $RH_1$, and $C_2$ means the capacitance obtained at $RH_2$. By selecting different values of $RH_1$ and $RH_2$, different sensitivities can be obtained. For this work, we chose 11% RH as $RH_1$ and 95% RH as $RH_2$ for the calculation of sensitivity. The sensitivity of the CIL@Cl-2 sensor is 27.95 pF/% RH.

The capacitance values of CIL@Cl-1–4 sensors during adsorption and desorption were recorded, as shown in Figure 3c–e. No significant humidity hysteresis was observed for all sensors. For the CIL@Cl-2 sensor, the humidity hysteresis was ~3.2% RH.

In addition, the accuracy of the sensors was defined by combining the humidity hysteresis with the standard error. The CIL@Cl-2 sensor showed the largest humidity hysteresis of 3.2% RH @~54% RH. The standard error at ~54% RH is 1.58 pF. The accuracy of the sensor is ±4.6% RH.

The response and recovery times are also very important parameters for humidity sensors. In this work, we exposed the sensors to 95% RH for 60 s, and then put them in 11% RH for recovery for 240 s; the curves were obtained after five cycles. The humidity environment was manually changed by the tester, and the change time between humidity bottles was less than 1 s. As shown in Figure 4a, when the humidity changed, the corresponding capacitance exhibited very little fluctuation. As for the CIL@Cl-2 sensor, the response time was 43 s. Interestingly, the recovery time of the sensors was only ~1 s (Figure 4b), which is much faster than that of cellular-based humidity sensors, as shown in Table 1. Researchers have introduced different materials into cellulose to improve the properties of cellulose-based humidity sensors. In this work, we strictly controlled the amount of the substance carrying the humidity-sensing electrolyte, which not only ensured the sensitivity of the sensors, but also endowed the sensors with good response and recovery characteristics.
3.3. Humidity-Sensing Mechanism

According to Sauerbrey’s relationship, the QCM sensor can effectively link the mass of water molecules adsorbed by the material with the frequency shift [25]. Based on that, we can obtain the physical adsorption/desorption characteristics and explore whether the fast recovery characteristics of the device are related to the adsorption amount of water molecules. Figure 5a,c shows the transformation curves of the QCM-5 sensor and the QCM-0 sensor in different humidities. The cycle curves between 11% RH and 95% RH for both sensors were amplified and shown in Figure 5b,d. The response times of the QCM-5 sensor and the QCM-0 sensor were 43 s and 9 s, respectively, while the recovery time was ~1 s for both sensors. The addition of (BMIM)Cl resulted in a higher frequency shift of the QCM-5 sensor, but it also led to an increase in the response time. The addition of (BMIM)Cl was beneficial to improve the ability of adsoring water molecules. Both sensors showed a similar fast adsorption process, demonstrating that the fast desorption properties of the sensors benefited from the cellulose matrix.

Table 1. Comparison of the sensing performance of the prepared sensor in this work with the reported cellulose-based humidity sensors.

| Sensitive Material                  | Sensitivity | Range (% RH) | Response/Recovery Time | Ref.  |
|-------------------------------------|-------------|--------------|------------------------|-------|
| wood-derived cellulose nanofibers   | -           | 7–94         | ~20 s/~2 s             | [18]  |
| cellulose/PPy                       | -           | 27.8–94.2    | ~418 s/~418 s          | [19]  |
| cellulose/nanofiber/graphene oxide  | -           | 11–97        | 30 s/11 s              | [20]  |
| CAB                                 | 2.36 ± 0.08 fF/% RH [a] | 10–70       | 24 ± 3 s/22 ± 4 s     | [21]  |
| cellulose/paper                     | -           | 25–90        | 90 min/35 min          | [22]  |
| CNF/PANI/PVA                        | 2 pF/% RH [a] | 40–100       | 4–5 min/-             | [23]  |
| cellulose/nanofiber/[BMIM]Cl        | 27.95 pF/% RH [a] | 11–95       | 43 s/~1 s              | this work |

[a]: S = \frac{C_3 - C_1}{C_3 + 2C_1}; [b]: S(%) = \frac{C_2 - C_1}{C_3} \times 100%.

Figure 4. Response and recovery curves of CIL@Cl-1–4 sensors: (a) five circles between 11% RH and 95% RH, and (b) is the enlarged shaded part of (a).
And at 500 Hz, the impedance characteristic was expressed completely at 54% RH. For the CIL@Cl-4 sensor, which was also the reason for the high sensitivity of the sensor. With the increase in humidity, the phase angle of CIL@Cl-3 and CIL@Cl-4 (Figure S6), more obvious phenomenon could be observed at low frequency. For the CIL@Cl-2 sensor, the phase angle decreased at 33% RH (Figure 7b). In this case, the sensor mainly exhibited capacitive characteristics. At 54% RH, the CIL@Cl-4 sensor shows an arc shape at 11% RH. As the amount of (BMIM)Cl added increased, EDL resulted in a lower humidity. The sensor could be described by the internal resistance (Rs) of the metal electrode, and closely gathered near the interface to form an electric double layer (EDL) [26], which was also the reason for the high sensitivity of the sensor. With the increase in humidity, the CIS showed a quarter-circle arc on the left half and a descending arc on the right half (Figure 6c–f), which indicates the emergence of Warburg impedance (Zw). Similar results were obtained for CIL@Cl-3 and CIL@Cl-4 (Figures S3 and S4). The CIS of the CIL@Cl-4 sensor shows an arc shape at 11% RH. As the amount of (BMIM)Cl added increased, EDL was formed at a lower humidity. For the blank CNFs sensor, the arc only appeared at 54% RH and the Zw appeared at a higher humidity (Figure S5).

Figure 7 shows the relationship between the phase angle and frequency of the sensors. For the blank CNFs sensor (Figure 7a), the phase angle was $\sim -90^\circ$ under 11% RH and 33% RH. In this case, the sensor mainly exhibited capacitive characteristics. At 54% RH, the phase angle decreased significantly at low frequencies, which also matched the parallel connection of the resistor and capacitor in the CIS. At a higher humidity, the blank CNFs sensor exhibited the impedance characteristic at low frequency and capacitive characteristic at high frequency. For the CIL@Cl-2 sensor, the phase angle decreased at 33% RH (Figure 7b). At 500 Hz, the impedance characteristic was expressed completely at 54% RH. For CIL@Cl-3 and CIL@Cl-4 (Figure S6), more obvious phenomenon could be observed at low humidity. The phase angle of CIL@Cl-4 sensor was only $\sim -12^\circ$ under 11% RH. It showed an impedance characteristic at low humidity.
Figure 6. The complex impedance spectroscopy plots and corresponding circuit diagrams of CIL@Cl–2 sensor in (a) 11% RH, (b) 33% RH, (c) 54% RH, (d) 75% RH, (e) 85% RH and (f) 95% RH.

Figure 7. The phase angles of (a) blank CNFs sensor and (b) CIL@Cl–2 sensor.

The humidity-sensing mechanism of cellulose-based sensors can be simplified as shown in Figure 8. When the humidity was low, the ionized ions of the sensitive film were fewer, and the interaction force with the electrons in the electrode was weak. With the increase in ambient humidity, more water molecules could be adsorbed on the sensing film, and more ions ((BMIM)+, Cl−, H+ and H3O+) would be generated. Polarization at the electrode contact interface occurred and an EDL was formed. The capacitances of the compact layer and the dispersed layer were superimposed on each other to increase the capacitance. During the entire humidity change process, water molecules were adsorbed on the surface of the sensitive film through hydrogen bonding, which plays a crucial role in the rapid adsorption and desorption of water molecules. Considering the small pore size and compact structure of CNFs materials, the desorption process of water molecules can quickly reach saturation, and the weak interaction between the hydroxyl groups and the water molecules determines the fact that the desorption is easy [16].
In order to investigate the polarization phenomenon of ions at the interface, another ionic liquid ((BMIM)Br) was selected for comparison. Since there is only an anion of difference between (BMIM)Cl and (BMIM)Br, the effect of the anion size on polarization can be verified. First of all, we researched the relationship between the capacitance response and working frequency as shown in Figure S7a. For both sensors, the capacitance increased with the humidity, and higher sensitivity appeared at low frequency. As shown in Figure S7b, the sensitivity of the CIL@Br-2 sensor was slightly higher than that of the CIL@Cl-2 sensor at 500 Hz. This is due to the fact that the atomic radius of the Br atom is larger than that of the Cl atom, and the polarization is more likely to occur at low frequencies.

3.4. Application of the Sensor

Due to its extremely high sensitivity and excellent recovery speed, the CIL@Cl-2 sensor can be used in many scenarios. As shown in Figure 9a, the CIL@Cl-2 sensor was attached to the inside of a face mask, near the nose and mouth. The capacitance of the sensor was real-time recorded, and the breathing state of the volunteer could be judged. Figure 9b shows the detection of mouth and nasal breathing. The difference in breathing patterns could be clearly observed in the circled area in the enlarged image. The exhaled gas from the mouth was usually more humid than that from the nose. The fluctuation in the response value of mouth breathing detection was significantly greater than that in nose breathing. The response curves of the sensor to different breathing frequencies are shown in Figure 9c. The capacitance change of the sensor was positively correlated with the breathing frequency. In addition, the CIL@Cl-2 sensor had a visible response to a micro-humidity unit such as the fingertip, as shown in Figure 9d. When the fingertip approached the sensor, the capacitance increased significantly. However, when the experimenter was wearing gloves, the transmission of water molecules was blocked and the sensor capacitance remained virtually unchanged.
Figure 9. Breath monitoring applications of CIL@Cl-2 sensor. (a) Photo of the sensor on the face mask for human breath monitoring. (b) Response of the sensor under various breathing modes. (c) Response of the sensor under different breathing rates. (d) Response of the sensor approached by a finger with or without gloves.

4. Conclusions

In summary, cellulose-based capacitive humidity sensors with high sensitivity and fast recovery were fabricated for this work. The humidity-sensing performance of the cellulose sensor was improved by the introduction of an ionic liquid, and the sensing properties could be tuned by the content of the ionic liquid in the sensing film. The optimized sensor showed a high sensitivity (27.95 pF/% RH) in a wide humidity range (11–95% RH), while the recovery time was as low as ~1 s. The as-prepared humidity sensor showed application potential in detecting human breathing and non-contact fingertip humidity.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/chemosensors10110464/s1, Figure S1: (a) The scheme of a platform for QCM humidity sensitivity measurement and analysis. (b) The photo of QCM-5 sensor; Figure S2: The capacitance vs. RH curves of (a) CIL@Cl-1, (b) CIL@Cl-2, (c) CIL@Cl-3 and (d) CIL@Cl-4 under different frequencies; Figure S3: The complex impedance spectroscopy plots of CIL@Cl-3 sensor under different humidities; Figure S4: The complex impedance spectroscopy plots of CIL@Cl-4 sensor under different humidities; Figure S5: The complex impedance spectroscopy plots of blank CNFs sensor under different humidities; Figure S6: The phase-angle diagrams of (a) CIL@Cl-3 and (b) CIL@Cl-4; Figure S7: (a) The capacitance vs. RH curves of CIL@Br-2 sensor measured under different frequencies. (b) Comparison curve of capacitance response values of CIL@Cl-2 and CIL@Br-2 at 500 Hz.

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