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NANOCELLULOSE-BASED RESISTIVE SENSORS FOR AIR HUMIDITY MEASUREMENTS

Introduction. *The measurement of relative air humidity plays a crucial role in various aspects of human life, such as climate control systems, medical breath and skin hydration monitoring. Typically, humidity sensors use inorganic materials and petroleum-derived polymers. However, there is a growing trend towards the transition to biodegradable materials, which eliminates the need for waste disposal.*

Problem Statement. *Currently, nanocellulose (NC) has been being explored as a promising material for humidity sensors. However, the influence of the chemical composition and nanoparticle size of NC on the sensor characteristics remains understudied.*

Purpose. *This study aims to investigate the influence of the chemical composition and structure of NC on the parameters of humidity sensors.*

Materials and Methods. *NC has been synthesized from reed stalks and wheat straw bz the oxidation and acid hydrolysis methods. NC-film sensors having a mass within 0.3—3 mg have been fabricated. The static parameters (response, sensitivity, reversibility, and repeatability) and the dynamic parameters (short and long-term stability, response and recovery time) of the sensors have been analyzed.*

Results. *The manufacturing method influences the NC chemical composition, while the origin material affects its structure. The sensors produced by the oxidation method have demonstrated improved sensitivity ($2.69 \cdot 10^6$), response ($0.2\ (\%RH)^{-1}$), recovery time (60 s) and long-term stability (1.44%) as compared with those made by the hydrolysis method. Additionally, the application of wheat straw NC as origin material has resulted in improved reversibility (5%), repeatability (5% deviation), short-term stability (30% deviation), and response time (1 s) as compared with the reed stalks NC.*

Conclusions. *It has been established that the origin material of nanocellulose influences the reversibility, repeatability, response time, and short-term stability of the sensors. The manufacturing method has effect on the sensitivity, response, recovery time, and long-term stability of the sensors.*

Keywords: nanocellulose, humidity sensors, biodegradable sensors, and resistive sensors.

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For the manufacture of electronic sensors, such inorganic materials as silicon [1, 2], gallium arsenide [3], indium antimonide [4], metals and their oxides [5, 6] are often used. But it is possible to use organic polymers [7—9], that could be applied for making of functional layers and for packaging. Common to both groups of materials is that they must be disposed after the end of device's service life. Otherwise, they accumulate in the form of electronic waste and lead to environmental pollution. One can observe that more and more studies are appearing on the use of biodegradable materials to produce electronic devices. These materials are capable of decomposition under the action of bacteria and fungi. Such materials include chitin-based polymers [10], almond resin-based polymers [11], nanocellulose-based polymers [12], etc. Among them, a promising material is nanocellulose (NC) that has unique properties: high elasticity and large specific surface area, high transparency and low weight, biodegradability and biocompatibility, low coefficient of thermal expansion and chemical reactivity, low production cost. NC can be used to produce "green electronics", that is, in electronic devices that do not require disposal and are capable of spontaneous decomposition in natural conditions [12].

Humidity sensors are the important electronic components because in modern realities the environmental humidity measurements are applied in many systems that improve human life. In particular, the measurement of air humidity is necessary in climate control systems, for breath monitoring, as well as for tracking of the skin sweating/moisturization of patients [13—16]. Also, the control of relative humidity is very important for certain technological operations that are used in the fabrication of electronic devices. Thus, silicon oxide growth can be carried out both in dry and wet oxygen atmosphere [17]. It is known that dry oxygen growth forms the silicon oxide films with high quality, but the rate of the process is very slow. The oxygen humidifying significantly increases the rate of oxide growth, but the quality of the films deteriorates. Combining dry and wet oxygen or selecting the required level of oxygen humidification, it is possible to obtain the layers of silicon oxide with required thickness and quality [17]. Therefore, because of the need of the operation of humidity sensors in various environments, the humidity-sensitive material should be characterized by high values of temperature and time stability and significant response.

Currently, many different humidity sensors have been developed, including capacitive [18—20], resistive [18, 19, 20], optical [22], acoustic [23, 24] and even power-generating devices [25]. Since nanocellulose is a hygroscopic material, it can be used as a sensitive layer for humidity sensors. This work presents the results of research on resistive humidity sensors based on nanocellulose. The working principle of these sensors is explained by the Grotthas mechanism, where the charge carriers are protons from adsorbed water molecules, which move by a jumping mechanism [18]. So, the changes in sensor's resistance depending on the absorbed humidity from the environment take place.

NC cellulose is traditionally divided into cellulose nanofibers (CNF), cellulose nanocrystals (CNC). CNF consists of fibers with diameter of 10—100 nm and a length of hundreds to thousands of nm. CNC typically has a relatively low aspect ratio, with typical diameters of 2—20 nm and lengths ranging from 100 to 600 nm. This material can be obtained from wood [26, 27] and non-wood plant raw materials, from stems and fibers of cereal and technical crops: wheat, flax, miscanthus, kenaf, reed, etc. [28—31]. NC can be obtained by various techniques, in particular, the oxidation and the acid hydrolysis methods. It is known that the structure and chemical composition of NC is determined by the origin material and manufacturing technology [29]. It is likely that the NC morphology and chemical composition can influence the humidity sensitivity. To date, there are no studies of this kind in the literature.

Therefore, the purpose of this paper is to establish the influence of the morphology and chemical composition, as well as the amount of nano-

cellulose on the parameters of resistive humidity sensors based on it.

1. Preparation of nanocellulose

For the extraction of nanocellulose, we used organosolv celluloses obtained by an environmentally safe method from wheat straw and reed stalks. Nanocellulose is obtained as a result of acid hydrolysis or oxidation of organosolv celluloses in the medium of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). Acid hydrolysis is carried out in a 43% solution of sulfuric acid at a liquid to solid ratio of 10 : 1, at a temperature of 60 °C for 60 min. Cellulose in the TEMPO medium is oxidized with a consumption rate of 1.6% of TEMPO at room temperature for 24 hours. The resulting nanocellulose is washed in distilled water by centrifugation and treated with ultrasound for its homogenization. Transparent, time-stable nanocellulose suspensions are stored in hermetic containers for further research.

2. Sensor fabrication

The structure of resistive humidity sensors based on a NC suspension is shown in Fig. 1. The manufacturing process of the sensors consists of the following technological steps: firstly, Ti/Ni bimetallic film is deposited on the surface of pre-cleaned glass-ceramic plate by the method of magnetron deposition in an argon atmosphere under the following technological parameters: the pressure in the chamber is $5 \cdot 10^{-3}$ mmHg, the voltage is 600 V, and the current is 1 A. As a result, the thickness of the obtained two-layered film is 0.25 μm.

The next step is photolithography that is necessary to form an electrode system with an interdigital configuration. Photolithography includes applying a photoresist coating by centrifuge, drying the photoresist, exposing the photoresist through a photo template, developing and hard-baking the photoresist, and etching a Ti/Ni two-layered film.

Then the electrical wires have been soldered to the sensor electrode pads. The last operation is the deposition of a nanocellulose layer top the surface of the electrodes by the drop-casting technique.

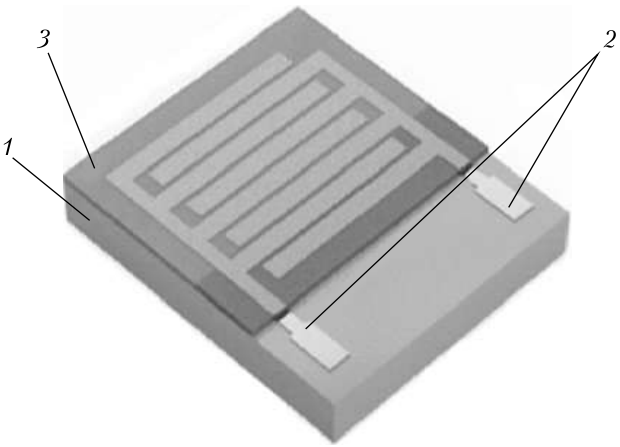

Fig. 1. Structure of a resistive humidity sensor based on NC: *1* — glass-ceramic substrate; *2* — Ni electrodes; *3* — NC film

To do this, NC suspension is dropped as layer by layer to obtain the required mass of nanocellulose film on the surface: 0.3 mg, 0.6 mg, 1.2 mg, 1.8 mg, 2.4 mg, 3.0 mg. Besides, four sets of sensors with different humidity-sensitive films have been obtained: RST (NC extracted from reed stalks using TEMPO method), RSH (NC extracted from reed stalks using acid hydrolysis method), WST (NC extracted from wheat straw using TEMPO method), WSH (NC extracted from wheat straw using acid hydrolysis method).

3. Measuring methods

To research obtained sensors, we used a set of hygrostats with different relative humidity levels. The principle of operation of hygrostats is based on Raoult's law. A saturated salt solution generates a specific value of relative humidity above its surface. The used hygrostats consist of such saturated solutions as: LiCl, $MgCl_2$, NaBr, NaCl, KCl and H_2O, which generate relative humidity (RH) of: 12, 33, 60, 75, 85, and 98% consequently.

The thermo-hygrometer sensor SHT-31 has been used to control the level of relative humidity and temperature at the measurement point. A thermo-hygrometer EZODO HT-390 has been used to calibrate the hygrostats. The resistance of the sensors has been studied with an RCL-P5030 meter at different frequencies of test signal of 100

and 1000 Hz. The weight of the humidity-sensitive film is controlled with an analytical balance OHAUS Pioneer PX163.

The static parameters (response, sensitivity, hysteresis, repeatability of measurements) and dynamic parameters (response and recovery time, short-term and long-term stability) of humidity sensors have been investigated.

The sensor's response is determined by measuring the dependence of sensor resistance on the relative humidity. The measurement adsorption and desorption curves are measured. The adsorption curve is measured when humidity levels increase, and the desorption curve is when humidity levels decrease. The sensor's response is the ratio of the maximum resistance value at the minimal relative humidity (12%) and the minimum resistance value at the maximal humidity (98%). The sensitivity of the sensor is determined from the exponential approximation of the adsorption curve as an indicator of the power of the exponent.

To determine the hysteresis of the sensors, two curves are measured: adsorption and desorption curves. The hysteresis of the sensors is determined by the following equation:

$$H = \pm \frac{\Delta R_{\max}}{\Delta R_{\max} - \Delta R_{\min}} \cdot 100\%,$$

where $\Delta R_{\max}$ — maximal difference between points on adsorption and desorption curves at same RH level; $R_{\max}$ — maximal resistance; $R_{\min}$ — minimal resistance.

The repeatability of device measurements is studied by cycling between RH values of 12% and 60%. This parameter is presented as a relative change in sensor resistance between adjacent cycles.

The short-term stability is studied by measuring of device resistance at stable humidity values of 12% or 60% for one hour. It should be noted that the samples are kept for 15 min before measurement to establish thermodynamic equilibrium. The sensor's deviation is defined as a normal deviation from the mean value of resistance.

The response time has been determined during sudden change in the RH level from 12% to 98% as the time for which the device resistance changes from 90% to 10% of initial value. The recovery time has been determined for sudden change in the RH level from 98% to 12% as the time during which the device resistance increases from 10% to 90% of the initial value.

The long-term stability of the sensors has been studied over a long period of time from 2 to 12 months. As a result, the specific change in the device resistance per day has been determined.

1. Surface morphology and wettability of the humidity-sensitive layer of nanocellulose

The surface morphology of different types of nanocellulose has been studied by atomic force microscopy. Figure 2, *a* shows that the NC extracted from reed by the TEMPO method consists of nanoparticles with a size of 60—150 nm, while the NC extracted from reed by the acid hydrolysis method consists of nanoparticles with a size of 50—140 nm (Fig. 2, *c*). The NC extracted from wheat, is nano-fibrillated for both extraction methods: WST and WSH consist of nanofibers with a size of 20—40 nm (Fig. 2, *b*) and 10—30 nm (Fig. 2, *d*) accordingly. Thus, the NC with particles with a larger diameter and length corresponding to nanofibrillated cellulose (CNF) has been obtained from wheat cellulose, while the NC extracted from reed cellulose has particles of smaller transverse size and shorter length, which are a mix of nanocrystalline (CNC) and nanofibrillated cellulose (CNF). Therefore, it can be assumed that the original material for the selection of NC has an effect on the shape of nanoparticles. It has been established that the synthesis method affects the size of nanoparticles: slightly larger nanoparticles have been obtained by the TEMPO method for both origin materials (reed and wheat).

To determine the hygroscopic properties of the NC film, the contact angle is measured by the sessile drop method. We coat the glass slide with a thin NC film by centrifugation to get a flat surface covered by NC. A drop of water is placed on the surface of the studied NC film, and a high-resolution photo is taken from the side projection.

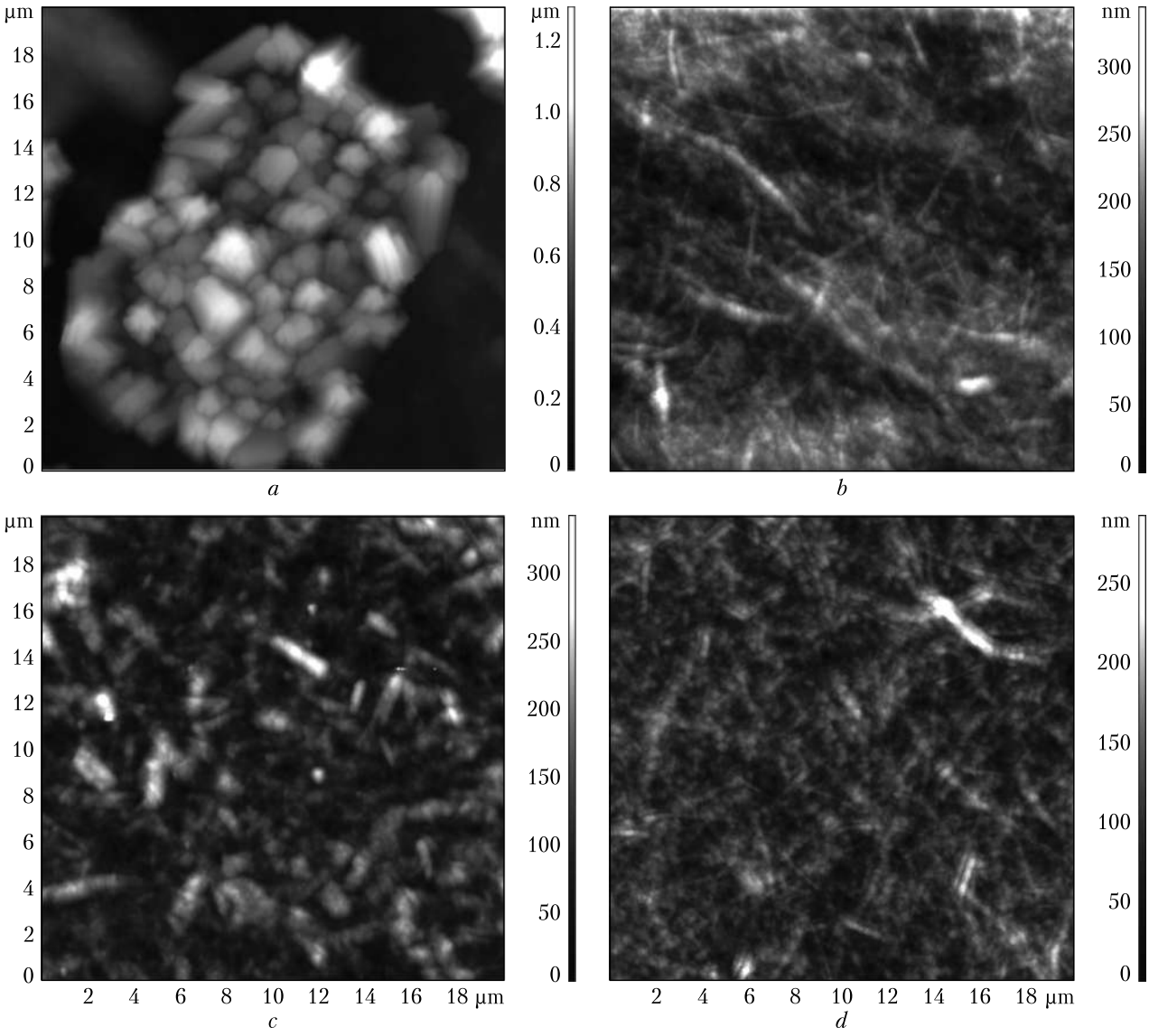

Fig. 2. AFM images of NC film surface: *a* — RST; *b* — WST; *c* — RSH; *d* — WSH

Figure 3 shows a comparison of the contact angle for RST — *b*, WST — *c*, RSH — *d*, WSH — *e* and clean glass — *a*. The angle between the surface of the film and the tangent to the arc formed by the water drop has been determined. It has been found that the contact angle is equal to 9.2°, for NC RST; 11.1°, for WST; 13.1° for RSH; and 19.6°, for WSH. At the same time, the glass slide has a contact angle of 50.8°. As one can see, the contact angle of pure glass significantly exceeds the measured angles for nanocellulose films, which indicates the high hygroscopicity of all NC films. Furthermore, it has been shown that NC obtained by the TEMPO method is more hygroscopic as compared with the NC obtained by the acid hydrolysis method. The higher hygroscopicity observed for NC extracted by the TEMPO method can be explained by the following: the carboxyl groups of cellulose macromolecules are characterized by high ability to interact with free water molecules.

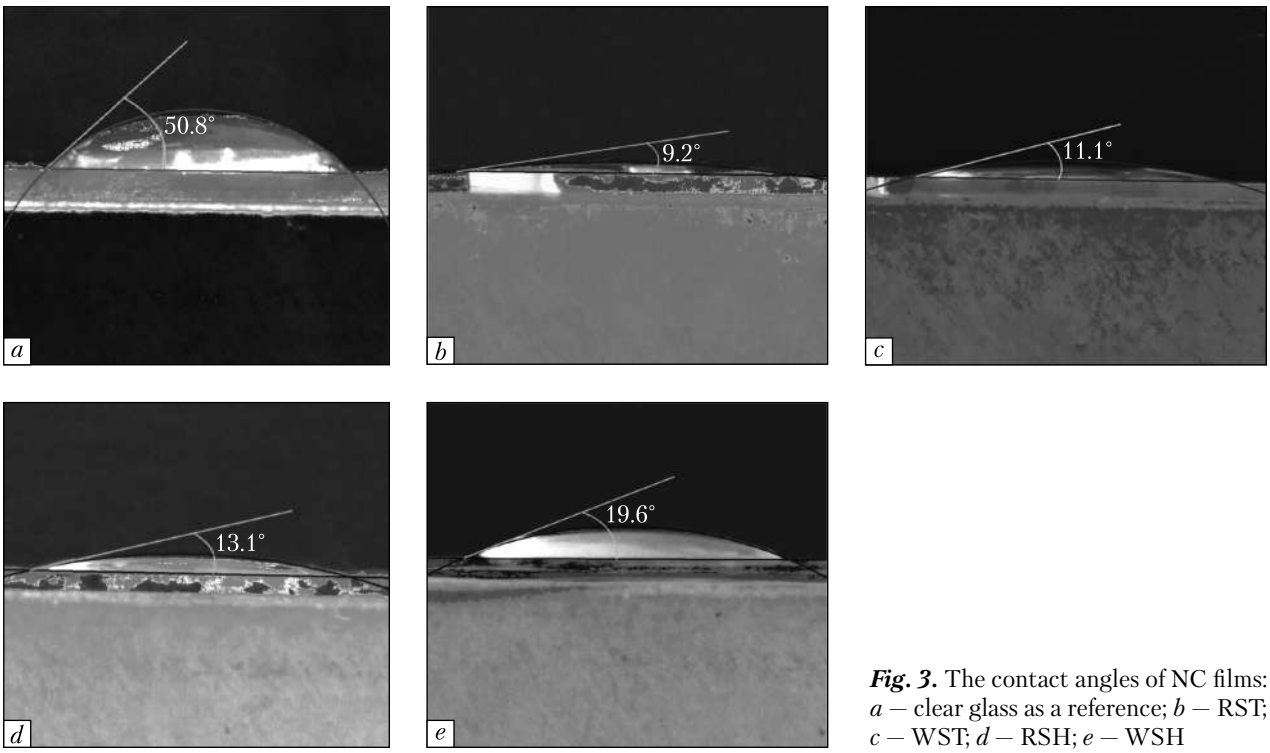

Fig. 3. The contact angles of NC films: *a* — clear glass as a reference; *b* — RST; *c* — WST; *d* — RSH; *e* — WSH

In the method of acid hydrolysis, the hydroxyl groups of cellulose are converted into esters with the formation of esters of sulfuric acid, which are less hygroscopic than the carboxyl groups that are formed during the oxidation process in the TEMPO environment.

2. Static parameters of the humidity sensors based on NC

Response and sensitivity. The working principle of the RH sensor is based on the increase in conductivity of the sensitive layer (nanocellulose) under humidity adsorbance from the environment. The conductivity in nanocellulose is explained by the Grothas mechanism. This mechanism is as follows: the electric charge in the sensitive NC layer is transferred due to protons that can jump between molecules that contain hydrogen bonds (for example, between water or cellulose molecules) under bias. Obviously, the higher humidity level, the greater number of water molecules that can be absorbed by NC film, which results in significant increase of the film conductivity.

The response of sensors, made from NC extracted by the TEMPO method, is significantly higher than for NC, extracted by the acid hydrolysis method. Moreover, the highest response ($2.69 \cdot 10^6$) is observed for RST-NC, while the WST-based sensor has a response of $1.64 \cdot 10^6$. For comparison, the sensors based on NC obtained by acid hydrolysis have a response of $1.75 \cdot 10^4$ and $4.69 \cdot 10^4$ for RSH and WSH accordingly. So, the TEMPO method provides the sensor with a response of 2 orders of magnitude higher as compared with the sensor obtained by the acid hydrolysis method. Such behavior is explained by smaller contact angle of TEMPO NC because of presents of carboxyl groups in its composition.

The device sensitivity to air humidity depending on the initial conditions of the NC synthesis (Fig. 4, *a*) has been determined. Similarly, to the TEMPO method provide better device sensitivity as compared with the acid hydrolysis me-

thod: 0.186 (%RH^{-1}) for RST and 0.2 (%RH^{-1}) for WST vs. 0.139 (%RH^{-1}) for RSH and 0.137 (%RH^{-1}) for WSH. However, the origin material has almost no effect on the device sensitivity.

The sensor with the smallest mass of NC humidity-sensitive film demonstrated the highest response. Figure 4, *b* features that the sensitivity of sensors based on the TEMPO extracted NC decreases with a mass much more sharply than for sensors made from the acid hydrolysis extracted NC. Thus, as the weight of the NC film increases from 0.3 mg to 3.0 mg, the sensitivity for RST-based sensors drops 3 times, 2 times, for WST, and by approximately 40%, for WSH and RSH. This behavior can be explained by the differences both in the chemical compositions and structure of NC, obtained by different methods. Also, one can clearly see, that the frequency of the test signal does not affect the sensitivity of resistive humidity sensors (Fig. 4, *a*).

Hysteresis. The hysteresis in relative humidity sensors is explained by the different speeds of humidity adsorption and desorption. So, the sensor resistance at a fixed humidity level on the adsorption and desorption curves is slightly different, which leads to the formation of a hysteresis loop.

Figure 5, *a* shows the dependence of hysteresis on the mass of the NC film, namely: for all samples, the hysteresis increases with the increase in the mass of the NC film. However, for sensors based on NC extracted from reed, the hysteresis increases much faster than for NC extracted from wheat straw. If you place the value of hysteresis from the largest to the smallest value, then the sequence for different types of NC will be as follows: RST — 26.75%, RSH — 8.15%, WSH — 6.22%, WST — 5.97% at the frequency of the test signal 100 Hz. This behavior can be explained by significantly smaller sizes of nanoparticles in the films made from wheat NC as compared with the films from reed NC. The smaller size of the nanoparticles means that the vacant places that can attach water molecules are more quickly filled during adsorption or emptied during desorption. That is,

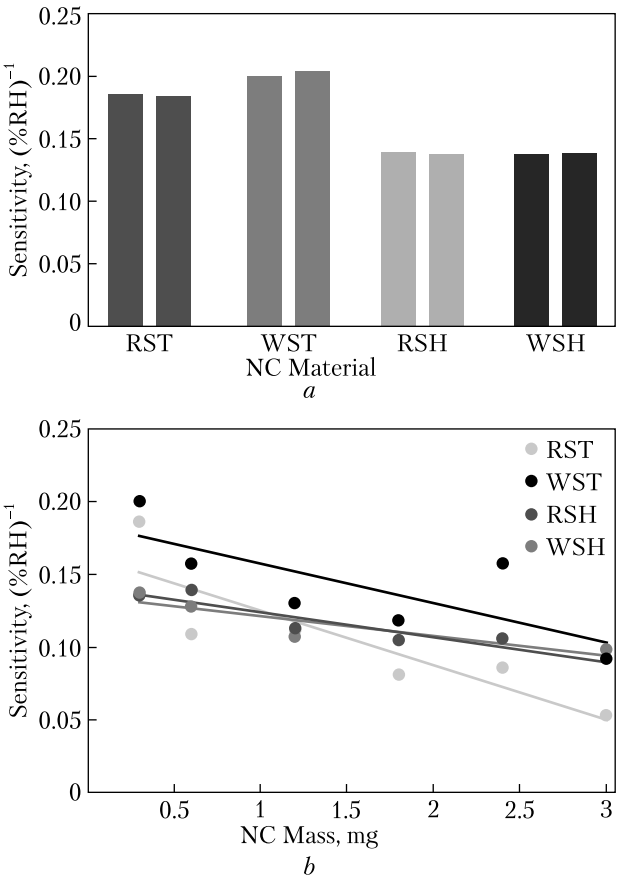

Fig. 4. Maximal value of sensitivity (*a*) and its dependence on NC film mass (*b*) for resistive humidity sensors based on NC

these processes proceed faster in relation to larger nanoparticles obtained from reed. Thus, for sensors based on NC from wheat, a smaller value of hysteresis is observed regardless of the manufacturing technology. We can also see that the frequency of the test signal has no effect on the hysteresis of the sensors (Fig. 5, *b*). For all sensors, the hysteresis at 1000 Hz is slightly higher than at 100 Hz, but this difference is negligibly small.

Cycling. Figure 6 features the cycling graphs for humidity sensors based on which the deviation has been calculated (Fig. 6, *b*). As can be seen, the sensors based on NC of reed stalks have shown a significantly worse repeatability of 20.46% for RST and 25.31% for RSH as compared with those based on NC of wheat straw of 7.52% for WST

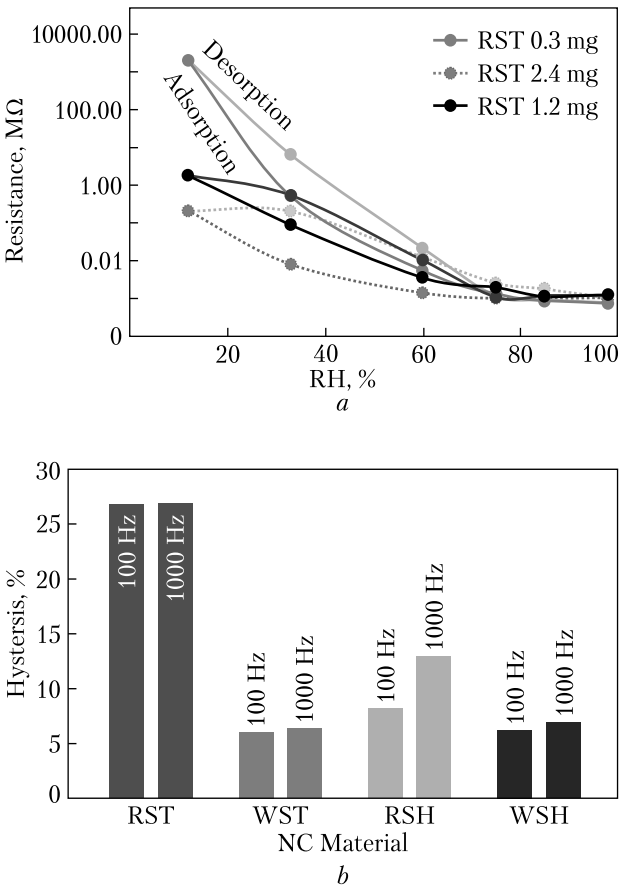

Fig. 5. The hysteresis curves (*a*) and the maximum values of hysteresis (*b*) for resistive humidity sensors based on NC

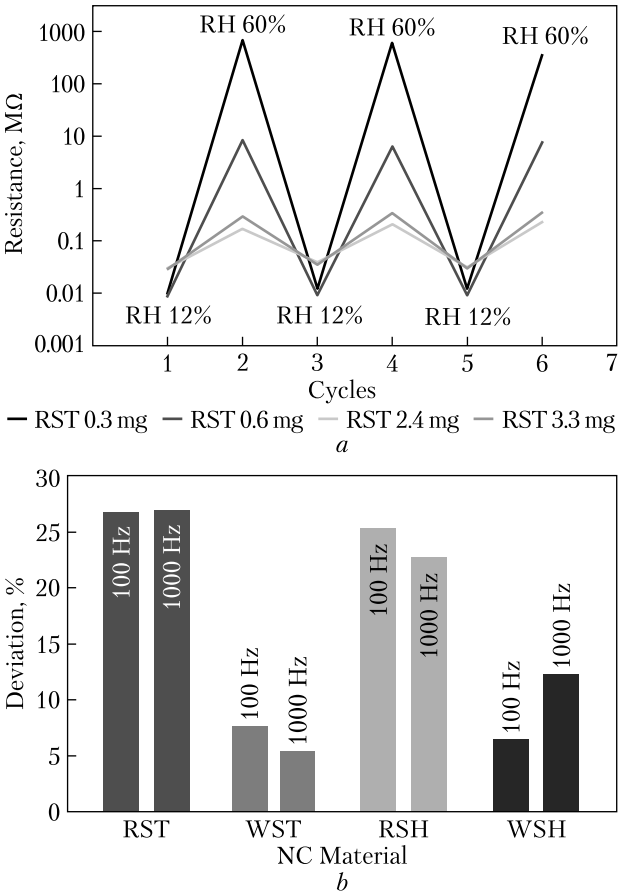

Fig. 6. The cycling graphs (*a*) and average values of deviation during cycling (*b*) for resistive humidity sensors based on NC

and 6.42% for WSH. Similarly, to the hysteresis, this can be explained by the significantly thinner nanoparticles obtained from wheat straw. Also, it has been found that the NC mass and the signal frequency do not affect the deviation during cycling test.

3.3. Dynamic parameters of the sensors based on NC

Reaction speed. Figure 7, *a* shows the response and recovery curves for sensors based on RSH in dependence on different mass of NC films. One can see that the larger NC mass, the longer response and recovery times (Fig. 7, *b*), the lowest response time have sensors based on NC from wheat for all NC mass and both synthesis methods (the response time is 1—92 s and 1—103 s for WST and WSH, respectively). The device response for NC from reed stalks is 3—6 times slower.

In the terms of recovery time, sensors based on nanocellulose extracted by the TEMPO method are faster than the devices made by the hydrolysis method (Fig. 7, *a*). So, the response time is 60—575 s, for TEMPO-extracted NC, and 520—690 s, for hydrolysis-extracted NC.

This can be explained by the different morphology of the obtained NC films. Thus, NC films extracted from wheat straw consists of nanoparticles with a relatively small diameter, which leads to a shorter response time for such sensors. At the same time, one can see that the extraction technology has almost no effect on the response time

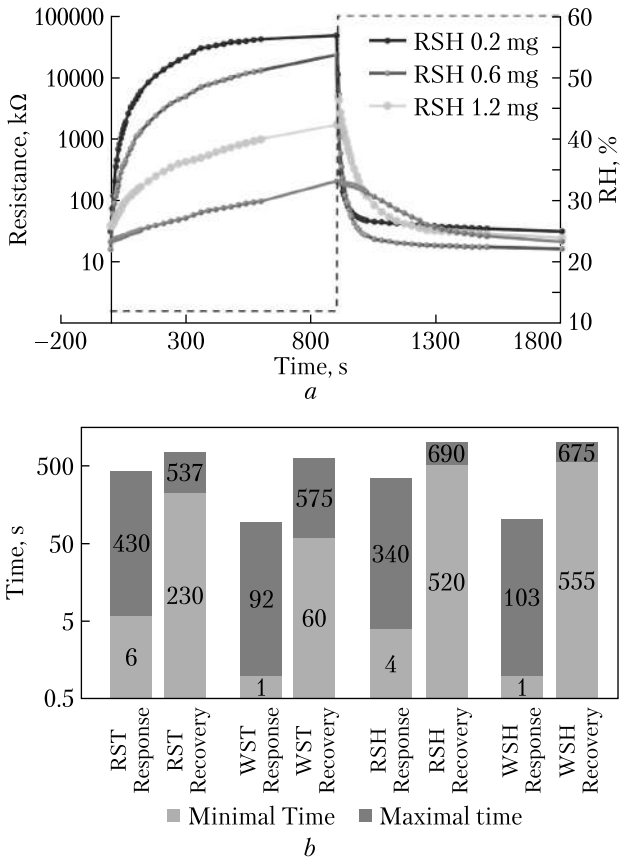

Fig. 7. The response and recovery curves (*a*) and minimum/maximum values of response and recovery times (*b*) for resistive humidity sensors based on NC

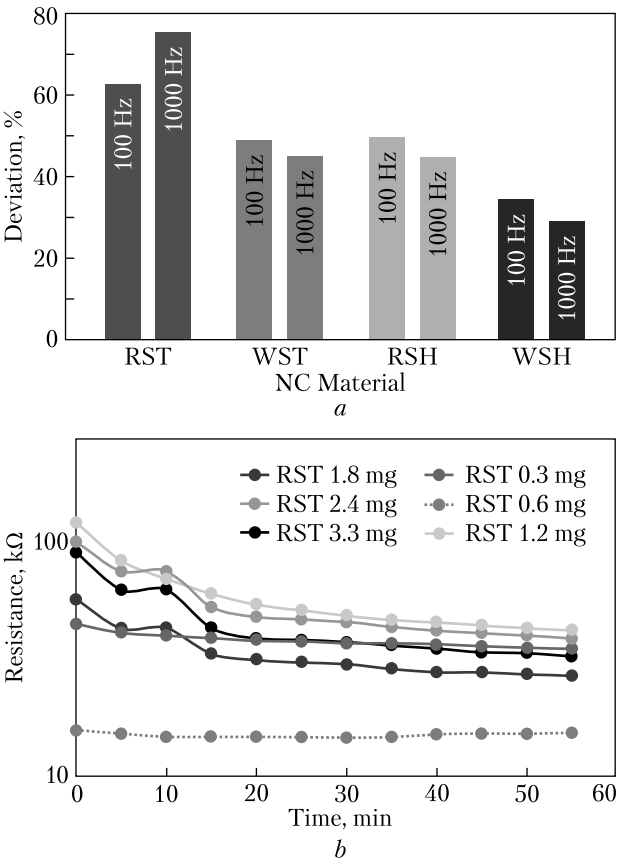

Fig. 8. The curves of short-term stability (*a*) and average values of deviation (*b*) for resistive humidity sensors based on NC

of the sensors, but it affects recovery time. This is due to the different chemical compositions of NC obtained by different methods. It means that water molecules are desorbed more easily from NC obtained by the TEMPO method, resulting in a reduction in recovery time.

Short-term stability. Figure 8, *a* shows that as the mass of the humidity-sensitive film increases, the device stability is worst. From Fig. 8, *b*, we can see that, regardless of the nanocellulose extraction technology, sensors obtained from reed stalks demonstrate worse stability. Thus, RST shows a deviation of 62.72% against 48.76% for WST, while RSH shows a deviation of 49.51% against 34.3% for WSH. If we arranged the sensors in order of improvement in their stability, we would get the following sequence: RST-RSH-WST-WSH. So, short-term stability is influenced by both the raw material from which the NC is made and the manufacturing technology.

Also, it has been found that the influence of the measurement frequency, is present for the most sensors The higher frequency of the test signals the lower instability, except of the RST material. This can be explained by the fact that some slow processes stop working.

Long-term stability. It has been determined that the resistance of humidity sensors increases for the year. The best long-term stability has been demonstrated by the sensors from WST, whose resistance changes about 1.44%/day. In general, the sensors, obtained by the TEMPO method,

are characterized by significantly better stability than sensors, obtained by the hydrolysis method (RSH shows 25.5%/day, WSH — 25.1%/day). The increase in resistance of the sensors over long period of time can be caused by both oxidation of the electrode system (and nanocellulose). So, the long-term stability required further investigation.

In this work, humidity sensors are made from NC extracted from organosolv cellulose from reed stalks and wheat straw by oxidation method in TEMPO environment and acid hydrolysis method. The sensors are obtained with a mass of humidity-sensitive nanocellulose film on their surface from 0.3 to 3.0 mg. It has been established that NC from wheat straw contains nanofibers and NC from reed stalks contains nanorods. Also, it has been shown that all NC films are hygroscopic and show wetting angles not exceeding 20°.

Static parameters (response, sensitivity, hysteresis, repeatability) and dynamic parameters (response and recovery time, short- and long-term stability) of resistive humidity sensors have been investigated. It has been established that the sensors made from NC by the oxidation method demonstrate significantly better response and sensitivity as compared with the sensors from NC extracted by the acid hydrolysis method. This is due to the different chemical compositions of nanocellulose obtained by different methods. However, the improved repeatability, reversibility and short-term stability are observed for the sensors based on wheat straw NC. This is explained by nanofibrillated structure of NC obtained from wheat, regardless of the manufacturing method. Also, the sensors based on NCs from wheat have the shortest response time, due to the small physical dimensions of the obtained nanoparticles. At the same time, the shortest recovery time is demonstrated by the sensors made by the oxidation method in TEMPO environment, which can be explained by the fact that this NC desorbs humidity much easier and faster. Such sensors are characterized much better stability too (1—8%/day). The direction of further research is to improve the long-term stability of the sensors.

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РЕЗИСТИВНІ ДАТЧИКИ НА ОСНОВІ НАНОЦЕЛЮЛОЗИ ДЛЯ ВИЯВЛЕННЯ ВОЛОГОСТІ ПОВІТРЯ

Вступ. Вимірювання відносної вологості повітря є важливим у таких сферах життєдіяльності людини як системи клімат-контролю, медичного моніторингу дихання, а також відслідковування потовиділення/зволоження шкіри пацієнтів. Зазвичай, сенсори виготовляють із неорганічних матеріалів та полімерів, отриманих із нафти. Сучасним трендом є перехід до біорозкладних природніх матеріалів, які не потребують подальшої утилізації.

Проблематика. На сьогодні існують досліди з використання наноцелюлози (НЦ) як чутливого елемента сенсорів, однак вплив хімічного складу та розміру наночасток НЦ на характеристики сенсорів не досліджено.

Мета. Встановити вплив хімічного складу та розміру наночасток НЦ на характеристики сенсорів вологості.

Матеріали й методи. Для виконання роботи було синтезовано НЦ із очерету та соломи пшениці методами ТЕМПО та кислотного гідролізу, виготовлено сенсори із масою плівки НЦ від 0,3 мг до 3 мг. Було досліджено статичні параметри (відгук, чутливість, реверсивність та повторюваність) та динамічні параметри (коротко- та довготривала стабільність, час відгуку та відновлення) сенсорів.

Результати. Встановлено, що метод виготовлення НЦ впливає на її хімічний склад, а вихідний матеріал синтезу наноцелюлози впливає на її структуру. Найкращі показники відгуку ($2{,}69 \cdot 10^6$ с), чутливості ($0{,}2(\%RH)^{-1}$), часу відновлення (60 с), а також довготривалої стабільності (1,44 %) показує метод ТЕМПО порівняно з методом гідролізу. Сенсори, виготовлені із НЦ з соломи пшениці, демонструють найкращу реверсивність (гістерезис 5%), повторюваність (відхилення 5 %), короткочасну стабільність (відхилення 30 %) та час відгуку (1 с).

Висновок. Визначено, що вихідний матеріал впливає на реверсивність, повторюваність, короткочасну стабільність та час відгуку сенсорів, а метод виготовлення — на чутливість, відгук, довготривалу стабільність та час відновлення.

Ключові слова: наноцелюлоза, сенсори вологості, біорозкладні сенсори, резистивні сенсори.