Polyacrylonitrile/CoCl₂ nanofibers based humidity sensor for human breath and ambient humidity monitoring

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Abstract

A novel humidity sensor was constructed using the hybrid nanofibers of polyacrylonitrile/CoCl₂ (PAN/CoCl₂), which were fabricated by electrospinning. Scanning electron microscopy (SEM) image demonstrated that the diameter of PAN/CoCl₂ nanofibers ranged from 100 - 500 nm. Energy-dispersive X-ray spectrometer (EDS) analysis confirmed that Co and Cl elements were homogeneously dispersed on the PAN nanofibers. CoCl₂ on the surface of PAN nanofibers play a dual function in humidity sensing performances. First, CoCl₂ serves as an indicator, which can change the color of nanofibers from blue to white-pink as the relative humidity changed from 11 to 98 %, to realize the colorimetric sensing. Second, CoCl₂ could remarkably improve the electric sensing performance. As a result, the PAN/CoCl₂ nanofibers offered much enhanced response currents compared to the pristine PAN nanofibers, as the humidity changed from RH 11 to 98 %. In addition, the PAN/CoCl₂ nanofibers based humidity sensor was employed to monitor human breath and the ambient humidity, which demonstrated the excellent sensitivity of this humidity sensor. Therefore, we believe that the highly sensitive and simply designed PAN/CoCl₂ humidity sensor is a promising candidate for various applications in the field of humidity monitoring.

Keywords: Humidity sensor; colorimetric sensing; PAN/CoCl₂; electrospun nanofibers; humidity monitoring.
Introduction

Humidity sensors are widely used in environmental monitoring, scientific research, as well as industrial and agricultural productions [1-4]. In particular, humidity sensor shows great potential in the application of health care, in which the humidity sensor could convert human respiratory into electrical signals, through real-time monitoring the moisture from human breath [5-10]. In various environmental parameters, the measurement of humidity is much more complicated than the measurement of other parameters, because humidity is susceptible to other environmental factors, such as atmospheric pressure and temperature. Therefore, the precision and accuracy of measuring humidity with wet bulb hygrometer or hair hygrometer are not high enough to meet the needs of modern technology development. Therefore, the research of new sensitive materials for humidity sensor has attracted more and more attentions [11-14]. Various types of sensors have been developed through utilizing the resistance, capacitor, field-effect-transistor, and optical response, to realize the purpose of humidity sensing. Among these types of sensors, the optical response type had attracted a lot of interests since it is easily detectable with the naked eye and suitable for applications in daily life [15-19]. Colorimetric detection can transform the object identification events into color changes; that is, through spectrophotometer or even the naked eye of the observer can directly conduct qualitative or quantitative detection of the target parameters that cause color changes. However, the measurement accuracy and sensitivity of the optical type sensors are very limited. Therefore, achieving humidity sensors with high accuracy and sensitivity is vital to its practical application. An excellent humidity sensor should meet other requirements, including wide humidity range, good linearity, short response time, stable chemical and physical characteristics, as well as low preparation cost.

Electrospun nanofibers have attracted wide attention to fabricate humidity sensors, due to their extremely high specific surface area and stable physical and chemical properties. For nanofibers-based humidity sensors, the high surface area and nanoporous structure regulate the water molecule adsorption and desorption. The electrons of adsorbed water molecules can be transferred within the nanofibers and result to the impedance, resistance, capacitance or other electric signals. ZnO/TiO₂ composite nanofibers on a ceramic substrate with Ag-Pd interdigitated electrodes, has been assessed for humidity sensing. The composite nanofibers of polyaniline/poly(vinyl butyral)/poly(ethylene oxide) has been also used to prepare an impedance type humidity sensor with good sensing linearity and repeatability as well as fast response times. In another study, conductive polyaniline was synthesized
on the surface of polyacrylonitrile (PAN) nanofibers and used for humidity sensing and moisture monitoring applications. Moreover, in order to improve the humidity sensing properties of polymeric nanofibers, addition of inorganic salts is one of the most used strategies. For example, LiCl was used to improve charge carrier transfer of polyvinylidene fluoride based nanofibers, obtaining a humidity sensor with linear impedance change with RH.

In this work, PAN/CoCl$_2$ nanofibers was prepared by means of electrospinning, with the PAN as the filament materials and the CoCl$_2$ utilized to provide the colorimetric potentials and to enhance the overall conductivity of composite nanofibers. Furthermore, Due to the hydration action, the CoCl$_2$ could adsorb water molecules and change its color under different relative humidity conditions. The humidity sensitive behavior of the obtained PAN/CoCl$_2$ humidity sensors was investigated in details; and the humidity sensitive mechanism was discussed. This work fully analyzed the humidity sensitive performance of PAN/CoCl$_2$ humidity sensor, and demonstrates the novel nanofibers-based humidity sensors could be used for monitoring human breathing and the ambient humidity.

2 Experimental

2.1 Materials

PAN (Mw = 150,000 g/mol), were purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF, anhydrous), CoCl$_2$·6H$_2$O, and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

2.2 Fabrication of PAN/CoCl$_2$ nanofibers humidity sensor

The electrospinning solution was prepared by dissolving PAN and CoCl$_2$·6H$_2$O into DMF with predetermined concentrations, under stirring for 10 h at the temperature of 60 °C. The resultant homogeneous solution was loaded into a plastic syringe with a 20 gauge metal needle. A high voltage of 15 kV was applied to the needle-tip using a power supply, and the solution was supplied with a flow rate of 1.0 ml/h using a syringe pump. Fibers were collected on a rotating metallic drum at a distance of 20 cm. Regulated relative humidity (45±5%) and temperature (25 ± 2 °C) were maintained throughout the process.

The humidity sensor mainly consists with three parts, including a piece of PET film (which was cut from a plastic file pocket with the size of 15 mm × 20 mm, this size allows the arrangement of conductive adhesive tape and the space for adhering PAN/CoCl$_2$ nanofibers), two paralleled double-side conductive adhesive tapes with 5 mm space between each other. As shown in Figure 1a,
the PET film and the conductive adhesive tapes were pasted on the PAN/CoCl$_2$ nanofibrous membrane, followed by peeled up the tapes from the membrane. In order to protect the nanofibers, the sensor was preserved in a sealed plastic bottle at room temperature, and used for the subsequent humidity sensing. For the aim of comparison, the humidity sensor based on pure PAN nanofibers was also prepared with the same method.

2.3 Method

The morphology of the samples was observed using scanning electron microscopy (SEM, QUANTA Q400, FEI, USA), combined with an energy-dispersive X-ray spectrometer. Fourier transform infrared spectroscopy (FTIR) tests were conducted on a Spectrum 100 FTIR spectrometer (PerkinElmer, US). The X-ray diffraction (XRD) patterns of the samples were recorded using an X-ray diffractometer (Rigaku D/Max 2200PC).

The colorimetric sensing behavior of the PAN/CoCl$_2$ sensor was performed in a closed flask. The sensor was hung up inside the flask. Means for humidity control are using saturated salt solution, which could produce a stable humidity circumstances of RH 11 % (Saturated LiCl solution, in 20 °C), RH 33 % (Saturated MgCl2 solution), RH 57 % (Saturated NaBr solution n), RH 75 % (Saturated NaCl solution), and RH 98 % (Saturated K$_2$SO$_4$ solution), respectively. More detailed quantitative measurements for the colorimetric detection were performed with UV-Vis spectrometer.

The humidity sensing properties of the nanofibers based humidity sensor were analyzed based on impedance variation under different humidity circumstances of RH 11%, RH 33%, RH 57 %, RH 75% and RH 98 % respectively. The controlled RH % circumstances were also achieved by using supersaturated aqueous solutions as aforementioned. The humidity sensitivity value is expressed as $R_0/R$, where RH 11% is considered as the initial humidity level. The $R_0$ and $R$ are the impedances taken at RH 11% RH and a detecting RH %, respectively. The response/recovery time was recorded as a sensor achieving 90% total impedance change during the sensing process.

3 Results and discussions

3.1 The concept of PAN/CoCl$_2$ nanofibers-based humidity sensor
Figure 1. (a) Preparation pathway of PAN/CoCl₂ nanofibers based humidity sensor. The inset picture is the SEM images of PAN/CoCl₂ nanofibers. (b) Element distribution of C, Co and Cl elements. (c) Photographs of the sensor and the response-time curves at the conditions of being covered and uncovered by human hand. (d) Photographs of patterns based on PAN/CoCl₂ nanofibers membrane at RH 11 % and RH 98%.

In order to investigate the structures of nanofibrous sensor, a sketch of the as-spun PAN/CoCl₂ samples are examined in Figure 1a. These SEM images indicates that the PAN nanofibers (15 wt%, 3.0 g PAN in 20 ml DMF), randomly oriented to form a nonwoven mat with large amount of micro-porous. The porous structure benefits to absorb moisture from the environment and resulted in the high humidity sensitivity. The morphology of nanofibers prepared from the PAN solution with the concentration of 10, 15 and 20 wt% were observed, as shown in supplementary Figure S1. As the PAN concentration was 10 wt%, part of the obtained nanofibers were adhered from each other; while the PAN concentration of 20 wt% produced the resultant nanofibers with large porosity, which is not conducive to the adsorption of water molecules or ion transmission. Therefore, the PAN concentration was set as 15 wt%.

In addition, as shown in Figure 1b, the energy dispersive X-ray spectrometry (EDS) results indicates that the C, Co and Cl elements are present; the EDS map demonstrated that these elements are
equally distributed throughout the electrospun nanofibers. The FTIR spectra of pure PAN, CoCl$_2$·(H$_2$O)$_6$ and PAN/CoCl$_2$ nanofibrous membrane are shown in supplementary Figure S2a. It is found that there was not any new characteristic peak present on the FTIR spectra of PAN/CoCl$_2$ nanofibrous membrane. All of the characteristic peaks attributes to PAN or CoCl$_2$. The incorporation of CoCl$_2$ in the nanofibers did not change the molecular structure of PAN. The similar results was also found in the XRD pattern, as shown in supplementary Figure S2b.

The present of CoCl$_2$ also modified the surface property of PAN nanofibers, leading significant improvement of conductivity, which resulted in high accuracy humidity sensitivity with very short response and recovery times. In addition, considering the large variation in humidity caused by human respiration, we chose a smaller variation to investigate the humidity sensor. As shown in Figure 1c, a hand-held multimeter was used to measure the resistance value of the PAN/CoCl$_2$ nanofibers-based humidity sensor. It can be observed that the resistance value of the sensor exceeds the measurement range of the multimeter, as the sensor exposed to air. Therefore, the "OL" (the abbreviation of OVER LOAD) is displayed on the LCD screen of the multimeter. The humidity of the air at this moment was about RH 50%. After being covered by human hand, the resistance reading of the multimeter decreases lower than 60 MΩ. It is important to note that the skin was not in contact with the sensor; therefore, the decrease resistance reading of the multimeter was entirely due to the fact that the nanofiber absorbs water molecules, which were emitted from human hand. Furthermore, the measurement of humidity was recorded. It is mentioned that the resistance value of the multimeter did not decrease significantly when we used the hand wearing a rubber glove to cover the sensor. It also indicates that the decrease in the sensor resistance is not caused by the temperature of human palm or the disappearance of the external light source. The current responses were also recorded during the processes of cover and uncover for 25 cycles in 10 min (supplementary Figure S3). The cover and uncover performances changed the humidity around the sensor and lead to the change in the current signals. The cover and uncover rate can be clearly distinguished from the number of peaks in the curve.

3.2 Humidity response performance via color
Figure 2. (a) Visible reflectivity spectra of PAN/CoCl$_2$ nanofibers in different humidity. (b) Reflectivity spectra of PAN/CoCl$_2$ nanofibers in as a function of detection time after exposure in RH 98 %. (c) CIE 1931 chromaticity diagram of PAN/CoCl$_2$ nanofibers in different humidity. (d) x, y value of CIE 1931 chromaticity corresponding to various humidity.

Due to the addition of cobalt chloride, the composite fibers show corresponding color changes under different humidity conditions. As shown in Figure 1d, the characters were blue at the RH 11 %, while changed to white-pink as the relative humidity increased to 98 %.

For evaluating the detection sensitivity of the PAN/CoCl$_2$ nanofibers, they were tested under the different environment humidity of RH 11 %, 33 %, 59 %, 75 % and 98 %, respectively. Cobalt chloride is a widely used moisture sensitive material. There is a dynamic equilibrium between [CoCl$_4$]$^{2-}$ and [Co(H$_2$O)$_6$]$^{2+}$, which induced by adsorption or desorption of water molecules. At high humidity, [CoCl$_4$]$^{2-}$ combines with water molecules to produce [Co(H$_2$O)$_6$]$^{2+}$, to present the red color, while [Co(H$_2$O)$_6$]$^{2+}$ loses crystal water and turns in to the blue. The process of these color changes could be expressed as:

$$[\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O} \rightarrow [\text{Co(H}_2\text{O)}_6]^2+ + 4 \text{Cl}^-$$

The color gradually varied from blue to pink, with the increase of environment humidity,
indicating the conversion of [CoCl₂]²⁻ into Co(H₂O)₆³⁺, due to the absorbance of water molecules. Since the information obtained from the human eyes is very limited and selfish, the absorbance and reflectivity curves from the RH 11 % to RH 98 % were quantified using UV-Vis spectrometer. As shown in supplementary Figure S4, at low humidity of RH 11 %, the absorption peak of PAN/CoCl₂ nanofibers was located between 500-700 nm. Correspondingly, as shown in Figure 2a, it is observed that almost 90 % of light reflected below 550 nm by the nanofibrous sample; while part of the light at 550-700 nm reflected by the nanofibrous sample. These reflections combined to create the blue color. With the increase of humidity, the absorption light at 550-700 nm gradually decreases, until the humidity is RH 98 %, it can be found that almost all the light is emitted by the fiber sample, thus making the sample present the white-pink color. This result is different with the pink color obtained by dissolving cobalt chloride in water, because the porous structure of nanofibers allows them to reflect the light completely, resulting in a mixture of white light. A kinetic study was performed to investigate the color changing process of PAN/CoCl₂ nanofibers in order to determine the measurement times. Figure 2b shows the reflectivity spectra of the nanofibers taken at different times during the first 240 min of exposure in RH 98 %. The image in Figure 2c display the color change as a function of the exposure time, exhibiting that the initial blue color was changed and saturated to white-pink within 240 s. Base on above study, an exposure time at least of 240 s was used for further measurements since it could provide enough time for color saturation.

3.3 Electric characterization of the PAN/CoCl₂ sensor.
Figure 3. (a) The schematic image of humidity sensing mechanism at low and high RH conditions and the schematic image of humidity sensing mechanism by using PAN sensor and PAN/CoCl$_2$ sensor. (b) Relationship between current and RH values; (c) Current (I–V) curves under different relative humidity. (d) Relationship between current and RH values. (e) I–V curves under different relative humidity.

As above mentioned, PAN/CoCl$_2$ nanofibers can characterize the environmental humidity ranged from RH 11 to 98% by means of colorimetry, which could be directly recognized by human eyes without any other equipment. However, we found that the colorimetry method has the following drawbacks including: 1) the color change of the nanofibrous membrane is not very obvious under the
humidity of RH 75%, and the relative obvious color change from blue to pink would only be detected as the humidity over RH 75%; 2) the response time of the colorimetric nanofibrous sensor to humidity is relatively long; even at the humidity of RH 98%, it still needs at least 3.0 min of exposed time before the color of the fiber membrane significantly changes; 3) there is not definite linear relationship between the color change of fibrous membrane and the humidity values. In order to solve these drawbacks, PAN/CoCl$_2$ nanofibers was designed as resistance-type sensor for the aim of humidity sensing.

As shown in Figure 3a, at the low RH of 11 % and 33 %, the intrinsic resistance of PAN and few water molecules adsorbed onto the PAN nanofibers results in the low conductivity of sensor, because the charge mainly transferred by protons hopping from site-to-site. When the RH further increased over 75%, water molecules began to accumulate at the interface between the sensing layer and the electrodes, resulted in much larger current value than that of lower relative humidity. Therefore, the increase of relative humidity definitely increase the amount of adsorbed water molecules on the surface of PAN nanofibers, which finally increased the overall current. As aforementioned, the reason for low sensitivity and low current values at the low RH conditions (RH 11%-33%) is the low conductivity of the polymer fibers for enabling the charge carrier to be transported. The dominant sensing mechanism for this range can be explained by proton (H$^+$) hopping and hydronium (H$_3$O$^+$) diffusion. The humidity sensitivity is greatly affected by the density of proton hopping sites. Therefore, in order to increase the sensitivity or current at the low RH, the media of the charge carrier should be enhanced or promoted, for example, adding salts or metals. In Choi’s reports, LiCl was used to increase the number of charge sites for obtaining greater hopping sites and finally enhanced the overall performance of nanofibers-based humidity sensors [20]. In this work, the aim of enhancing sensitivity was achieved by adding CoCl$_2$ into the PAN nanofibers, in the form of greater currents. Co$^{2+}$ ions could be served as the transport media for the charge carrier, which leaded to a decrease in the electric resistance and increase the current in the sensing processes.

As shown in Figure 3b and d, the PAN/CoCl$_2$ sensor present the similar response values with that of PAN nanofibers based humidity sensor. However, the sensitivity of PAN/CoCl$_2$ sensor was much greater than that of PAN sensor. The greater sensitivity under various relative humidity that obtained from the PAN/CoCl$_2$ sensor mainly caused by the incorporation of salt in the PAN nanofibers. Figure 3c and e shows the dynamic response and recovery curve of nanofibrous sensor between RH 11% and
33, 57, 75, and 98 %; and each humidification or dehumidification process lasted 5 min. For each RH condition, three repeated response-recovery processes were performed. It can be detected that the PAN nanofibers based humidity sensor can make a fast response to the change of RH, and the largest $R_0/R$ value is achieved at 98% RH. The PAN sensor showed very low current value under the humidity of RH 11 % and RH 33%. Since PAN is one of the excellent insulating materials, the enhance of $R_0/R$ value was mainly conducted by the $H^+$ and $OH^-$ ions which were dissociated from the adsorbed water molecules on the nanofibers surface. The fact is that the surface of PAN nanofibers can only adsorbed a certain amount of water molecules, which can hardly dissociated into enough $H^+$ and $OH^-$ ions for large current. Therefore, the amount of water molecules limited the sensitivity of PAN based humidity sensor. Moreover, with the increase of humidity, the $R_0/R$ value was increased and finally reached to about 3000 times under the humidity of RH 98 %; while $R_0/R$ value was increased about $10^5$ times, which demonstrated the much greater sensitivity of PAN/COCl$_2$ humidity sensor. These results also demonstrated that the amount of adsorbed water molecules was the determinant for the response values under various humidity.

3.4 Application performance in breath and environment detection

The PAN/CoCl$_2$ sensors are highly desirable for various applications relative to humidity measurements. In this work, the novel humidity sensor was used in monitoring the human breath and the ambient humidity. The breath monitoring was to reflect the sensor sensitivity, while the ambient humidity monitoring was to reflect the durability.
As shown in Figure 4a, the PAN/CoCl$_2$ humidity sensor with high sensitivity performance were demonstrated in the application of breath monitoring. The sensor was placed under the nose, and the $R_o/R$ value was recorded during breathing. The exhaled and inhaled breath can change the humidity around the sensor and lead to the change of $R_o/R$ value. The breathing rate can be clearly distinguished from the number of peaks in the curves.

In order to invested the sensor durability in the application of real-time humidity monitoring, the PAN/CoCl$_2$ sensor was exposed in an ambient condition in Wuxi (East in China: East longitude of 120.299 and North latitude of 31.568) from the Beijing time 6-12 o’clock on 6th/Oct 2019. The
resultant I-V curve was shown in Figure 4b. It can be seen from the curve that the relative humidity decreased gradually from 6-12 o’clock. Thereafter, the humidity data were calculated using the current responses based on the following equation.

\[ y = -2.29104 + 0.07159 \times \]  

(1)

where y is the value of \( \log \left( \frac{R_0}{R} \right) \), x is the relative humidity. This equation is obtained from the data between RH 59 % and 75 %.

The data points of relative humidity was drown in Figure 4b in the form of red circles. We also got the humidity data (in form of black squares) of Wuxi on 6th/Oct 2019 from the official weather report website. It was found that the data points calculated using equation (1) were close to that of the official report.

4 Conclusions

In summary, electrospinning technology was used to fabricate nanofibers based humidity sensor, in which the PAN served as filament material, and CoCl\(_2\) was used to realize the colorimetric sensing property and enhance the overall electric sensing performances. The results proved that the PAN/CoCl\(_2\) nanofibers exhibited the colorimetric sensing capability and excellent electric humidity sensing performances, including high sensitivity and stability, which are attributed to the nanofibrous structure and the COCl\(_2\) can improve the efficiency of charge transfer. Furthermore, the present humidity sensor displays a high response over the range of RH 11%-95%, which is critical for the practical humidity measurement. In addition, it was also demonstrated to monitor human breath, and the ambient humidity. Therefore, the PAN/COCl\(_2\) nanofibers open a new avenue for the construction of high performance humidity sensors.

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