A flexible humidity sensor based on KC–MWCNTs composites

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Abstract

Multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) were dispersed in the biopolymer kappa-carrageenan (KC) to form a flexible composite via evaporative casting method. The glycerin was used as plasticizer to increase the flexibility of the composite. The KC–CNTs was examined by using FESEM and Raman, and then the humidity sensing properties of the samples were characterized under alternating current (AC). The purpose for using AC power supply is to avoid the possible polarization effect during measurements of the humidity properties. The experimental data exhibit that the fabricated sensors have high response to relative humidity (RH) with good repeatability, stability, and low hysteresis. A phenomenon that the impedance of the sensor decreases with ascending RH was also found and the basic sensing mechanisms were discussed.

Keywords: polymer kappa-carrageenan, carbon nanotube, flexible humidity sensor

1. Introduction

Carbon nanotubes (CNTs) have attracted many researchers due to their unique electronic, mechanical, optical and thermal properties which make them suitable for current and future application in nanotechnology [1-4]. Lighter, more flexible, and cheaper than conventional solar-cell materials, CNTs show promise for the application as solar cell. A recent application of CNTs is the promising candidate as novel humidity sensing materials owing to their large surface to volume ratio [5], high chemical inertness, nanoscale structure and hollow center [6, 7]. The measurement and control of humidity is quite important for the ticklish matters as water molecules are easily adsorbed on the surface of electronic equipment and finally damage them. A number of recent groups have reported the sensor based on Multi-walled carbon nanotubes (MWCNTs). Cao et al. [6] compared the humidity sensing properties of both untreated and chemically treated MWCNT thin films. It's found that the chemical treatment makes CNT shorten, more open ends, and more defects, which makes water molecules adsorb tubes easily and then improve the sensing performances. Liu et al. [8] presented a resistor-type humidity sensor based on deposited MWCNTs networks using AC dielectrophoresis between interdigitated electrodes on silicon substrate. The sensor exhibits as a promising humidity sensing material with good reversibility, high response and good linearity, etc. Karimov et al. [9] studied the humidity sensing properties of MWCNTs films fabricated with drop coating method on glass substrates. The sensing mechanism had been explained by the polarization effect. Zhao et al. [7] also investigated the effect of applied frequency on the impedance variation of the MWCNTs grown on glass substrate. Despite of the performance these sensors achieved, they are all based on inflexible substrates, which make them difficult to embed in integrated circuits. In contrast, the advantage of using flexible materials to build the humidity sensor is to make them less fragile and easy to integrate into human-friendly, flexible electronics. As for flexible sensor, Feng et al. [10] synthesized an flexible humidity sensor based on MWCNTs but the resistance of the sensor change according to the bending radius due to the different densities of

MWCNTs.

For humidity sensing measurements, the polarization effect frequently occurs under direct current (DC) circuit due to the existence of physisorption of water when relative humidity (RH) is high enough [11,12]. As an attempt to avoid the polarization effect, the response characteristic of the humidity sensor should be explored under alternating current (AC) testing.

This study provides the biopolymer kappa-carrageenan (KC) as the dispersant of carbon to build the KC-CNTs composite as an impedance-type humidity sensing material. The surface morphologies and the crystalline properties of the composite are analyzed by Field Emission Scanning Electron Microscope (FESEM), and Raman Spectroscopy. The proposed sensor exhibits a high performance during the humidity measurements. The mechanism of the humidity sensing is clearly discussed as capillary condensation and dielectric loss.

2. Experimental details

KC-CNTs films including KC-SWCNTs and KC-MWCNTs with or without glycerin (G) were prepared using evaporative casting method. The biopolymer KC is shown as a suitable dispersant for the stabilization of SWCNTs and MWCNTs in water, and the glycerin is used as a plasticizer to increase the flexibility of polymer films. The detailed preparing process has been reported previously [13]. In brief, solutions of KC were prepared by adding appropriate amounts of KC to Milli-Q water. Homogenous KC-CNTs dispersions were prepared by using a digital sonicator horn. Glycerin was added to KC-CNTs dispersions at a concentration of 0.25% w/v. Free-standing films were prepared by pouring the KC-CNTs composite dispersion onto a petri dish for drying under controlled conditions in a temperature-humidity chamber for 24 h. The resulting films were peeled off the substrate to yield uniform free-standing flexible films, as shown in Fig. 1. The size of the prepared sample depends on the size of the petri dish. In our case, the films with 5.5 cm in diameter, 0.2 mm in thickness are obtained, which are cut into small pieces with the area of 1 cm² for characterization of sensing properties. The detailed descriptions of the

components of 4 samples marked as A1-A4, respectively, are displayed in table 1, where the naming of the dispersion indicates the concentrations of biopolymer, CNTs and glycerin, i.e. KC 0.5–SWCNT 0.01–0.25G corresponds to dispersion with KC, SWCNT and G concentrations of 0.50 %w/v, 0.10 %w/v and 0.25 %w/v, respectively. Similar indications are suit to others.

The samples were characterized by FESEM and Raman. Humidity sensitive properties of the as-prepared sensors were investigated by recording their impedance response to RH at room temperature using a home-made equipment [14]. The samples are serially connected to a precise resistor and a power supply to form a voltage–current–resistor (V–I–R) electrical circuit to monitor the variation of the sensor’s electrical property. In this work, we applied an AC power supply (1 V, 1 MHz) to avoid any possibility of polarization effect that usually happened in humidity sensing characterization process. The variation of sensor’s impedance was estimated based on the measurement of the voltage drop across the precise resistor according to the formula: $\frac{Z_{\text{sensor}}}{R_{\text{precise}}} = \frac{V_{\text{sensor}}}{V_{\text{precise}}}$, where the Z_{sensor} , R_{precise} , V_{sensor} and V_{precise} are the impedance, resistance and voltage drop across the KC–CNTs based sensors and the precise resistor, respectively. The flexible samples were fixed directly on a silicon platform with two ends of the samples sandwiching by two copper sheets as electrodes.

3. Results and discussions

3.1. Characterizations of the KC–CNTs

Fig. 2 shows the images acquired using a JEOL JSM-7500F Field Emission Scanning Electron Microscope. Samples were prepared by mounting small pieces of films onto a brass stage using double-sided conductive carbon tape. CNTs with diameters about 10 nm (A1, A2) and 5 nm (A3, A4) were observed in all samples. The background of the CNTs is KC (A1, A3) and KC-G (A2, A4), respectively. It have been will know that film porosity plays an important role in detecting ambient gases. In this case, the MWCNTs A1 and A2 are more porous because the surface area of

inner wall is larger for the SWCNTs A3 and A4.

Fig. 3 show the Raman spectra of the KC-CNTs. Characteristic peaks are identified in the Raman spectra between 1000 and 2000 cm^{-1} . The one at around 1340 cm^{-1} called the D band is associated with disorder allowed zone edge modes of graphite that became Raman active due to the lack of long range order in amorphous carbon based materials. The G band at around 1590 cm^{-1} corresponds to the G line associated with the optically allowed E_{2g} zone centre of crystalline graphite [15]. Two separated G band were observed in KC-SWCNTs which are called G+ and G- band, respectively. It is also noted that the Raman signal ratio I_D/I_G of KC-MWCNTs is much stronger than that of KC-SWCNTs.

3.2. Humidity sensing properties of the KC-CNTs

To investigate the sensing properties, such as: selectivity, responsivity, reproducibility, and stability, the static and dynamic testing of the sensor device at different RH were performed. The temperature of the chamber remained unchanged at room temperature ($\sim 25^\circ\text{C}$), and provided different humidity levels in incremental steps. Each step was maintained at constant parameters until the voltage reading reached a steady value to make sure the corresponding impedance change was correctly monitored. The humidity response (S) is defined by the following formula: $S = (Z_0 - Z_h) / Z_0 \times 100\%$, where Z_h refers to the impedance at certain humidity and Z_0 represents the original resistance of the sensors at air of 10% RH. The preliminary results are shown in Fig. 4 where KC is one as carrier with flexibility. But the effect of KC can be ignored because KC polymer without CNT or with very few CNT is a completely insulate material with huge resistance. KC does not have contribution for conductive properties but just a carrier for CNTs and water molecule. The obtained KC-CNTs composite films show almost linear response of the fabricated sensor to RH over the range of 10-90%. The KC-MWCNTs films display high response comparing to the corresponding KC-SWCNTs films, and the response is slightly reduced upon incorporation of glycerin over the RH range from 10 to 90%.

Due to much defects on the KC-MWCNTs, vapor molecules can be easily adsorbed and diffused, which contributes to the high response. Consequently, the KC-MWCNTs composite based sensor shows the highest response, as exhibited in Fig. 4. Therefore in the following characterizations, we would mainly focus on this sample.

Fig.5 shows the typical I-V characteristics of the films A1 based sensor in different static air of 30-90% RH at room temperature. The KC-CNTs resistor shows a good ohmic contact with the copper electrodes. The different impedance is constant over the supply voltages. From experimental data shown in Fig.5, it can also be found that the impedance of the sensor decreases with the increase of RH in air. This is in good agreement with the results shown in Fig.4.

The characterization of response of the fabricated humidity sensor to different gases including ammonia, gas, hydrogen gas, and methane gas were also conducted at room temperature in the home-made calibration chamber [14]. No obvious variation of the impedance was observed, indicating its poor sensitivity to the selected gases. In general cases, the obtained response of the sensor to (35%) humidity is more than 7 times higher than the target gases with 100 ppm concentration, from which we can conclude that the fabricated sensor has high selectivity to humidity.

The response-recovery property of the present humidity sensor is shown in Fig. 6. When the sensor in an ambient of RH= 20% was exposed to RH= 80% air, the resistance of the sensor promptly decreased and then reached a relatively stable value. When the humidity was switched back to 20%, the resistance abruptly increased and gradually reached a relatively stable value. Further testing after three additional cycles indicates that the sensor has good reproducibility. This indicates that the interaction between water vapor and KC-MWCNTs networks is mainly dominated by physisorption in a weak bond. Moreover, the dynamic response shows that the impedance at a given humidity is identical.

The humidity mechanism of the resistor-type CNTs have been well established [16–18]. The CNTs network shows global p-type semiconducting behavior, and holes are the dominated electrical carrier [19]. The H₂O molecules adsorbed on the surface

behave like electron donors. An increase in humidity results in a reduction of hole density of the p-type nanotubes and thus decreasing the conductance of the sample. Besides the electron donation model, other humidity sensing mechanisms have also been proposed: one is the hydrogen bonding on the oxygen defect sites present on the nanotubes; another one is the possible introduction of charge traps on the nanotubes arising from direct adsorption of water molecules on the substrate [16]. But in our case, the conductance increase with the increasing RH, which implies the possibility of some other mechanism. For example, the distribution of CNTs may be not continuous and the conductivity is resulted from channel effect. After water molecules are adsorbed on to the surface of KC-CNT, the channel effect is enhanced, resulting in an increase of conductivity of material.

The similar results has been reported by Zhao et al.[7], and the phenomenon that the conductance increases with the rising RH level can be interpreted by dielectric physics and capillary condensation [20]. MWCNTs are the highly porous 3D structures, which can be regards as the framework and the capillary condensation can take place in them and fewer vapors molecules from a lower RH level are required to saturate in these pores and induce vapors to condense into water. At humidity environment, the physisorbed water molecules on the carbon film surface have dipole moment [21, 22], the equivalent circuit of the sensor under humidity environment can be consider as a parallel combination of a resistance component of sensor material: a resistance component of physisorbed water and then a capacitance component of physisorbed water. Considering the contact conductance G_0 , circuit model of the sensor can be depicted in Fig. 7. G_0 and G_1 denote two frequency independent conductance, and $G_{(\omega)}$ is frequency dependent conductance in parallel with a capacitor C. Then the sensor resistance R is:

$$R = \frac{1}{G_0} + \frac{1}{G_1 + G_{(\omega)}} = \frac{1}{G_0} + \frac{1}{G_1 + \frac{A\omega^2}{(1 + \omega^2\tau^2)}} \quad (1)$$

where A is a constant coefficient, ω is the angular frequency, and τ is molecular

relaxation time. In general, the dielectric capacitance of water is always higher than air. Therefore, the relaxation strength and the dielectric constant of the sensing film increases when capillary condensation happens in the porous nanostructures of MWCNTs film. Correspondingly, the conductance would increase when RH level ascends. This is because the parameter of $G_{(\omega)}$ is proportional to the relaxation strength [7]. Actually, if we functionalized the CNT, more porous and open ends will appear than that of the pristine CNT, the capillary condensation would happen in bigger area for the functionalized CNT. Consequently, the functionalized CNT would have a better sensing performance than that of the pristine CNT. So, our future work will focus on the functionalization of CNT to achieve better performance.

Fig. 8 shows the humidity hysteresis characteristics in adsorption and desorption process of the as-prepared humidity sensor. The moisture absorption started from 20% RH and ended at 90% RH with incremental steps of about 10%, and then dehumidified to 20% RH again. The maximum humidity hysteresis is about 3.99% under 60% RH for our sensor. The narrow hysteresis loop indicates that the rate of adsorption process of the water has almost the same rate with the desorption process of water. The impedance of the sensor decreases almost linearly with an increase RH about three times changing in the resistance during the RH variation of 20–90%.

Fig.9 shows the long-term stability of the sensor under air with different RH. The impedance-RH characteristics of the humidity sensor were measured everyday at the same time. One can clearly see in Fig. 9 that the gas response changes slightly and keeps at a nearly constant value during the long experimental cycles, which confirms the excellent longtime stability and repeatability of the prepared sensor. It is needed to mention here the sensitivity, response/recovery time, and transient behaviors are coincident for bent and flat KC-MWCNTs sensor devices. The main reason is that the carbon nanotubes are dispersed uniformly in the biopolymer kappa-carrageenan to form a flexible and homogenous composite so that the sensing surface area won't be changed when the sensor is bent. All the performances above indicate KC-MWCNTs based sensor could be a good candidate for long-term humidity sensor.

4. Conclusions

We have successfully synthesis flexible KC-MWCNTs and KC-SWCNTs composites by evaporative casting method. The samples' sensing properties were then measured at room temperature by applying a U-I-R circuit with AC power supply to avoid the as-known polarization effect. The KC-MWCNTs show better sensing performance than the KC-SWCNTs due to the more defects. I-V characteristics of the KC-MWCNTs indicate the ohmic behavior of the sample. The KC-MWCNTs exhibit selectivity to moisture air with high response. Fast and reversible changes in the impedance have been measured as the RH is varied. A slight hysteresis has been recorded, with a maximum variation of 3.99%. A 40-days long-term measurement at 20%, 50%, 80%, and 90% RH environments demonstrates the good stability of the developed sensor. The conventional mechanism for carbon to humidity air, i.e., electron donation model, is not suitable to the MWCNTs for the conductance of the MWCNTs decreases with the ascending RH. And the dielectric physics and capillary condensation were introduced to explain the humidity sensing mechanism.

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Table caption

Table 1. Sample information. The naming of the dispersion indicates the concentrations of biopolymer, CNTs and glycerin, i.e. KC 0. 50–SWCNT 0.10–0.25G corresponds to dispersion with KC, SWCNT and G concentrations of 0.50 %w/v, 0.10 %w/v and 0.25 %w/v, respectively.

Figure captions

Fig. 1. (a) Poured the composite dispersion onto a petri dish for drying, (b) KC and KC–CNT films, (c) Flexibility of the film, (d) A 1 cm×1 cm piece of KC–CNT films for sensing test.

Fig. 2. FESEM images of (A1) KC–MWCNTs, (A2) KC–MWCNTs–G, (A3) KC–SWCNTs, (A4) KC–SWCNTs –G prepared by evaporative casting methods.

Fig. 3. Raman spectroscopy of KC–CNTs films prepared by evaporative casting methods.

Fig. 4. Humidity sensing properties of KC–CNTs composite films based sensors.

Fig. 5. I–V characteristics of the KC–MWCNTs based sensor in different static RH atmosphere from 30% to 90% RH at room temperature.

Fig. 6. Response–recovery property of the KC–MWCNTs based sensor to dynamic switches between 20% and 80% RH.

Fig. 7. The equivalent circuit of the KC–MWCNTs based humidity sensor.

Fig. 8. Absorption-desorption behavior of KC–MWCNTs based sensor under different humidity conditions.

Fig. 9. The long-term stability of KC–MWCNTs based sensor at room temperature.

Film	Dispersion
A1	KC 0.50 – MWCNT 0.10
A2	KC 0.50 – MWCNT 0.10 – 0.25 G
A3	KC 0.50 – SWCNT 0.10
A4	KC 0.50 – SWCNT 0.10 – 0.25 G

Table 1

Figure

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