บทความวิจัย

DEVELOPMENT OF HUMIDITY SENSOR USING SEMICONDUCTING ORGANIC POLYMER IN CELLULAR FORMS

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ABSTRACT

Humidity sensor was developed in cellular forms using semiconducting organic polymer. Poly (3,4-ethylenedioxythiophene) : polystyrene sulfonate (PEDOT:PSS) was the key material that played the important role in the humidity sensing. It was embedded in the structure of melamine foam by dip and dry process for thin film formation. In order to distribute PEDOT: PSS film in the cellular structure, LF-221 surfactant was added in the PEDOT : PSS solution and the concentration of surfactant was varied. The impedance and capacitance responses were observed in different relative humidity, and the results revealed that the relative humidity response of the obtained sensor depended on the concentration of surfactant. The appropriate concentration should be in the range of 0.1% - 1%. Moreover, the results showed that the frequency of electrical measurement affected the dynamic switch behavior for humidity sensing. The frequency of 1 kHz is the best values for electrical measurement. The results of electrical measurement indicate that the obtained sensor from PEDOT:PSS in a cellular form has potential to be a humidity sensor in the capacitive mode more than the resistive mode due to the better in humidity response and dynamic switch behavior for humidity sensing.

Keywords: humidity sensor, cellular form, PEDOT : PSS, melamine foam

Introduction

The moisture is an essential thing in the human's life and many activities. Therefore, the way how to control and monitoring humidity is interesting for benefit from it. A humidity sensor is the best for measuring, detecting and sensing in moisture content. The most common types of humidity sensors are the relative humidity (RH) sensors that based upon organic and inorganic materials. Moreover, the fabrication technologies of humidity sensors are various types such as conventional ceramic/semiconductor processing, thick film, thin film, p-n heterojunction and etc. that determine the working principle and properties of the sensor. Dunmore (1938) developed an electrolytic humidity sensor based on lithium chloride (LiCl) in 1938. A porous medium was used as the supporting material that was immersed in a humidity sensitive partially hydrolyzed polyvinyl acetate which was impregnated with LiCl solution. The conductivity of the sensor was changed and the amount of humidity detected by absorbing the atmospheric water vapors via the porous medium. Salehi et al. (2006) reported that the porous humidity sensor exhibited higher humidity sensitivity than the nonporous counterparts. So, the porosity that associated with the concept of surface area is the important parameter for the humidity sensing. Generally, an inorganic humidity sensor is not easy to process and high production cost. Therefore, the organic polymer is then a candidate which is the low-cost and simpler in fabrication process. The fundamental working principle of organic polymer humidity sensor can be both the resistive-type and capacitive-type categories.

The review of Farahani et al. (2014) mentioned that this classification was based upon the sensing mechanism in which the prior one contained polyelectrolytes respond to water vapor variation by changing their resistivity, while in the latter humidity was measured based on the variation of the dielectric constant of the polymer dielectrics and hence changed in capacitance. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is a semiconducting organic polymer that have been extensively used for various applications such as, light emitting diodes (Dai el at., 2014), sensors (Aziz el at., 2015), and solar cells (Ho el at., 2016). PEDOT itself is an insoluble polymer but it becomes aqueous if it is synthesized in the presence of poly(4-styrenesulfonate) (PSS). PEDOT is used as a hole injection layer in organic electronics by doping PSS and the change of conductivity depending on the environmental conditions such as humidity and temperature.

Kuş et al. (2009) studied the effect of relative humidity on DC and AC electrical resistivity of PEDOT:PSS film for humidity sensor applications. They reported that the resistivity of the sensor increased in accord with RH up to 80% and then it started to decrease when the moisture goes above it. The reproducible humidity detection could be observed by cyclic humidity conditions between 40% and 80% RH that showed the stability of sensor in both DC and AC resistivity. The simply way to test the humidity sensor, Feng el at. (2015) used seven kinds of saturated salt solution which were utilized to control the environmental humidity. Their free-standing films of graphene oxide humidity sensor was put inside the top of sealed glass container for humidity sensing measurement. The covered beaker with the different kinds of saturated salt solution placed at the bottom of container and then the electrical measurement was carried out by ohmmeter. By this method, the humidity sensing of the sensor could be determined by the dynamic switch behavior. As mentioned above, the surface area is a key of the humidity sensing, so the structure of foam is probably used as supporting material. Because of the open-cell and the three-dimensional network structure, the melamine foam is used as the scaffold for PEDOT:PSS thin film formation and also advantage in surface enhancement. The properties of this foam are light-weight, flame and chemical resistance, wide operating temperature range and thermal insulation.

In this work, we are interested in inventing the humidity sensor in the form of foam. The prototype of humidity foam sensor has been built up by embedding PEDOT : PSS thin film in cellular network of melamine foam that utilized as humidity sensing material. After that, the preliminary results of this device have been demonstrated. In the first, the concentration of surfactant is investigated for studying the effect of surfactant to humidity sensing behavior. The appropriate frequency is determined for electrical measurement. The stability of humidity foam sensor is inspected by repeating cyclic humidity conditions. In the last, the category of the obtained humidity foam sensor is identified.

Methods

The melamine foam (Basotect®) was purchased from BASF that used as scaffold for surface enhancement and humidity sensing thin film network. The size of 3x3x3 mm^3 melamine foam were prepared by CO_2 laser cutting machine. Prior to dip coating process, the processes of ultrasonic cleaning in deionized (DI) water and drying in an oven were followed for removing ashes and water. The mixture of PEDOT : PSS (Clevios™ PH 1000) solution, obtained from Hereaus, and Plurafac® LF-221 nonionic surfactant, purchased from Thanant chemical, were used as the humidity response material that embedded within the structure of melamine foam. The concentration of surfactant was varied from 0 to 5 vol%. The melamine foams were dipped into PEDOT : PSS aqueous solution for 10 minutes, then removed and dried in a drying oven at 80°C for 1 hour and 100°C for 1 hour. The electrodes of sensor were painted with silver paste and dried at 100°C for 30 minutes. For electrical measurement, the copper plates and the electrodes of sensor were connected with solder paste and wired with copper wires.

For characterization method, the humidity responses were demonstrated by switching the humidity environments and measured the electrical responses by precision LCR (inductance, capacitance and resistance) analyzer (Keysight, Model E4980A). The humidity environments were prepared in the closed system by silica gel, air at the room temperature and saturation salt solutions as shown in Table 1. Each system was contained in the sealed glass bottle at the bottom. The sensor was put inside the covered bottle in the area of the air over silica gel or saturation salt solutions and then the electrical measurement was started for testing the response of the sensor. The sensor was switched between the desired humidity environment and the humidity baseline that used the silica gel as the substance for two aims, humidity environment 10% RH and moisture desorption. The electrical response was measured in each relative humidity system for 5 minutes. Firstly, the relative humidity system at 90% was selected for determining the appropriate concentration of surfactant, the suitable frequency of electrical measurement and the repeatability of the sensor. In the step of finding the appropriate surfactant concentration, the frequency of LCR meter was set at 50 Hz for resistance measurement. After that the frequency was changed from 50 Hz to 1 kHz and 100 kHz for frequency dependent verification. The stability of the sensor in both resistance and reactance responses were observed by repeating cyclic humidity conditions between 10% RH and 90% RH about 12 times. The correlation between dynamic response behavior and relative humidity were performed in the last step by putting the sensor into the different humidity system and then carried out the data by resistance and capacitance measurements.

Table 1 Relative humidity systems were prepared by the different substances

Substances	Amount	Relative Humidity (RH)
1. Silica gel	60 g	~ 10% RH
2. Saturation LiCl soln	84.25 g / 100 ml	~ 20% RH
3. Atmospheric air	-	~ 40% RH
4. Saturation KNO3 soln	36 g / 100 ml	~ 50% RH
5. Saturation KCl soln	34 g / 100 ml	~ 60% RH
6. Saturation NaCl soln	35.9 g / 100 ml	~ 70% RH
7. Deionized water	100 ml	~ 90% RH

Results and Discussions

The humidity response of PEDOT : PSS in melamine foam was tested by measuring the electrical parameters such as resistance, reactance and capacitance as a function of time. The cyclic humidity condition was applied to this measurement for observing the response behaviour. Figure 1 shows the humidity responses of different surfactant concentrations of PEDOT : PSS foam sensor in the term of resistance. These results are obtained from the same batch of fabrication for comparing the responses. The results reveal that the characteristics of resistance of the samples fabricated without and with 5% LF surfactant change via cyclic humidity condition do not clearly present the cyclic response via humidity switch. The tendency of resistance changes of the sample without surfactant is increasing as seen in Figure 1(a) while the tendency of the sample fabricated with 5% LF surfactant is decreasing as shown in Figure 1(e). On the other hand, Figure 1(b) - (d) exhibit the characteristics of humidity responses of the samples fabricated with 0.1% - 1% LF surfactant that show the repetition pattern and constant changes in resistance. By these results, they can be summarized that the suitable concentration of surfactant that will promote the distribution of PEDOT : PSS thin film formation in the structure of foam are in the range of 0.1% to 1%. Moreover, the effect of surfactant can reduce the resistance of device that can be obviously observed in Figure1

Since, the results of resistance responses in Figure 1 were set the frequency of measurement at 50 Hz due to the concept of household frequency. To study the effects of frequency on measurement, the frequency of LCR analyzer was varied from

50 Hz to 100 kHz and the sample which 0.5% LF surfactant concentration was chosen to prove it. The results of verification are shown in Figure 2. For observing this effect, all samples were prepared in the new batch for comparison. The characteristics of changes in resistance of all frequency depict the cyclic response patterns and repetition. The patterns of resistance changes of frequency 50 Hz (in Figure 2(a)) and 100 kHz (in Figure 2(c)) are similar but the pattern of frequency 1 kHz is different, as shown in Figure 2(b). The difference of them is a sharp spike observed on each humidity cycle during 10% RH and 90% RH. In addition, it is found that the frequency at 1 kHz performs the pretty pattern of resistance responses and the baseline of humidity at 10% RH is not fluctuation. So, the appropriate frequency for obtained humidity foam sensor is 1 kHz. After this experimental results, this frequency is applied to measure the electrical properties at different conditions. Moreover, the results of changes of frequency 50 Hz between the new batch (Figure 2(a)) and the old batch (Figure 1(c)) are different. This difference can be used to confirm that the low frequency is not appropriate for measurement.

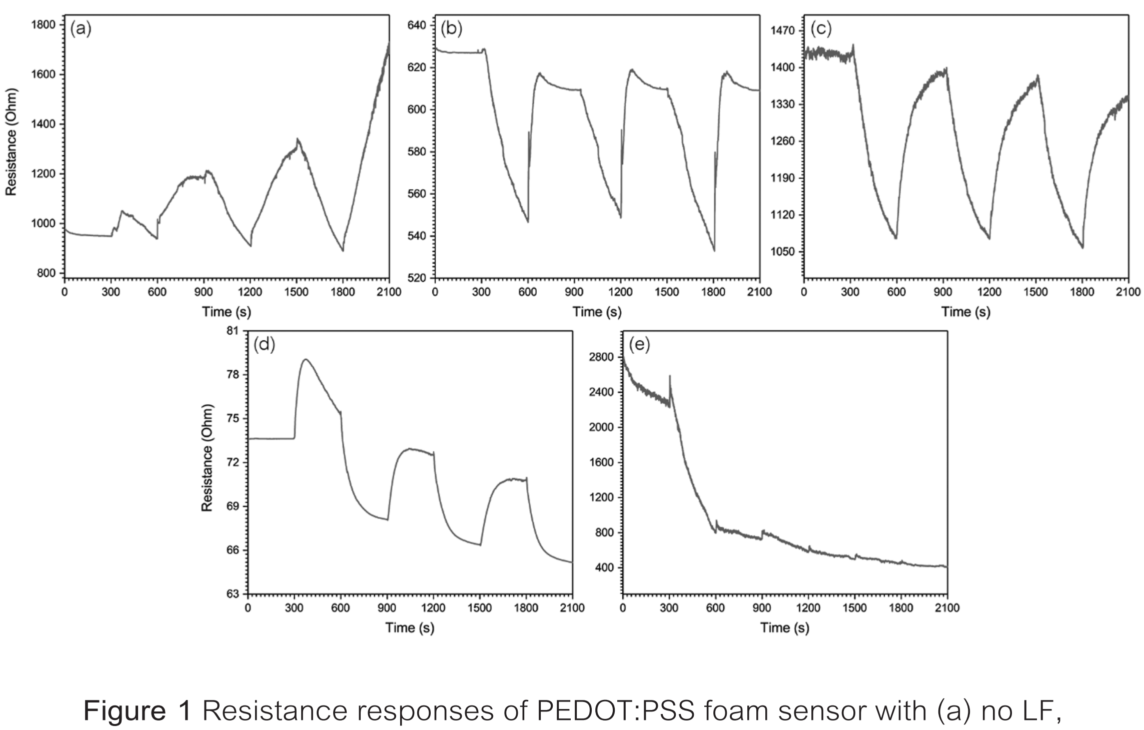

Figure 1 Resistance responses of PEDOT:PSS foam sensor with (a) no LF, (b) 0.1% LF, (c) 0.5% LF, (d) 1% LF, and (e) 5% LF to cyclic humidity conditions between 10% RH and 90% RH at frequency 50 Hz.

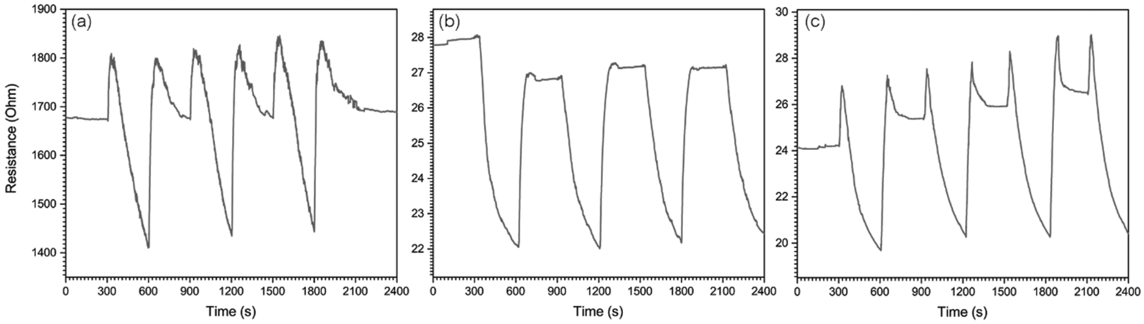

Figure 2 Resistance responses of PEDOT:PSS foam sensor with 0.5% LF to cyclic humidity conditions between 10% RH and 90% RH at frequency (a) 50 Hz, (b) 1 kHz, and (c) 100 kHz.

The stability of the samples fabricated with 0.1% - 1% LF was verified in both resistance and reactance responses by repeating cyclic humidity measurement between 10% RH and 90% RH. The results of resistance and reactance cyclic responses as a function of time are exhibited in Figure 3 and Figure 4, respectively. The resistance cyclic responses of the samples fabricated with 0.1% and 0.5% LF surfactant give a better response than the sample fabricated with 1% LF surfactant. Because the deviation of changes compared with the difference of resistance changes due to humidity switch of the prior foam sensors is low and the level of the baseline is nearly constant whereas the latter shows the higher deviation and the level of baseline is increasing. In results of the reactance cyclic responses, all samples perform the changes in negative value that associated with the capacitance and the stability of changes is better than the resistance. So, the obtained humidity foam sensors should be applied as capacitive-type sensor more than resistive-type sensor. However, the changes in resistance and reactance via humidity switch as a function of time of all samples are almost constant and the deviations of these changes are low when they are compared with the values of changes. The average values of the changes in both resistance (ΔR) and reactance (ΔX) via humidity switch between 10% RH and 90% RH and the values of standard deviation are shown in table 2. It can be mentioned that the obtained humidity foam sensors fabricated with 0.1% – 1% LF surfactant are stable and can be applied in both resistive and capacitive modes.

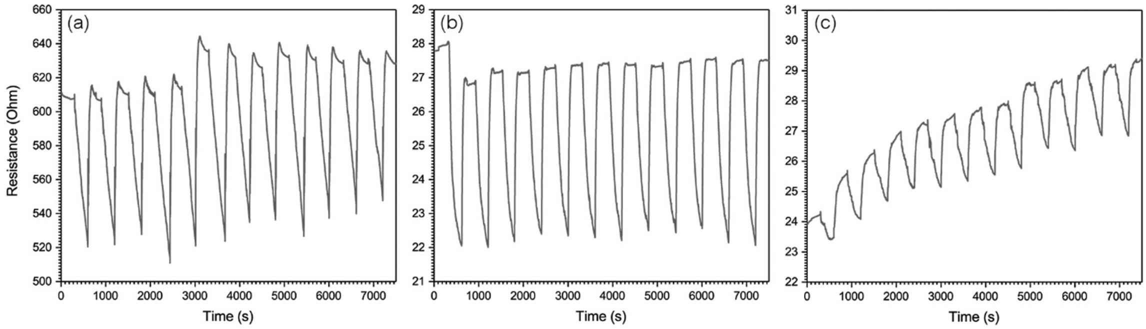

Figure 3 Cyclic responses of resistance of PEDOT:PSS foam sensor with (a) 0.1% LF, (b) 0.5% LF, and (c) 1% LF as a function of time between humidity condition 10% RH and 90% RH at frequency 1 kHz.

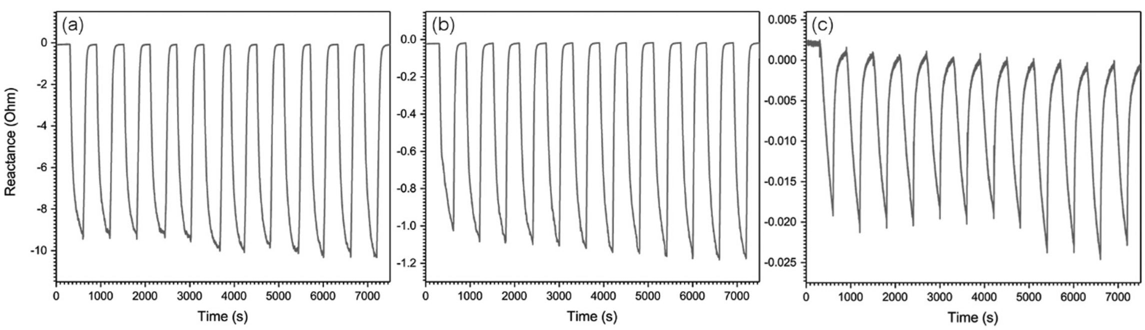

Figure 4 Cyclic responses of reactance of PEDOT:PSS foam sensor with (a) 0.1% LF, (b) 0.5% LF, and (c) 1% LF as a function of time between humidity condition 10% RH and 90% RH at frequency 1 kHz.

Table 2 Average value and standard deviation of the change in resistance and reactance via the humidity switch between 10% RH and 90% RH for 12 times

Surfactant concentration	ΔR (Ohm)	ΔX (Ohm)
0.1% LF	87.85 ± 6.76	9.50 ± 0.35
0.5% LF	5.02 ± 0.25	1.09 ± 0.05
1% LF	3.17 ± 1.19	0.037 ± 0.004

In order to test humidity responses directly on resistance and capacitance measurements, the samples fabricated with 0.1% - 1% LF surfactant were examined in various humidity conditions. Figure 5 shows the correlation between the relative humidity and the resistance responses as a function of time. It is found that the characteristics of resistance of 0.5% and 1% LF addition demonstrate the better response than 0.1% LF addition. The evidence that indicates the bad responses of the samples fabricated with 0.1% LF surfactant is the variation of the baseline at 10% RH as seen in Figure 5(a). This variation may be the cause of unreliable responses. When the characteristics of the humidity changes are specified in the resistance responses between Figure 5(b) and Figure 5(c), they can be suggested that the sample with 1% LF surfactant should be applied as resistive humidity sensor than 0.5% LF surfactant. Because the changes in resistance values of 1% LF addition when the relative humidity of the system is increased and then goes back to the beginning are almost the same values but the values of 0.5% LF addition are not. Moreover, the sensitivity of the sample with 1% LF surfactant shows the humidity responses started from 40% RH faster than the samples with 0.1% and 0.5% LF addition that respond at above 40% RH. The results of capacitance responses that shown in Figure 6 manifest inversely. The characteristic of 0.1% LF addition as seen in Figure 6(a) reveals the best responses in the changes of relative humidity. The level of the baseline is constant and the levels of the changes in each relative humidity are the same when they are increased and then go back to the original. The characteristic of 0.5% LF addition in Figure 6(b) performs the better response than 1% LF addition as shown in Figure 6(c). The characteristic of 1% LF addition is noisy that is difficult to utilize as the capacitive humidity sensor. The sensitivity of 0.1% or 0.5% LF addition in capacitance responses is more quickly than 1% LF addition. The humidity response of the lower surfactant concentration starts at the humidity about 40% RH while the higher concentration senses to humidity at the greater than 40% RH. From all discussions, they can be summarized that PEDOT : PSS fabricated with 1% LF surfactant should be utilized as the resistive-type humidity foam sensor while 0.1% LF addition should be applied as capacitive-type sensor. On the results of dynamic switch behavior, they can be confirmed that the device could be classified in capacitive category.

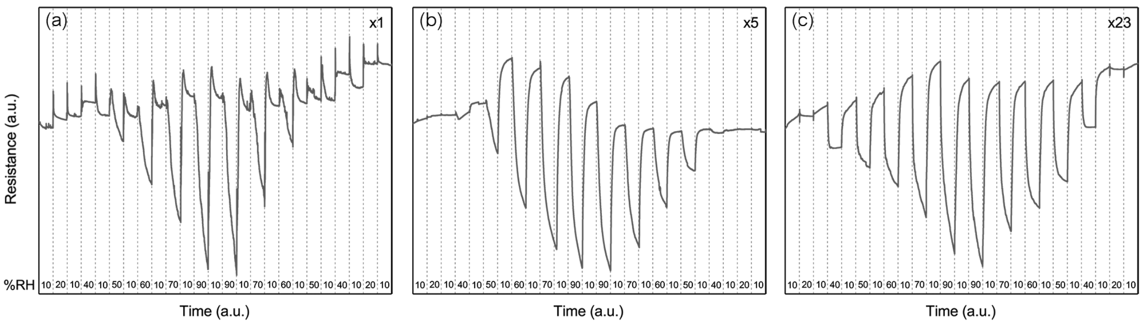

Figure 5 Relationships between resistance and relative humidity of PEDOT:PSS foam sensor in different concentrations of surfactant (a) 0.1% LF, (b) 0.5% LF, and (c) 1% LF at frequency 1 kHz.

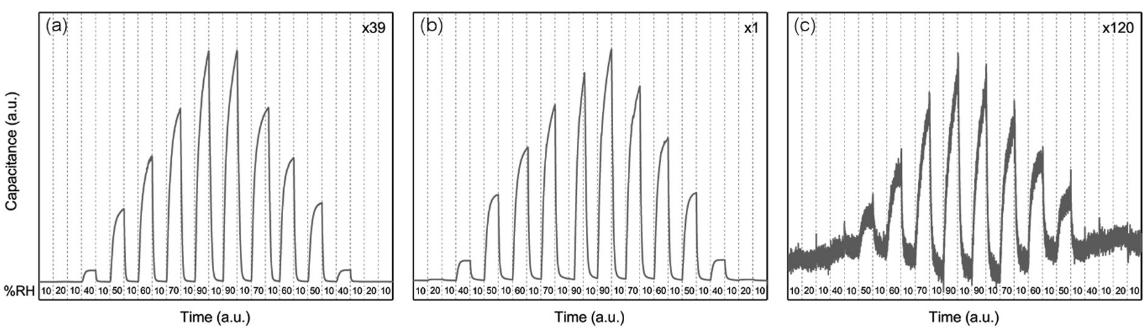

Figure 6 Relationships between capacitance and relative humidity of PEDOT:PSS foam sensor in different concentrations of surfactant (a) 0.1% LF, (b) 0.5% LF, and (c) 1% LF at frequency 1 kHz.

Conclusions

The addition of surfactant plays the necessary role in a cellular form of humidity sensor which required to help in distribution and adhesion of semiconducting polymer PEDOT:PSS thin film within the melamine foam structure. The suitable concentration of surfactant is in the range of 0.1% to 1%. In addition, a frequency of electrical measurement is a key factor that affects to the response of humidity sensor. The appropriate frequency is 1 kHz. From the results, it can be concluded that the humidity sensor made from melamine foam has a responsibility to relative humidity in the resistive and capacitive modes. The moisture content which is trapped by PEDOT : PSS thin film polymer in the foam structure is the causes of change in the value of resistance and dielectric constant. The PEDOT : PSS with 1% surfactant addition should be candidate for resistive-type humidity sensor application while the capacitive-type sensor should be PEDOT : PSS with 0.1% surfactant addition. However, a suitable application for humidity foam sensor should be selected in the capacitive form.

Acknowledgements

The authors gratefully acknowledge the Integrated Nanosystem Laboratory (INS), National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA) for the access to the equipment and facilities, and would also like to thank our senior project students, Phanwira Kaewkrajang and Sirilak Chana, for their helps in this work.

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