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Humidity Sensing Material Based on Doped Polyaniline

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ABSTRACT

Functional gas sensors should have main properties of high sensitivity/selectivity, fast response, and repeatability. Most of the commercial gas sensors conform to the above advantages, but the drawbacks of these sensors are expensive, hard fabrication, and operated at high temperature. The Fe-Al doped polyaniline (PANI) based humidity sensor is developed to overcome these obstacles. The PANI was chemically synthesized by copolymerization of aniline and formaldehyde. Then the advisable concentration of Fe and Al salts act as dopants to make the doped PANI specific for vapor sensing. Furthermore, the fabrication of Fe-Al doped PANI thin film on the golden interdigitated electrodes was simple to use drop-coating method. The developed humidity sensor was accomplished. The fabrication processes and optical characterization, surface morphology, and sensing properties which are investigated at room temperature are reported here.

Keywords: Polyaniline, Humidity, Vapor, Sensor

1. INTRODUCTION

The humidity sensing has been one of the most important functions for both living and manufacturing environmental monitoring [1-3]. Besides, asthma may be triggered by moist air and dust mites surround us. A necessary condition for dust mites growth is sufficient relative humidity about 75% to 80%. If we can measure and control relative humidity less than 60%, dust mites will become dormant and may die to reduce the asthma morbidity. Therefore, many novel materials and processes have been developed to investigate the humidity sensing. There are many kinds of humidity sensors, such as ceramic humidity sensors [4-6], semiconducting humidity sensors [7-8], and conducting polymer-based humidity sensors [2, 3, 9-19], etc. Ceramic humidity sensors based on Al_2O_3, TiO_2, SiO_2, and spinel compounds which show very high sensitivity, fast and linear response and long term stability. But these kinds of sensors are temperature-dependent, energy wasting, hard fabrication, expensive and hard to miniaturize [1-2]. Humidity sensors based on semiconductor, such as In_2O_3 and ZnO, which show high sensitivity, selectivity and fast response but require high temperature operation and consume a lot of power. As the consequence, these kinds of sensing devices suffer from high power consumption and long set-up time. In addition, they are also relatively complicated from the point of fabrication process. To overcome these obstacles, a novel humidity sensing materials based on doped-PANI is developed in this work. Polymer-based humidity sensors have attracted much attention because of its flexibility, simplicity of fabrication, and low cost [10]. Conducting polymers such as polyaniline (PANI), polypyrrole, and polythiophene, etc are widely used in many aspects, including various gas sensors. Among the different conducting polymers, PANI is one of the promising candidates because of its environmental stability, ease of synthesis and directly doping by protonic acids [10, 14]. The conductivity, sensitivity, and selectivity of PANI can be easily controlled by modification the doping level and the dopants species of the base polymers [2, 3, 9-19]. In Specific, we will report the fabrication processes of the PANI based thin films humidity sensor which has been estimated for electrical characterization, sensitivity, selectivity, response time, repeatability, and temperature response.

2. EXPERIMANTAL SECTION

The fabrication processes of PANI thin films humidity sensor divide into two parts.

The formation of precipitate

All the chemicals were used without purification. To add aniline (ACROS 99%) monomers to hydrochloric acid (10M) which was diluted with deionized water. Then add formaldehyde (ACROS 37%) to this solution and add ferric chloride (ACROS 98%) and aluminum chloride (ACROS 99%) solution with specific concentration. This is the most important step because the metal ions as the dopants can affect the selectivity of analyte [10, 12, 13, 16]. The PANI was chemically synthesized by copolymerization of aniline and formaldehyde. The process is shown as Fig. 1. Then the deep red precipitation was obtained after the solution of copolymer was poured into 10% NaOH solution and stirred for 1 hour [12, 13]. Subsequently, the precipitation was washed with distilled water to prevent etching the electrodes.

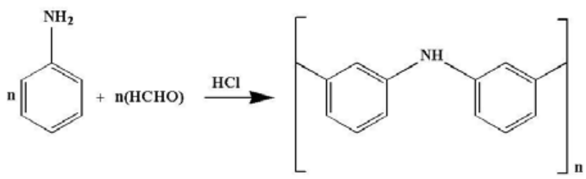

Fig. 1. Copolymerization of aniline and formaldehyde

Preparation of thin films

To use the drop-coating method to drop the precipitation on the golden interdigitated electrodes which was coated chromium 300Å and aurum 1200 Å by E-gun evaporator on the glass substrate. The interdigitated electrodes structures are showed in Fig. 2. The width of the golden electrodes was 0.2cm and the gap between two electrodes was 0.3cm. Then the humidity sensor was already prepared.

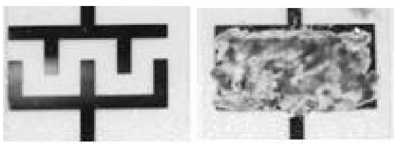

Fig.2. Interdigitated electrodes. (a) without PANI, (b)with PANI

3. RESULTS AND DISCUSSION

3-1. Characterization of undoped and Fe-Al doped PANI

To examine the structure of the undoped and Fe-Al doped PANI materials, the FTIR spectra of the precipitation was observed and shown as Fig. 3. The basic conjugated structure of Fe-Al doped PANI is close to undoped PANI. The peak around 3460-3490 cm^{-1} conformed the presence of amino group. A strong peak at 1600 cm^{-1} is characteristic of C=C in benzene ring. The result implies that the influence of dopants on basic structure of Fe-Al doped and undoped PANI unapparent.

To analyze the surface morphology of PANI before and after doping Fe-Al, scanning electron microscopy (SEM) is used to scan and capture the surface of the precipitation. The surface morphology of the undoped and Fe-Al doped PANI is shown as Fig. 4(a) and Fig. 4(b). This observation indicates that the surface morphology changes from compact slice to irregular porous structure.

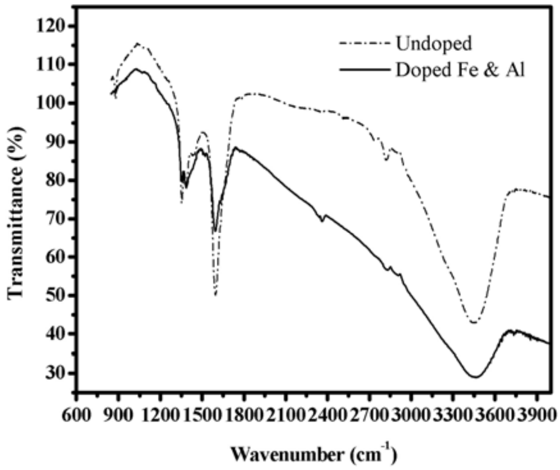

Fig. 3. The FTIR spectra of undoped(···) and Fe-Al doped(—) PANI.

3-2. Sensitivity

There are two speculated sensing mechanism as following: the stable resonance structure of the analyte and the amine nitrogen of the PANI transfer the electron to each other [10, 11]. Another was explained as the reduction of the barrier height at intercrystallite boundaries when PANI was exposed to vapor [12, 13]. Consequently, the surface potential and barrier height are reduced, which increases the electrical conductivity.

To demonstrate the sensitivity characteristics of the developed humidity sensor, the device is placed in the controlled environment which to fix at room temperature 24℃ and bias at 3V. As the device exposed to the different relative humidity (RH), the current flowing through the doped PANI thin film is measured by Keithley 6485 pico-ammeter and the results are plotted in Fig. 5. It clearly illustrates the device current has low power consumption, and high sensitivity, i.e. the current increases one to two orders when the sensor exposed to the vapor. The behavior of the sensor between relative humidity 35 and 70% shows good divinable and then helpful to measure humidity. The experimental relative humidity range is restricted by the glass chamber. The vapor condenses into water when the relative humidity is high than 80%. It will affect the experimental results. However, the sensing range from 35 to 70% is suitable for requirement of human life.

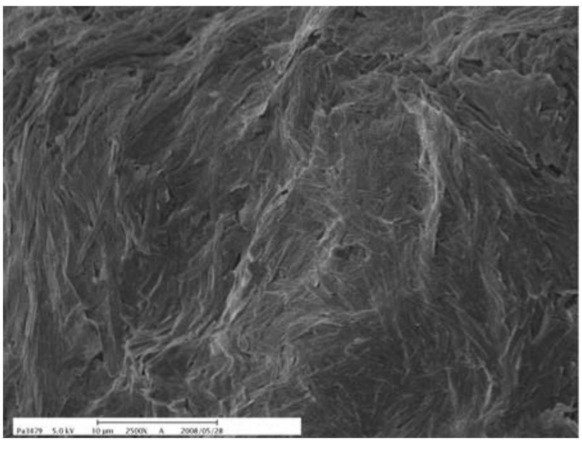

Fig. 4(a) Surface morphology of the undoped PANI.

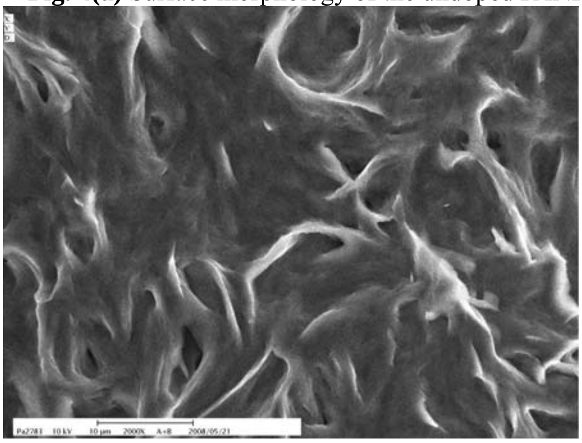

Fig. 4(b) Surface morphology of the Fe-Al doped PANI.

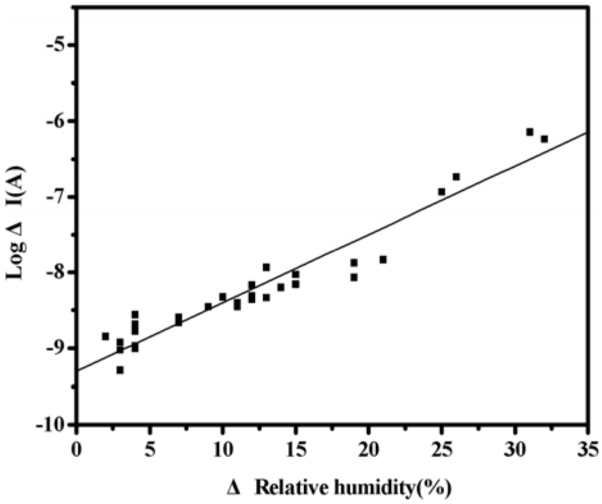

Fig. 5. The experimental results of the humidity measurement (N=45). It shows the relationship between the current changes and relative humidity. It demonstrates good exponential relationship.

3-3. Selectivity

There are many kinds of gas sensors which are able to detect various gases based on doped PANI. In order to prove the developed humidity sensor based on PANI which doped with specific concentration of Fe and Al salts has the high selectivity to vapor. Therefore, the sensor is exposed to CO, N_2, CO_2, C_2H_5OH, and NH_3 at 3v to demonstrate the sensor selectivity. When the sensor is exposed to the vapor, the current increases one to two orders in a few seconds. The same sensor is exposed to CO, N_2, CO_2, C_2H_5OH, and NH_3, but it showed slight variations in current. The various gases are not dry to affect the variations of current when the gases are injected into the chamber. These results were showed in Fig. 6. The definition of the normalization is {(the average current induced by the various gases- the average current induced by the background relative humidity)/ the average current induced by the background relative humidity}. Apparently, the current difference generated by other kinds of gases is smaller than 12%. These showed that the dopants as Fe-Al with specific concentration made the sensor specific only for vapor.

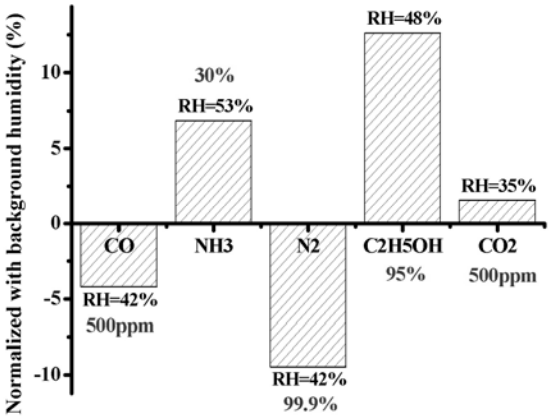

Fig. 6. The selectivity experimental result of the developed humidity sensing device. The testing concentration of CO, NH3 (evaporated from liquid phase), N2, C2H5OH (evaporated from liquid phase), and CO2 are 500ppm, 30%, 90.9%, 95%, and 500ppm respectively. In addition, the relative humidity (RH) of different experimental tests was also shown in the figure. As the consequence, the measured current was subtracted by the fitting current obtained in Fig. 5. to demonstrate the crosssensitivity to different gases.

3-4. Repeatability

Repeatability is very important to practical humidity sensors, including the developed low power consumption humidity sensor in this work. Many kinds of humidity sensors have good repeatability, but they often consume additional power to achieve initial state, such as ceramic humidity sensors which need additional heater to remove the physisorbed water [4]. The Fe-Al doped PANI based humidity sensor recovers the initial state rapidly at room temperature when the surrounding vapor has been removed. A repeatability test of the device is carried out by exposing the sensor to the water vapor repeatedly, as shown in Fig. 7. It shows not only repeatability but also response-recovery and sensitivity properties of the Fe-Al doped PANI based humidity sensor exposed to different concentration of vapor. It is clear that the current following through the developed humidity sensor increases rapidly when exposed to vapor, and then decreases dramatically when removed the vapor. To exhibit the Fe-Al doped PANI based humidity sensor has fast response-recovery time, high sensitivity and good repeatability.

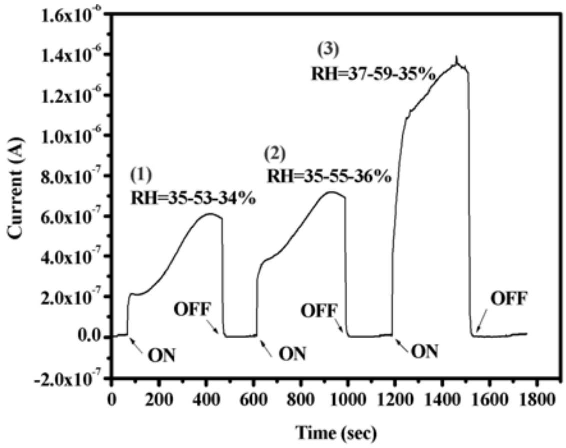

Fig. 7. The repeatability experimental results of the developed humidity sensor. The initial relative humidity of experiments (1), (2), and (3) are about 35%.Then injecting the water vapor (ON state), the relative humidity become 53%, 55% and 59% respectively. After about 400 s, to remove the vapor (OFF state) the current falls to its initial value rapidly.

4. CONCLUSIONS

In this work, we have developed a doped PANI humidity sensor which can operate under room temperature. The developed sensor has been proved to have high sensitive/ selective, fast response, repeatability characteristics. The simple solution-based fabrication process and interface circuit for resistance measurement facilitate the decrease of manufacturing costs. In conclusion, the developed PANI thin film doped with optimized Fe-Al ions has the potential to be implemented as the humidity sensing material for various applications.

REFERENCES

[1] Z. Chen and C. Lu, " Humidity Sensors: A Review of Materials and Mechanisms," *Sensor Letters*, Vol.3, pp.274-295 (2005).

[2] Scott T. McGovern, Geoffrey M. Spink, Gordon G. Wallace, " Micro-humidity sensors based on a processable PANI blend," *Sens. Actuators B,*Vol. 107, pp.657-665 (2005).

[3] Shilpa Jain, Sanjay Chakane, A.B. Samui, V.N. Krishnamurthy, and S.V. Bhoraskar, " Humidity sensing with weak acid-doped PANI and its composites," *Sens. Actuators B,* Vol. 96, pp.124-129 (2003).

[4] C. Cantalinic, M. Pelino, " Microstructure and humidity sensitive characterstics of α-Fe2O3 ceramic sensors," *J. Am. Ceram.,* Vol.75, pp.546–551 (1992).

[5] M. Li, Y. Chen, "An investigation of response time of TiO2 thin film oxygen sensors, " *Sens. Actuators B*, Vol. 32,
pp. 83–85 (1996).

[6] H.Yagi, M. Nakata, "Humidity sensor using Al2O3, TiO2 and SnO2 prepared by sol–gel method," *J. Ceram. Soc. Jpn.*, Vol. 100, pp. 152–156 (1992).

[7] J. F. Boyle and K. A. Jones," Effects of CO, Water-Vapor and surface-temperature on conductivity of a SnO_2 gas sensor," *J. Electronic Mater.*, Vol. 6, pp. 717-733 (1977).

[8] G. N. Avani and L. Nanis," Effects of humidity on hydrogen-sulfide detection by SnO_2 solid-state gas sensors," *Sens. Actuators B*, Vol. 2, pp. 201-206 (1981)

[9] Huiling Tai, Yadong Jiang , Guangzhong Xie, Junsheng Yu, Xuan Chen, Zhihua Ying,"Influence of polymerization temperature on NH3 response of PANI/TiO2 thin film gas sensor," *Sensors and Actuators B*, Vol. 129, pp. 319–326 (2008).

[10] Hua Bai and Gaoquan Shi.," Review Gas sensors based on conducting polymers," *Sensors*, Vol. 7, pp.267-307 (2007).

[11] Densakulprasert, N.; Wannatong, L.; Chotpattananont, D.; Hiamtup, P.; Sirivat, A.; Schwank, J. ,"Electrical conductivity of PANI/zeolite composites and synergetic interaction with CO," *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.*, Vol. 117, pp. 276-282 (2005).

[12] Dixit, V.; Misra, S.C.K.; Sharma, B.S.,"Carbon monoxide sensitivity of vacuum deposited PANI semiconducting thin films," *Sens. Actuators B*, Vol. 104, pp. 90-93 (2005).

[13] Misra, S.C.K.; Mathur, P.; Srivastava, B.K.,"Vacuum-deposited nanocrystalline PANI thin film sensors for detection of carbon monoxide," *Sens. Actuators A*, Vol. 114, pp. 30-35 (2004).

[14] Partha Pratim Sengupta, Satyananda Barik, and Basudam Adhikari,"PANI as a Gas-Sensor Material, "*Materials and Manufacturing Processes*, Vol. 21, pp. 263–270 (2006).

[15] Xie, D.; Jiang, Y.D.; Pan, W.; Li, D.; Wu, Z.M.; Li, Y.R.," Fabrication and characterization of PANI-based gas sensor by ultra-thin film technology," *Sens. Actuators B*, Vol. 81, pp. 158-164 (2002).

[16] Misra, S.C.K.; Mathur, P.; Yadav, M.; Tiwari, M.K.; Garg, S.C.; Tripathi, P. "Preparation and characterization of vacuum deposited semiconducting nanocrystalline polymeric thin film sensors for detection of HCl," *Polymer*, Vol. 45, pp. 8623-8628 (2004).

[17] Virji, S.; Fowler, J.D.; Baker, C.O.; Huang, J.X.; Kaner, R.B.; Weiller, B.H., "PANI manofiber

composites with metal salts: Chemical sensors for hydrogen sulfide," *Small*, Vol. 1, pp. 624-627 (2005).
[18] Li, G.F.; Martinez, C.; Semancik, S.," Controlled electrophoretic patterning of PANI from a colloidal suspension," *J. Am. Chem. Soc.*, Vol. 127, pp. 4903-4909 (2005).
[19] M. L. Singla, Sajeela Awasthi, and Alok Srivastava," Humidity sensing; using PANI/Mn_3O_4 composite doped with organic/inorganic acids," *Sens. Actuators B* , Vol. 127, pp. 580-585 (2007).