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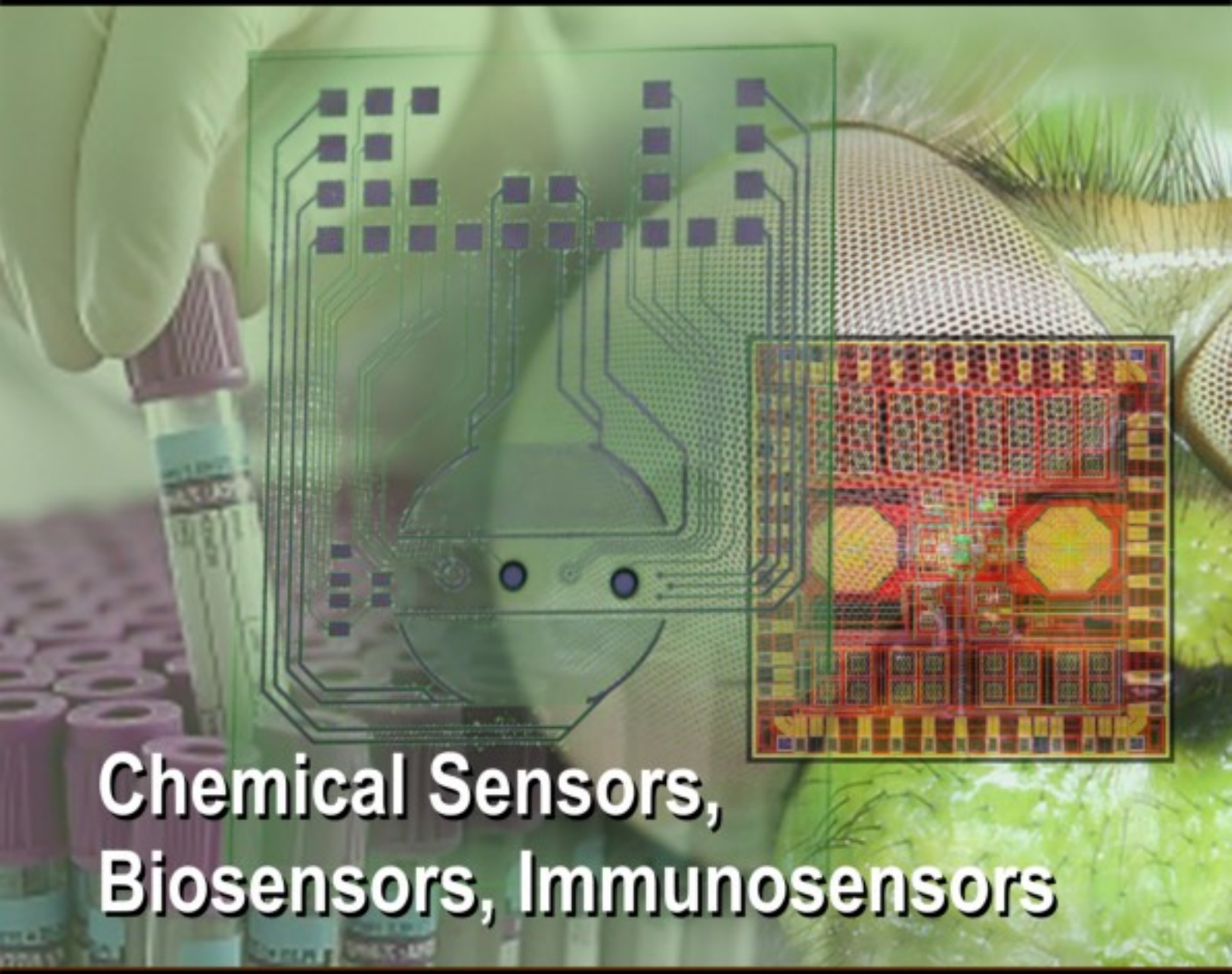

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Humidity Response of Polyaniline Based Sensor

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Abstract: This paper presents hitherto unreported humidity sensing capacity of emeraldine salt form of polyaniline. Humidity plays a major role in different processes in industries ranging from food to electronic goods besides human comfort and therefore its monitoring is an essential requirement during various processes. Polyaniline has a wide use for making sensors as it can be easily synthesized and has long stability. Polyaniline is synthesized here by chemical route and is found to sense humidity as it shows variation in electrical resistance with variation in relative humidity. Results are presented here for a range of 15 to 90 RH%. The resistance falls from 5.8 to 0.72 Giga ohms as RH varies from 15 to 65 % and then falls to 13.9 Mega ohms as RH approaches 90 %. The response and recovery times are also measured. *Copyright © 2010 IFSA.*

Keywords: Humidity sensor, Scanning electron microscopy, FTIR spectra

1. Introduction

There is a continuing need for accurate, reliable, inexpensive sensing systems for measuring relative humidity (RH), not only for human comfort but also for a broad spectrum of applications in chemical industry, process control, atmospheric sciences, agriculture [1], air conditioning systems, electronic devices, tyre industries, sugar industries and drying processes for ceramics and food [2].

Humidity is one of the most common constituents present in the environment and its measurement is indispensable when it comes to monitoring of various environmental parameters. For instance, detecting organic pollutants in indoor atmosphere [3], organic vapor monitoring [4], maintenance of Green houses, performance of air/ smoke filters [5], hydrocarbon sensing [6] are all affected by

relative humidity conditions. Therefore, sensing and controlling relative humidity is of great importance.

There is a growing demand for a sensing system that has high sensitivity, wide dynamic range, good stability, quick response, good reproducibility, simple structure and minimal cost. Metal oxide films sensitive to humidity have been reported earlier [7, 8] where sensing has been done using optical means. However, metal oxide humidity sensors depending upon measurements of electrical parameters require high temperature operation and consume significant amount of power [9]. In the recent years there has been significant progress in the field of polymer based humidity sensors [10-13]. According to their sensing mechanisms these can be either resistive type or capacitive type [14]. In addition to the traditional quaternary ammonium and sulfonate compounds [15, 16], polymers containing phosphonium [17] have also been studied for humidity sensing. Copolymers, mutually reactive copolymers [18] and conjugated polymers have also been reported for humidity sensing. Conjugated polymers especially conducting polymers like polypyrrole [19], polyethylene, polypropylene [20] etc. have shown humidity sensing properties. Besides these metal-polymer nanocomposites for instance iron oxide-polypyrrole [21] have also been reported for relative humidity sensing.

Among all the conducting polymers, polyaniline is important owing to its simple synthesis, environmental stability and high enough electrical conductivity. The conductivity of polyaniline depends on two variables: the degree of oxidation and the degree of protonation and can reversibly be controlled by the protonation of the charged amine sites and/or the oxidation of the main polymer chain [22, 23]. It can be modified to conduct across a wide range, from being utterly non-conducting for insulation use to conducting for other electrical purposes [24].

2. Experimental

There are two major polymerization approaches to synthesize polyaniline: electro-polymerization and chemical polymerization [25]. In this paper, the chemical polymerization technique, a standard procedure [26] for the synthesis of emeraldine salt form of polyaniline is followed. The synthesis of polyaniline is done by oxidative polymerization with ammonium peroxysulphate [27]. The starting material taken is aniline hydrochloride (99.95% pure) since; efficient polymerization of aniline is achieved only in acidic medium, where aniline exists as anilinium cation [28].

0.2 M aniline hydrochloride and 0.25 M ammonium peroxysulphate solution are prepared in two volumetric flasks. Both the solutions are kept separately for 1 hour at room temperature before mixing. It is then briefly stirred and left for polymerization for 24 hours. Next day, the precipitate of polyaniline is collected and washed by three 100 ml portions of 0.2M HCl and acetone solutions. The precipitate is then dried in air first at room temperature and then at 60°C. As a result a green colored emeraldine salt form of polyaniline is formed.

It is crushed using a mortar and pestle and then three pellets are prepared with the help of a hydraulic press machine by applying a pressure of 7 tons. The thickness of the pellets is found to be 0.55, 0.62 and 0.89 mm respectively. Diameter of all the pellets is 13 mm.

The surface morphology of the pellet is investigated with the help of Scanning Electron Microscope (SEM). The FTIR spectra of the composites are recorded on Perkin-Elmer Spectrophotometer.

The variation in the resistance of the pellet is studied by controlling the humidity in a closed chamber within a range of 15 to 90% RH. Relative Humidity is measured using a hygrometer and the resistance is measured using Keithley electrometer. All the observations have been taken at room temperature i.e at 24^0C.

3. Results and Discussion

3.1. Characterization

The study of surface morphology of the pellet is carried out using SEM (Model No. 430, LEO Cambridge, England). The specimens are mounted on 10mm diameter stub with the help of conducting adhesives and are sputtered with a thin layer of Au-Pd to make them conducting. These stubs are then fixed on the viewing stage of the SEM instrument having three-dimensional movement as well as rotation and tilt facility. The specimens are scanned thoroughly to check the uniformity of the pellet.

The SEM of 0.62 mm thickness (Fig. 1) shows the formation of a spongy amorphous structure. The particle formation in polyaniline takes place by heterogeneous nucleation. As a result granular coral-like structures are formed. As a characteristic of polyaniline, secondary nucleation [29] also takes place because of which the granular coral-like particles come together to form aggregates.

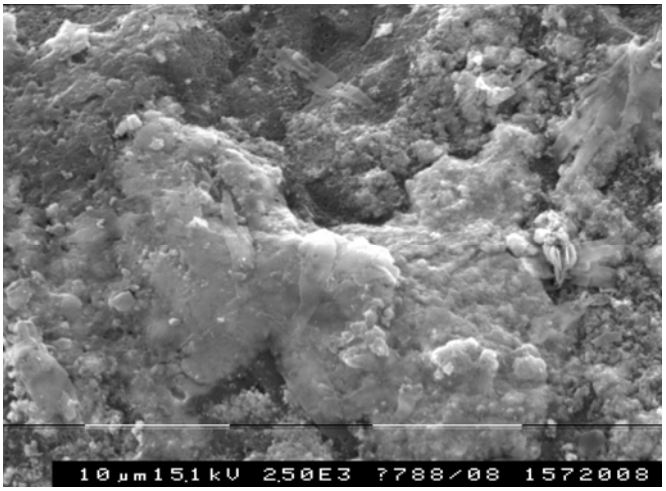


Fig. 1. SEM image of polyaniline pellet having 0.62 mm thickness.

The FTIR transmission spectrum (Fig. 2) is recorded on Perkin-Elmer spectrophotometer. In FTIR, the infrared radiation is split into two beams, out of which one is kept static and the other moving. These are combined to give a modulated beam which is passed through the sample. It is then digitized and Fourier-transformed by the computer to give the infrared spectrum [30].

The spectrum of polyaniline pellet is recorded in the range 450-4000 cm^{-1} [31]. The spectrum shows strong bands in the region 750 to 1800 cm^{-1} which is characteristic of polyaniline [32]. It also shows aromatic C-C stretching at frequency 1555 cm^{-1} and C-N stretching at frequency 1305 cm^{-1} as also mentioned in Ref. [33].

3.2. Humidity Sensing

The variation of resistance with variation in relative humidity (Fig. 3) is recorded for the three polyaniline pellets. A laboratory set-up is designed for humidity sensing in which the humidity is first lowered by introducing $CaCl_2$ in the chamber [34]. Then water vapors are introduced in the chamber with the help of air compressor which is already attached to a flask containing water in order to increase humidity inside the chamber from 15 to 90% RH. The polyaniline pellet with 0.55 mm

thickness shows response only in the high humidity range i.e. 53 RH% onwards which does not follow any regular pattern and therefore the response is not shown here. The sample with 0.62 mm thickness shows almost linear response in two regions i.e.15 to 70 % and 70 to 90 %. The resistance falls from 5.8 GΩ to 93.5 MΩ as RH increases from 15 to 70 % and then falls to 13.9 MΩ as RH approaches 90 %. Similarly, the sample with 0.89 mm thickness also shows almost linear response, with resistance falling from 6.45 MΩ to 1.04 MΩ in the 15-50 % relative humidity range and then falling to 0.04 MΩ as relative humidity approaches to 90 % . It is also seen that the resistance of the pellets decreases with increasing thickness.

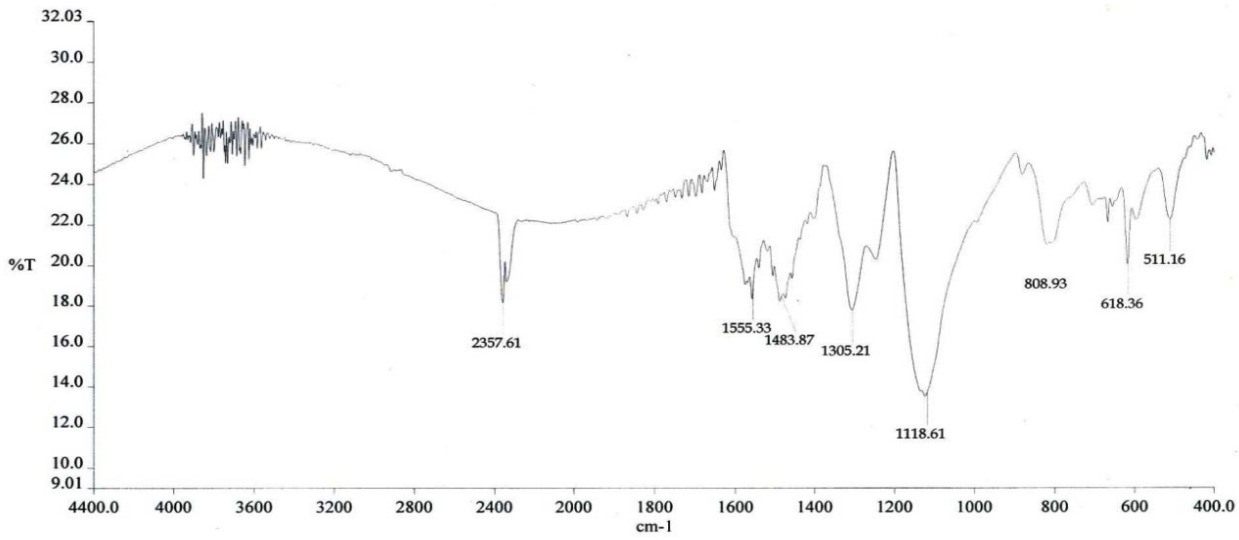


Fig. 2. FTIR spectra of Polyaniline.

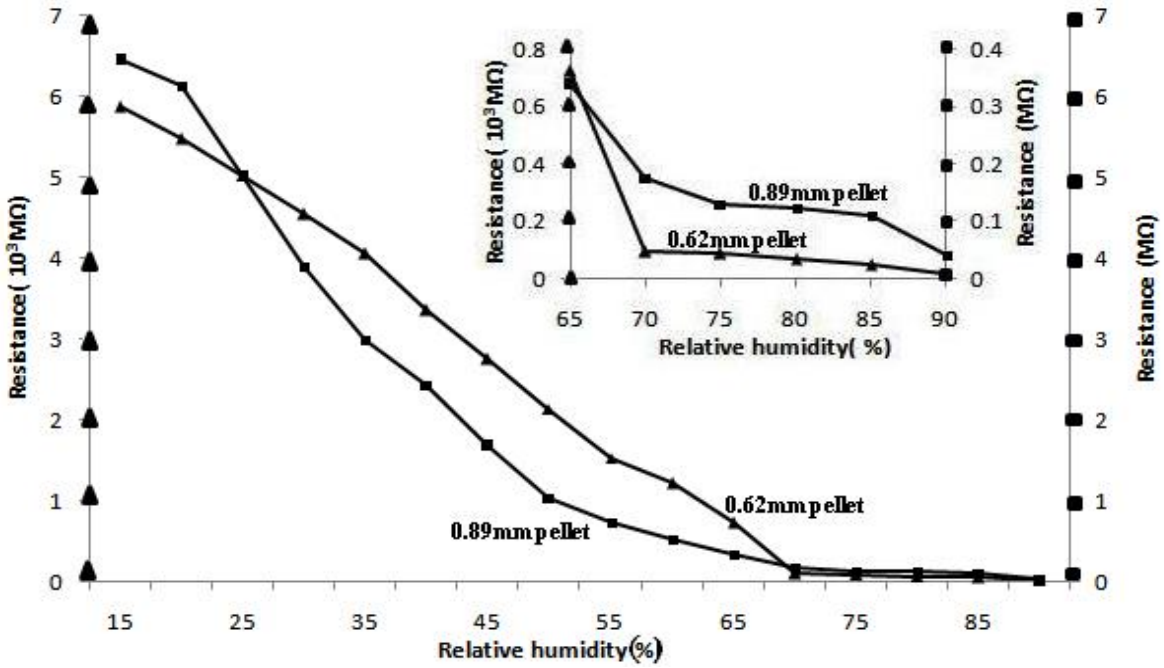


Fig. 3. Variation in resistance of polyaniline pellets with variation in relative humidity. Inset shows enlarged view of the curves in the range 65 to 90 RH%.

The variation of sensitivity as a function of relative humidity is calculated and is given in the Table 1. Here, the sensitivity is defined as the ratio of resistance in dry condition R_d (value taken at 20% RH) to R_h (resistance at a particular RH value), i.e. $S= R_d/R_h$ [21].

Table 1. Sensitivity of the polyaniline pellets.

RH %	Sensitivity of 0.62 mm thick pellet	Sensitivity of 0.89 mm thick pellet
15	0.93	0.95
20	1.00	1.00
25	1.09	1.23
30	1.20	1.57
35	1.35	2.05
40	1.63	2.52
45	1.98	3.65
50	2.56	5.90
55	3.57	8.30
60	4.47	11.81
65	7.58	18.06
70	58.50	34.11
75	64.25	47.23
80	81.78	51.17
85	110.75	55.82
90	391.18	153.50

For both the pellets sensitivity rises gradually in the range 15-65 % and then rapidly in the 65-90 % as shown in the table. However, when the sensitivities of both the pellets are compared with each other in the first range of 15-65 % and in the second range of 65-90 %., it is seen that the 0.62 mm pellet shows smaller rise in the sensitivity in the first range and a much faster rise, around three times, in the second range. Since, the pellet with 0.62 mm thickness exhibits greater sensitivity in the higher humidity range its response and recovery curves are shown in Fig. 4. The response and recovery time of this sample is found to be 1minute for a humidity change of 30RH% i.e. 51 to 80RH%. Here the response time is defined as the time taken by the sensor to reach 75 % of the total resistance change [35]. The observations using the pellets are repeated twice, initially after a time gap of 1 month and then after two months. The results are found to be reproducible.

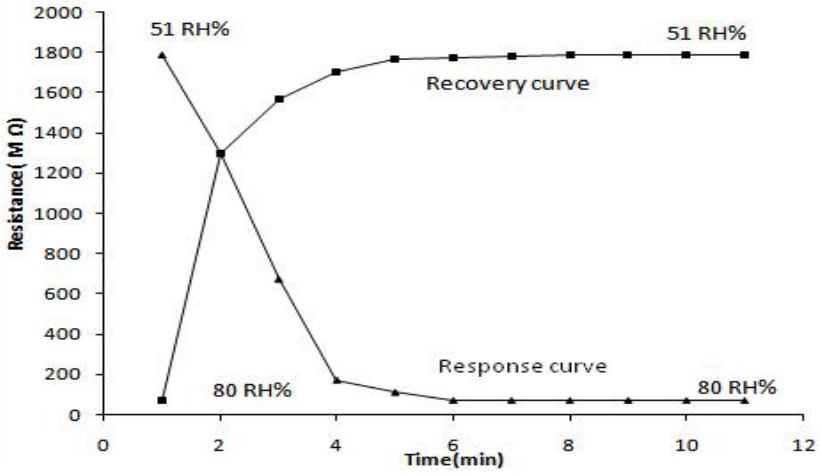
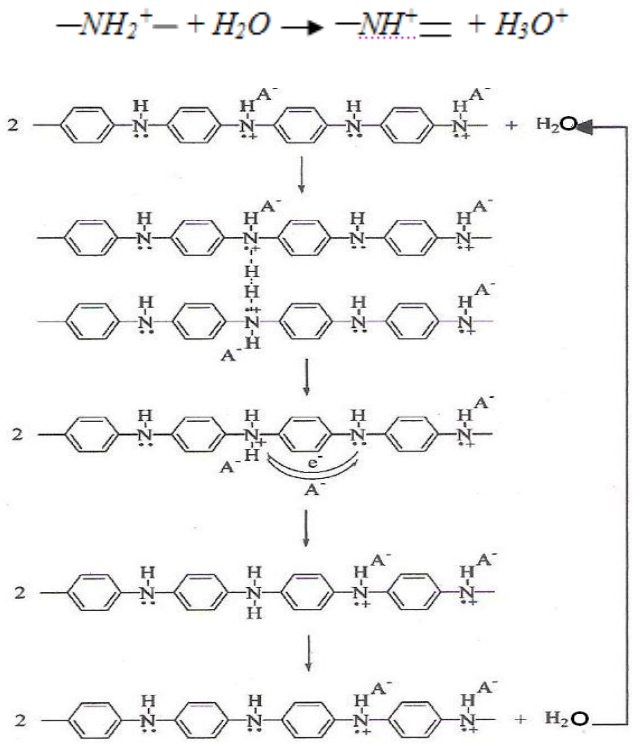


Fig. 4. Response and recovery time for 0.62 mm polyaniline pellet for the humidity change from 51 to 80 RH%.

3.3. Sensing Mechanism

The decrease in resistance with increase in relative humidity is because of adsorption of water molecules by the pellet surface. Typically on exposure to water vapor, polyaniline becomes protonated, and an increase in conductivity is observed. The humidity sensing property of polyaniline to water vapor can be regarded as electron hopping assisted by proton transfer mechanism [36] as shown below. The acid base reaction is given by



The protonation is occurring at the charged amine nitrogen sites and since water has a higher binding affinity to these sites as compared to hydrogen gas, interference of H_2 gas is not likely to occur while sensing humidity using polyaniline pellets. Moreover, oxygen will also not interfere with the sensing of humidity as the hydrogen bonding is the basis of sensing mechanism.

5. Conclusion

This paper presents hitherto unreported humidity sensing capacity of emeraldine salt form of polyaniline. Polyaniline has been successfully synthesized by oxidative chemical polymerization of aniline hydrochloride and its formation is confirmed by FTIR study. The SEM studies show uniform, spongy, amorphous surface morphology which is suitable for humidity sensing application. The electrical conductivity of polyaniline pellets is found to increase with their increasing thickness. At room temperature the polyaniline samples exhibit good sensitivity towards humidity with a response and recovery time of 1 minute for 30 RH% change i.e. from 51 to 80 RH%. It is expected that sensing humidity with polyaniline pellets is comparatively advantageous as the gases falling short of hydrogen bonding or having lesser binding affinity as compared to water molecule will not interfere.

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References

[1]. M. Penza, G. Cassano, Relative humidity sensing by PVA-coated dual resonator SAW oscillator, *Sensors and Actuators B*, 68, 2000, pp. 300-306.
[2]. E. Bracken, Combating humidity: the hidden enemy in manufacturing, *Sens. Rev.,* 17, 4, 1997, p. 291.
[3]. Maneerat Ongwandee and Glenn C. Morrison, Influence of Ammonia and Carbon Dioxide on the Sorption of a Basic Organic Pollutant to Carpet and Latex-Painted Gypsum Board, *Environ. Sci. Technol.*, 2008, 42, 15, pp. 5415–5420.
[4]. Naohide Shinohara, Tomohisa Kajiwara, Masato Ohnishi, Kenichi Kodama and Yukio Yanagisawa, Passive Emission Colorimetric Sensor (PECS) for Measuring Emission Rates of Formaldehyde based on an Enzymatic Reaction and Reflectance Photometry, *Environ. Sci. Technol.*, 2008, 42, 12, pp. 4472–4477.
[5]. Stuart Batterman, Christopher Godwin, and Chunrong Jia, Long Duration Tests of Room Air Filters in Cigarette Smokers' Homes, *Environ. Sci. Technol.,* 2005, 39, 18, pp. 7260–7268.
[6]. Bobby Pejcic, Peter Eadington, and Andrew Ross, Environmental Monitoring of Hydrocarbons: A Chemical Sensor Perspective, *Environ. Sci. Technol.*, 2007, 41, 18, pp. 6333–6342.
[7]. Shobhna Dixit, Anchal Srivastava, R. K. Shukla, and Atul Srivastava, ZnO Thick Film Based Opto-electronic Humidity Sensor for a Wide Range of Humidity, *Optical Review*, Vol. 14, No. 4, 2007, pp. 186-188.
[8]. Shobhna Dixit, Anchal Srivastava, Atul Srivastava, and R. K. Shukla, Effect of toxic gases on humidity sensing property of nanocrystalline ZnO film, *J. of Applied Physics*, 102, 2007, pp. 113-114.
[9]. D. Hodgins, The electronic nose using conducting polymer sensors, *Sens. Rev.,* 14-4, 1994, pp. 28-31.
[10]. B. Adhikari, S. Majumdar, Polymers in sensors applications, *Prog. Polym. Sci.*, 29, 2004, pp. 699-766.
[11]. G. Harsanyi, Polymer films in sensor application: a review of present uses and future possibilities, *Sens. Rev.,* 20-2, 2000, pp. 98-105.
[12]. Milind V. Kulkarni, Annamraju Kasi Viswanath, Spectroscopic, thermal and electrical properties of sulphonic acids doped poly(o-anisidine) and their application as humidity sensor, *Sensors and Actuators B*, 107, 2005, pp. 791-797.
[13]. Razat Nohria, Rajneek K. Khillan, Yi Su, Rohit Dikshit, Yuri Lvov, Kody Varahramyan, Humidity sensor based on ultrathin polyaniline film deposited using layer-by-layer nano-assembly, *Sens. Actuators B*, 114, 2006, pp. 218-222.
[14]. Neetika Gupta, Shalini Sharma, Irfan Ahmad Mir and D. Kumar, Advances in sensors based on conducting polymers, *J. of Scientific and Industrial Research*, 65, 2006, pp. 549-557.
[15]. L. G. Wade, Jr., Organic Chemistry, *Prentice Hall*, NJ, 2001.
[16]. K. L. Rauen, D. A. Smith, and W. R Heineman, J. Johnson, R. Seguin and P. Stoughton, Humidity Sensor Based on Conductivity Measurements of a Poly(dimethyldiallylammonium chloride) Polymer Film, *Sens. Actuators, B*, 17, 1993, pp. 61–68.
[17]. S. Y. Son, M. S. Gong, Polymeric humidity sensor using phosphonium salt-containing polymers, *Sens. Actuators B: Chem*., 86, 2002, pp. 168-173.
[18]. M. S. Gong, J. S. Park, M. H. Lee and H. W. Rhee, Humidity sensor using cross-linked polyelectrolyte prepared from mutually reactive copolymers containing phosphonium salt, *Sens. Actuators B: Chem.,* 86, 2002, pp. 160-167.
[19]. M. K. Ram, M. Adami, P. Faraci, C. Nicoloni, Physical insight in the in situ self-assembled films of polypyrrole, *Polymer*, 41, 2000, pp. 7499-7509.
[20]. T. Maddanimath, I. S. Mulla, S. R. Sainkar, K. Vijayamohanan, K. I. Shaikh, A. S. Patil, S. P. Vernekar, Humidity sensing properties of surface functionalized polyethylene and polypropylene films, *Sens. Actuators B: Chem.*, 81, 2002, pp. 141-151.
[21]. R. P. Tandon, M. R. Tripathy, A. K. Arora, Surat Hotchandani, Gas and humidity response of iron oxide—Polypyrrole nanocomposites, *Sens. Actuators B*, 114, 2006, pp. 768-773.

[22].Huang W S, Humphrey B D and MacDiarmid A G, Polyaniline, a novel conducting polymer: Morphology and chemistry of its oxidation and reduction in aqueous electrolytes, *J. Chem. Soc. Faraday Trans*., Vol. 82, No. 8, 1986, pp. 2385-2400.
[23].A. Z. Sadek, W. Wlodarski, K. Shin, Richard B. Kaner, and K. Kalantar-zadeh, Polyaniline nanofiber based surface acoustic wave gas sensors- Effect of nanofiber diameter on H-2 response, *Nanotechnology*, 17, 17, 2006, pp. 4488-4492.
[24].http://www.wisegeek.com/what-is-polyaniline.htm
[25].N. J. Pinto, P. D. Shah and P. K. Kahol, B. J. McCormick, Conducting state of polyaniline films: Dependence on moisture, *Physical Review B*, Vol. 53, No. 16, 15April 1996, II.
[26].J. Stejskal, R. G. Gilbert, Polaniline, Preparation of a conducting polymer, *Pure Appl. Chem.,* Vol. 74, No. 5, 2002, pp. 857–867.
[27].S. C. Raghavendra, Syed Khasim, M. Revanasiddappa, M. V. N. Ambika Prasad and A. B. Kulkarni, Synthesis, characterization and low frequency a. c. conduction of polyaniline/fly ash composites, *Bull. Mater. Sci.*, Vol. 26, No. 7, December 2003, pp. 733-739.
[28].M. D. Catedral, A. K. G. Tapia, and R. V. Sarmago & J. P. Tamayo and E. J. del Rosario, Effect of Dopant Ions on the Electrical Conductivity and Microstructure of Polyaniline (Emeraldine Salt), *Science Diliman*, July-December 2004, 16, 2, pp. 41–46.
[29].Dan Li and Richard B. Kaner, Shape and Aggregation Control of Nanoparticles: Not Shaken, Not Stirred, *J. Am. Chem. Soc*., 128, 3, 2006, pp. 968 – 975.
[30].P. S. Kalsi: Spectroscopy of Organic Compounds, edition 6, pp. 83-84.
[31].M. C. Gupta: Atomic and Molecular Spectroscopy, 2001, p. 231.
[32].P. R. Somani, R. Marimuthu, A. B. Mandale, Synthesis, characterization and charge transport mechanism in conducting polyaniline/V2O5 composites, *Polymer*, 42, 2001, pp. 2991-3001.
[33].P. S. Kalsi: Spectroscopy of Organic Compounds, p. 112.
[34].S. Jain, S. Chakane, A. B. Samui, V. N. Krishnamurthy, S. V. Bhoraskar, Humidity sensing with weak acid-doped polyaniline and its composites, *Sens. Actuators B*, 96, 2003, pp. 121-129.
[35].Dewyani Patil, You-Kyong Seo, Young Kyu Hwang, Jong-San Chang and Pradip Patil, Humidity sensing properties of poly(o-anisidine)/WO3 composites, *Sens. Actuators B: Chem*., Vol. 128, Issue 2, 15 January 2008, pp. 374-382.
[36].Shabnam Virji, Richard B. Kaner, and Bruce H. Weiller, Hydrogen Sensors Based on Conductivity Changes in Polyaniline Nanofibres, *J. Phys. Chem. B*, 110, 44, 2006, pp. 22266-22270.

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