

ORIGINAL RESEARCH PAPER

Electrical Behaviour of Chitosan-Silver Nanocomposite in Presence of Water Vapour

Bal Chandra Yadav^{1*}, Ritesh Kumar², Ravindra Kumar⁴, Subhasis Chaudhuri³, Panchanan Pramanik³

¹Department of Applied Physics, School of Physical Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow-226025, U.P., India

²Department of Physics, University of Lucknow, Lucknow-226007, U.P., India

³Department of Chemistry, IIT Kharagpur, W.B., India

Received: 2016-12-27

Accepted: 2017-02-18

Published: 2017-04-08

ABSTRACT

This paper presents the synthesis, characterization of the nanocomposite of silver and chitosan polymer composite reinforced by cellulose fibre and its electrical behaviour in presence of water vapour. The coated paper has been characterized by XRD, IR, SEM and EDX techniques. The size of silver nanoparticles is found to be around 9 nm and deposited uniformly. Chitosan, as well as cellulose, contain a hydrogen attached to electronegative nitrogen and oxygen. This gives a favourable environment for the formation of hydrogen bonds. IR peaks of the composite infer the intermolecular hydrogen bonding between the two constituents. The SEM pictures show that the coating of the fibres with nanoparticles is quite uniform. EDX analysis shows that the coated filter paper has sufficient amount of silver along with carbon and oxygen. The coated paper shows good sensitivity towards humidity. It gives excellent linearity in response with a concentration of water vapour after heat treatment of composite at 130 °C. The sensitivity of the sensor is 0.8 MΩ per unit of relative humidity. Sensing properties originate from protonic conductivity from adsorbed water molecule.

Keywords: Chitosan, Humidity Sensor, Nanocomposite, Silver Nanoparticles

How to cite this article

Bal Chandra Y, Kumar R, Chaudhuri S, Pramanik P. Electrical Behaviour of Chitosan-Silver Nanocomposite in Presence of Water Vapour. J. Water Environ. Nanotechnol., 2017; 2(2): 71-79. DOI: [10.22090/jwent.2017.02.001](https://doi.org/10.22090/jwent.2017.02.001)

INTRODUCTION

Several different kinds and varieties of polymers have been used as different kinds of chemical sensors. Polymers show chemical sensing properties [1-9]. The polymer having the reasonable backbone for hydrogen bonding has the promise to act as a humidity sensor. Thus humidity sensing using polymers has been a major part of the research for a long time. Humidity sensors have attracted increasing attention recently due to its applications in food quality and storage, meteorological studies,

environmental humidity for air conditioning systems and also for feedback control in household electric appliances such as drying machines and microwave ovens [10-14]. Humidity sensors based on polymers offer many advantages such as long-term stability, reliability, ease of processing and low fabrication cost. Commonly there are two categories for the humidity sensors: resistive-type [15-17] and capacitive-type [18-19]. However, the poor specific conductivity of polymer sometimes poses great impedance to use a sensor. This problem may be solved by embedding metal particles in the polymer matrix.

* Corresponding Author Email:
balchandra_yadav@rediffmail.com

The properties of silver nanoparticles have been extensively studied in the past few years for their unique optical, sensing and anti-microbial properties. In fact, silver nanoparticles have been one of the most widely studied of all the nanoparticles. Over the years various techniques have been used to synthesized silver nanoparticles [20]. Chitosan, on the other hand, is a polymer which has found widespread application in recent years. Chitosan is a copolymer of glucosamine and N-acetylglucosamine derived from the natural polymer chitin. This biopolymer can be physically modified to give different forms (e.g., powder, nanoparticles, gel, film, and beads), crosslinked with different substances (e.g., glutaraldehyde, carbodiimide, epichlorohydrin, and tripolyphosphate) and used in various fields of application [21-22].

The present paper reports a unique and very simple technique for making nanocomposite of nano-sized silver and chitosan to use as a humidity sensor. Silver has a high value of conductivity. The addition of silver to the chitosan has ensured that the background resistance value of the sensor material is well within measurable range. Moreover, silver is chemically stable and does not react with the polymer. The deposition of composite material would be carried out on filter paper made of cellulose fibers consisting ether or esters of cellulose. Thus the sensor developed using chitosan and nano-sized silver has a background resistance well within the measurable range.

The success of humidity sensor lies in linearity of the response curve. This composite shows reasonable linearity in response after the proper heat treatment.

EXPERIMENTAL

Preparation of Sensing Material and Its Characterization

0.2% chitosan purchased from Sigma-Aldrich (weight by volume) in 1 % acetic acid (volume by volume) has been prepared. This solution is mixed with 0.2 (M) silver nitrate in a ratio of 1:1 by volume. Strips of filter paper (Whatman 42) have been taken and soaked in this solution followed by soaking in N/10 ammonium hydroxide for 15 mins. The strips are then exposed to hydrazine vapours for 10 mins which produced Ag nanoparticles. On exposure to ammonia gas, chitosan is precipitated on the filter paper along with silver nanoparticles. Thus on the strips of filter paper chitosan and silver

nanoparticles composite are deposited. The strips are washed with water to remove soluble inorganic compounds. The washing is followed by drying. These strips having a smooth deposition are used as a humidity sensor. The amount of silver added to the sample has been optimised. The various different concentration of Ag^+ has been tried ranging from 0.05(M) to 0.4(M). But it is found that on using 0.2(M) Ag^+ the background resistance comes in a measurable range. Too much of silver leads to a decrease in background resistance whereas too little leads to a drastic increase. When 0.05(M) Ag^+ has used the background resistance increases to around 600 M Ω but when 0.4(M) Ag^+ is used the background resistance drops down to around 0.5 M Ω . The concentration of Ag^+ in the range of 0.2(M) produces the background resistance within the range of 100 M Ω to 120 M Ω . This value is comfortable for designing the hardware of the sensor. This value is chosen since it is neither too high nor too low, thus, ensuring that on absorbing moisture there is a sufficient and detectable change in resistance. After deposition of the composite, the thick films have been backed in the oven at 130 °C which makes the thick film mechanically stable. The thermal treatment is necessary to eliminate any hysteresis during measurement. The strips having length 5 cm and breadth 1cm are cut from the sheet of thick film for measurement. The contacts of the strips are made with silver paint.

Device assembly for Humidity Detection

A controlled humidity chamber has been designed [23]. A saturated solution of potassium hydroxide in distilled water is used as a dehumidifier and saturated solution of potassium sulphate as a humidifier. A variation in resistance has been noted by using a digital multimeter (Keithley 6541A). Relative humidity is measured using standard hygrometer associated with a thermometer (Huger, Germany) as illustrated in Fig. 1(a). Schematic of proposed sensing structure is shown in Fig. 1(b).

The humidifier/dehumidifier is kept in a dish on a stand. In this process, the temperature of the chamber remains the same throughout the experiment which is being constantly monitored. The ends of the sensor were connected to the Keithley Electrometer which recorded the changes in resistance values. The sensor has been investigated by exposing humidity inside a specially designed controlled humidity chamber. The sensitivity of humidity sensor has been defined as the change

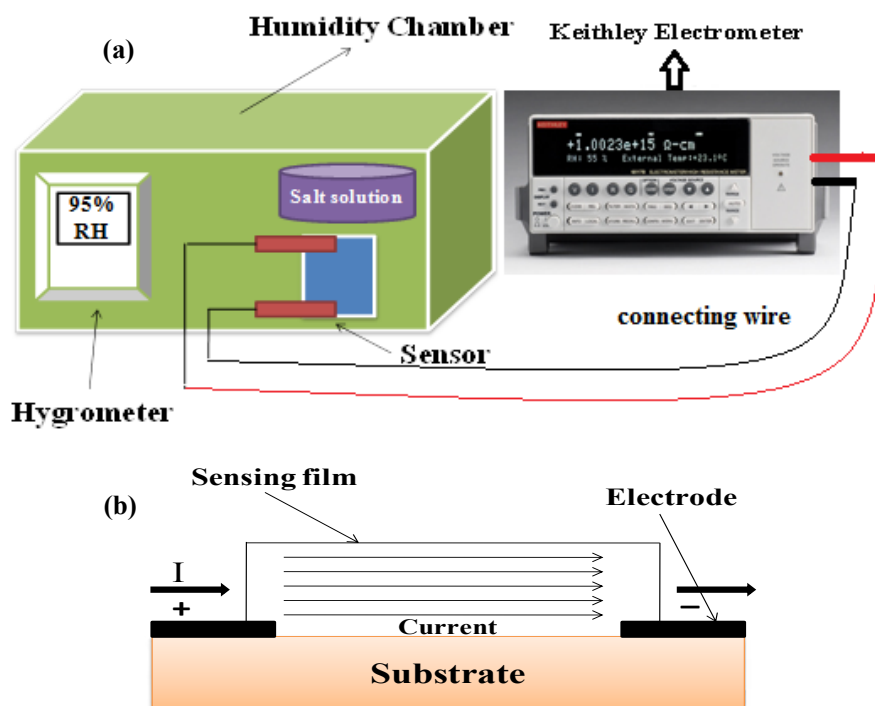


Fig. 1. (a) Device assembly for humidity detection and (b) Schematic of sensing element

in resistance of sensor per unit change in relative humidity (%RH) [24].

Variations in resistance with the variations in %RH for the sensor at room temperature which is around 30 °C have been studied.

RESULTS AND DISCUSSION

XRD Studies

XRD studies were done using Philips PW1710 diffractometer with Cu K α as the target material in which 3 major peaks were obtained apart from some other minor peaks as shown in Fig. 2. The peak at $2\theta = 38.13^\circ$ is due to silver nanoparticle formation.

Using the Scherrer's equation given as under:

$$\beta_{hkl} = \frac{K\lambda}{L_{hkl} \cos \theta_{hkl}}$$

β is the breadth of the peak of a specific phase (hkl).

K is a constant that varies with the method of taking the breadth ($0.89 < K < 1$ in this case taking $K = 0.89$).

λ is the wavelength of incident X-rays. θ is the center angle of the peak. L is FWHM of the peak.

The crystallite size of the silver nanoparticles

is calculated using this equation. The crystallite size thus obtained is around 9 nm. The peak corresponding to (111) is the plane of the silver nanoparticle. However, the largest peak obtained is at $2\theta = 22.67^\circ$ which is due to the chitosan. Any XRD of the chitosan-based sample gives a peak at around 22° . This peak is large owing to the crystallinity of chitosan which is very well known. The other small peak may originate from the AgCl or Ag₂O crystals in the sample.

IR Studies

FTIR spectra of the prepared samples (finely chopped up into very tiny pieces) were done in KBr medium with Thermo Nicolet Nexus FTIR spectrometer (model 870). The IR data was taken for the coated filter paper (sensor) and the data was compared with that of an ordinary filter paper and of chitosan as shown in Fig. 3. Filter paper contains cellulose as its constituent. Chitosan and cellulose have very similar functional groups in its structure. Some of the hydroxyl groups of cellulose have replaced by $-\text{NH}_2$ and $-\text{NHCOCH}_3$. So this makes the IR data quite similar to both these polymers except some additional peaks in chitosan. When the data were compared, it was found that the coated filter paper (sensor) showed almost all the

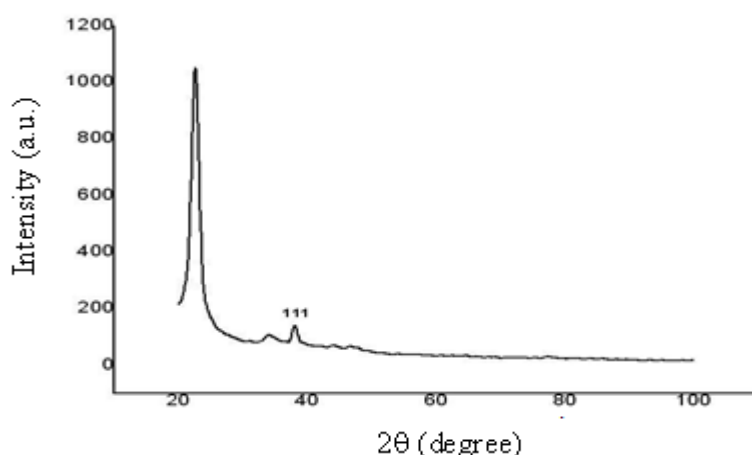


Fig. 2. XRD data of the coated filter paper.

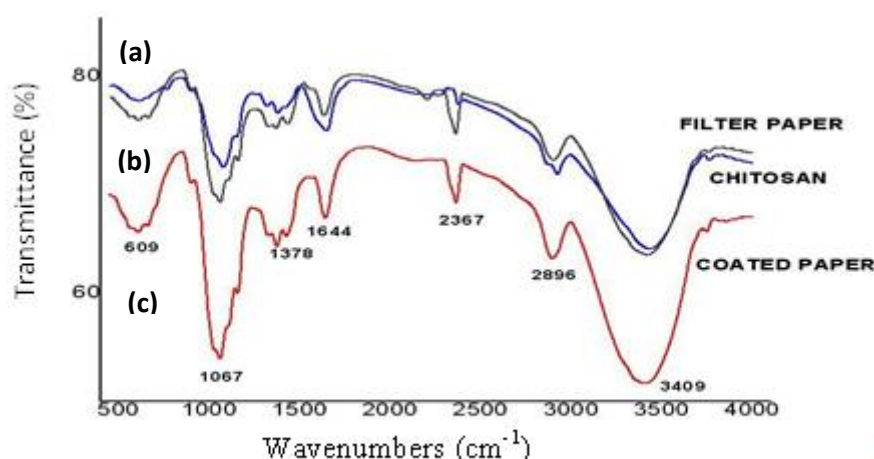


Fig. 3. IR data for ordinary filter paper, chitosan and coated filter paper.

peaks corresponding to both the species. But there is slight shifting and sharpening of peaks in some cases. This can be attributed to the formation of hydrogen bonds between chitosan and cellulose. Chitosan, as well as cellulose, contain a hydrogen attached to electronegative nitrogen and oxygen. This gives a favourable environment for the formation of hydrogen bonds. Thus the changes in IR peaks of the composite infer the intermolecular hydrogen bonding between the two constituents.

The silver nanoparticles loaded chitosan film (Fig. 3c) shows the characteristic peaks with a slight shift of the peak 1350 to 1378 cm⁻¹ corresponding to amide III band. In addition, the stretching vibration at 2896 cm⁻¹ conforming to OH/NH₂ groups has shifted to 3409 cm⁻¹, which indicates that the silver particles are bonded to the functional groups present both in chitosan. The shifting of the peak is due to the formation of coordination

bond between the silver atom and the electron rich groups (oxygen/nitrogen) present in chitosan. This causes an increase in bond length and frequency. Binding of silver with N of the amine and amide group results in decreasing of the intensity of amine and amide peaks at 1644 cm⁻¹. Division of combined peak of amine and amide at 1644 cm⁻¹, also indicates the binding of Ag with O and N of those groups. The peak intensities in the range 1000 cm⁻¹ and 1350 cm⁻¹ due to C–N stretching and bending is very less in silver loaded chitosan nanoparticles because of the complexation of chitosan with silver.

SEM Studies

SEM analysis reveals that fibrous structure of composite due to deposition of composite on cellulose fiber which is depicted in Fig. 4(a) and Fig. 4(b). The SEM of uncoated filter paper is also

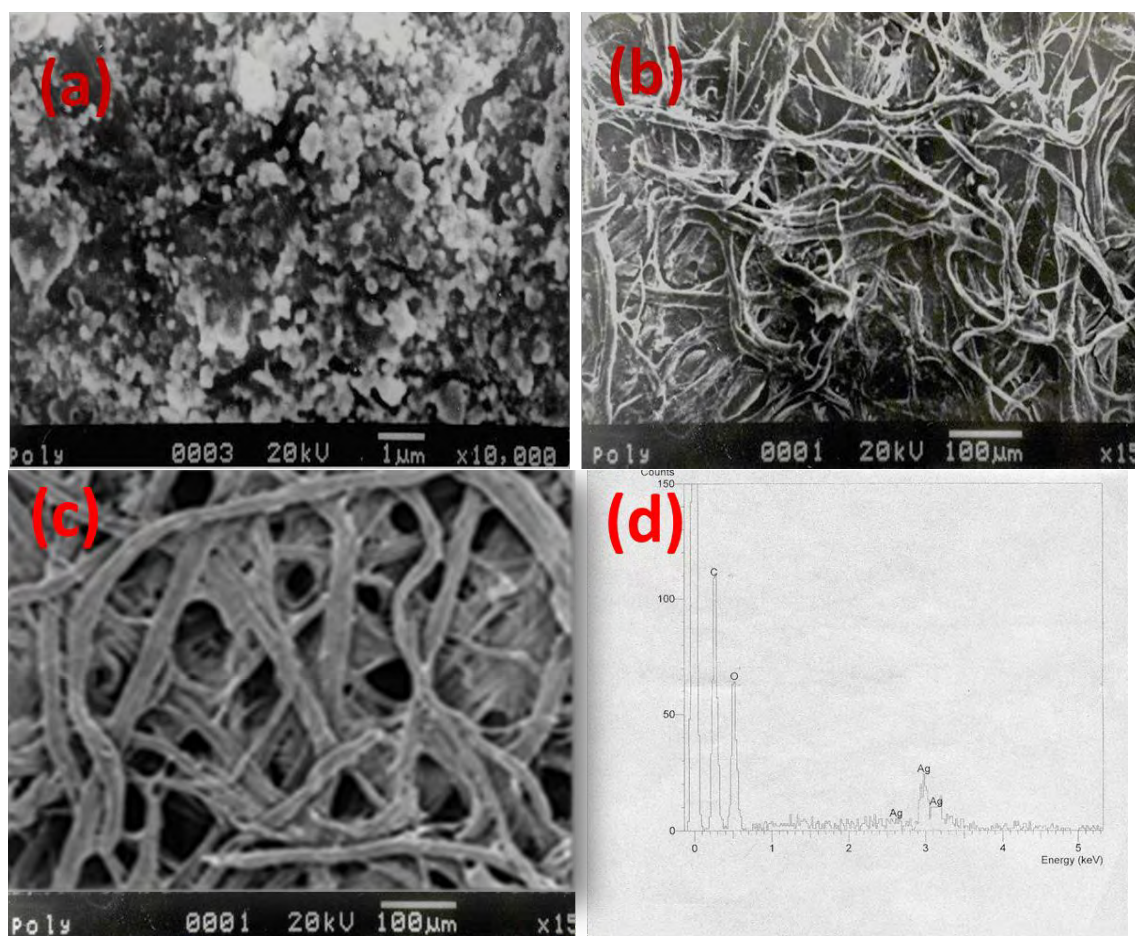


Fig. 4. (a) SEM pictures of the coated filter paper on scale 1μm, (b) SEM pictures of the coated filter paper on scale 100 μm, (c) SEM of the uncoated filter paper, (d) EDX data of the coated filter paper.

shown in Fig. 4(c). A filter paper has a high fibrous network. Such a highly fibrous network with nanoparticle deposition gives a good opportunity for the water molecules to get trapped in this material. As seen in the SEM pictures nanoparticle deposition is formed along the fibres. The coating of the fibres with nanoparticles is quite uniform. Such a uniform deposition enables the sample to be used as a good sensor material.

EDX Analysis

EDX analysis (Fig. 4 d) shows that the coated filter paper has sufficient amount of silver along with carbon and oxygen. The filter paper contains cellulose. So the carbon and oxygen come from the filter paper as well as chitosan. Mapping of silver particle shows that the distribution is very uniform. After mapping at different positions along the coated filter paper, almost same values were obtained.

Moisture Sensing

Sensitivity of a humidity sensor can be defined as the change in resistance (ΔR) of sensing element per unit change in relative humidity (%RH) [25] i.e.

$$S = \frac{\Delta R}{\Delta \%RH} \text{ M}\Omega/\%RH$$

The average sensitivity is calculated by taking the average of all sensitivities ranging from 10%RH to 90%RH.

The variation of resistance with a variation of %RH prepared by coating on the paper strip has been shown in Fig. 5(a). The curve for the sensing element shows that resistance decreases slowly with the increase in %RH. The average sensitivity is found to be 0.80 MΩ/%RH. In this case, it is found that the curve of resistance versus relative humidity is nearly linear as supported by the Fig. 5(a). The linearity of the sensing element arises early from 10% relative humidity onwards.

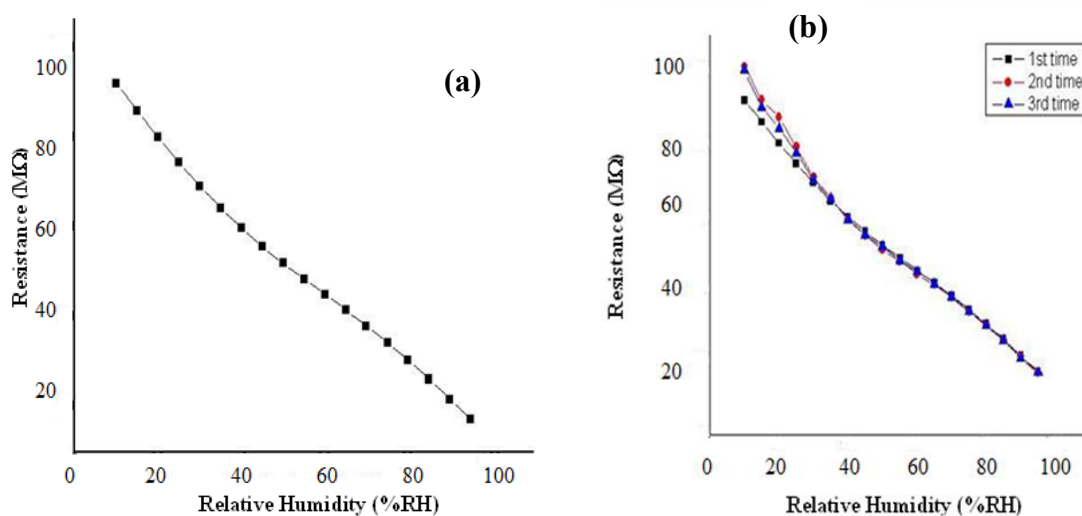


Fig. 5. (a) Variations in resistance with the variations in relative humidity for the sensing element (b) Variations in resistance with the variations in relative humidity after 3 and 6 days respectively.

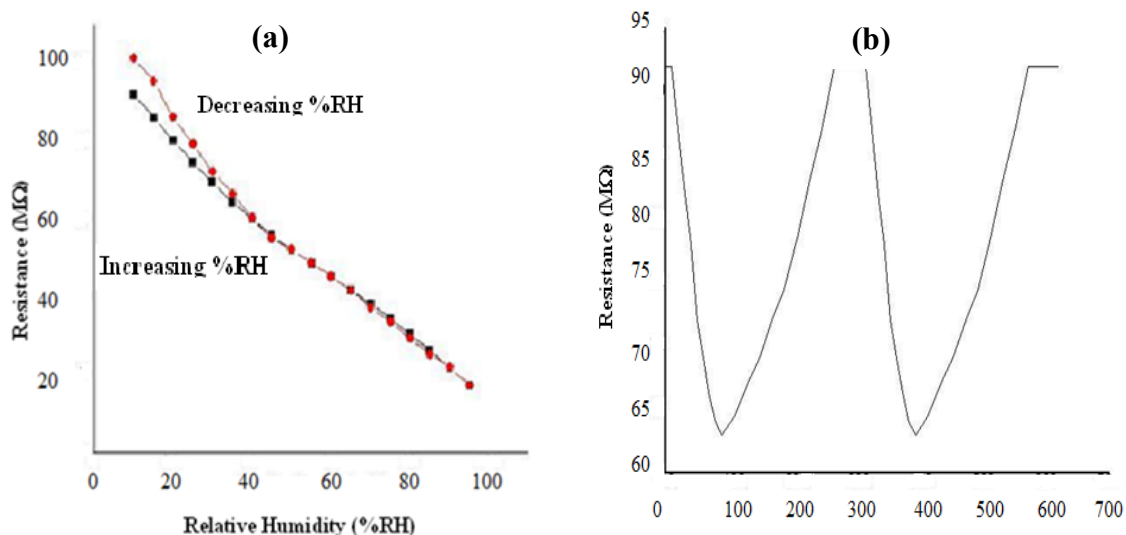


Fig. 6. (a) Hysteresis curve, (b) Response curve at a constant humidity.

The repeatability of the results has also been studied for the sensing element and the characteristics are shown in Fig. 5(b). The results are reproducible in multiple measurements. The hysteresis of the sensor is also tested as shown in Fig. 6(a). Hysteresis is observed especially at low humidity region. With the increase in humidity, the hysteresis loop becomes thinner. It takes in water vapour but during its release does not do so completely. There might even be mild structural changes occurring due to which this phenomenon is being observed. The

sensor is backed in the oven at 130 °C which makes the thick film mechanically stable. The thermal treatment is necessary to eliminate hysteresis during measurement. The response time has also been measured by the sensor. The response curve has been shown in Fig. 6(b) at a constant humidity of around 35%. As shown in the figure, the sensor takes about 80 seconds to reach a stable value of resistance under the given humidity conditions. The recovery time of the sensor is about 3 mins. Thus response curve shows the sensing behaviour is excellent as a humidity sensor.

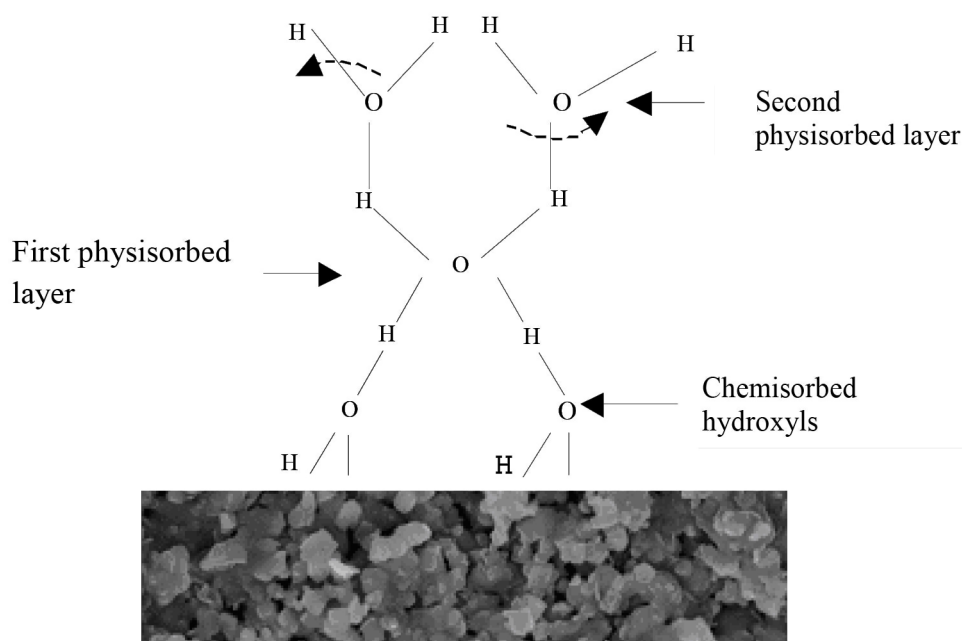


Fig. 7. Schematic of humidity sensing mechanism through a porous film.

Moisture Sensing Mechanism

The sensor material is a highly fibrous network as evident from the SEM analysis. Along these fibers silver nanoparticles are deposited. These silver nanoparticles are distributed all along the fibers. Thus these nanoparticles form small islands along these fibers. There is no long continuous chain between these nanoparticles and hence they are like islands over this fibrous network. Due to the absence of the continuous connectivity, the resistance of the sensor material in the absence of humidity is quite high. The discontinuity has been played upon the action of the sensor. If a higher concentration of silver is used in the fabrication of the sensor then the continuity of the background increases and thus sensitivity of the sensor becomes poor.

When this sensor is exposed to moisture water molecules are adsorbed on the surface of the sensor where highly fibrous networks exist. These water molecules get trapped in between the islands formed by the silver nanoparticles and introduce reasonable conductivity from H^+ generated there. Overall the conduction is due to proton generation through dissociation of H_2O through surface hydrolysis [26-27]. It may be facilitated by proton dissociated from OH group of chitosan. When the film is coated with any nonpolar low boiling organic solvent vapour after adsorption of moisture, the conductivity is

drastically reduced and gain to the original value after some time in the open atmosphere. This indicates that surface conductivity is probably due to protonic conductivity. Thus the mechanism of sensing action is simply due to proton conduction as per Grotthus Chain Reaction [25].

Schematic of sensing mechanism is shown in Fig.7. At low humidities, conduction is due to proton hopping between hydroxyl ions on the first layer of chemisorbed water vapour. The chemisorbed hydroxyl ions enhance the electrical conductivity of the sensor either by donating electrons to the conduction band of the base material or through proton hopping between adjacent hydroxyl groups upon application of an electric field. The process of chemisorptions occurs at very low humidity levels and is unaffected by further changes in humidity. However, an increase in humidity makes the water molecules physisorbed onto this hydroxyl layer. The effectiveness of physisorption depends upon the cation charge complexes from the material or the impurities and the water molecules present at the surface of the base material i.e. the hydroxyl ions. During formation of the first physisorbed layer, a water molecule attaches to two neighbouring hydroxyl groups through hydrogen double bonds and a proton may be transferred from a hydroxyl group to the water molecule. At higher humidity levels, the number of physisorbed layers increases,

allowing each water molecule to be singly bonded to a hydroxyl group, and proton hopping between adjacent water molecules in the continuous water layer takes place.

CONCLUSION

The sensing element prepared by the nanocomposite of silver and chitosan shows average sensitivity 0.8 MΩ/%RH for the entire range of humidity. The graph of resistance versus relative humidity is found to be linear in all the samples prepared by the same process. The results are also reproducible. The deposition of the silver in the composite is uniform as observed from EDX. The optimization of silver concentration is crucial to maximizing the sensitivity. The measured resistance of the strips (5 cm x 1 cm) ranges from 100 MΩ to 120 MΩ which is a very comfortable range of measurement by the simple electronic gadget. Instruments which can measure resistance up to about 100-150 MΩ will easily do the job. The sensor can be used over and over again due to its reproducibility after its heat treatment. Thus the sensor reported here is user-friendly, cost-effective, easy to fabricate and its operation range is quite large.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

- Kozłowski M, Frąckowiak S. Chemical sensors based on polymer composites. *Sensors and Actuators B: Chemical*. 2005;109(1):141-5.
- Kumar R, Singh S. Conducting Polymers: Synthesis, Properties and Applications. *International Advanced Research Journal in Science, Engineering and Technology*. 2015;2(11):110-24.
- Singh S, Singh A, Yadav BC, Tandon P, Kumar S, Yadav RR, et al. Frontal polymerization of acrylamide complex with nanostructured ZnS and PbS: Their characterizations and sensing applications. *Sensors and Actuators B: Chemical*. 2015;207, Part A:460-9.
- Pomogailo DA, Singh S, Singh M, Yadav BC, Tandon P, Pomogailo SI, et al. Polymer-matrix nanocomposite gas-sensing materials. *Inorganic Materials*. 2014;50(3):296-305.
- Meanna Pérez JM, Freyre C. A poly(ethyleneterephthalate)-based humidity sensor. *Sensors and Actuators B: Chemical*. 1997;42(1):27-30.
- Lee C-W, Nam D-H, Han Y-S, Chung K-C, Gong M-S. Humidity sensors fabricated with polyelectrolyte membrane using an ink-jet printing technique and their electrical properties. *Sensors and Actuators B: Chemical*. 2005;109(2):334-40.
- Singh S, Singh A, Yadav BC, Tandon P, Shukla A, Shershnev VA, et al. Synthesis, characterization and liquefied petroleum gas sensing of cobalt acetylenedicarboxylate and its polymer. *Sensors and Actuators B: Chemical*. 2014;192:503-11.
- Lee C-W, Park H-S, Kim J-G, Choi B-K, Joo S-W, Gong M-S. Polymeric humidity sensor using organic/inorganic hybrid polyelectrolytes. *Sensors and Actuators B: Chemical*. 2005;109(2):315-22.
- Saxena V, Choudhury S, Gadkari SC, Gupta SK, Yakhmi JV. Room temperature operated ammonia gas sensor using polycarbazole Langmuir-Blodgett film. *Sensors and Actuators B: Chemical*. 2005;107(1):277-82.
- Kulwicki BM. Humidity Sensors. *Journal of the American Ceramic Society*. 1991;74(4):697-708.
- Arai H, Seiyama T, W. Göpel, Hesse J, Zemel JN. Humidity Sensors, in *Sensors Set: A Comprehensive Survey*: Wiley-VCH Verlag GmbH, Weinheim, Germany; 1995.
- Traversa E. Ceramic sensors for humidity detection: the state-of-the-art and future developments. *Sensors and Actuators B: Chemical*. 1995;23(2):135-56.
- Sikarwar S, Yadav BC. Opto-electronic humidity sensor: A review. *Sensors and Actuators A: Physical*. 2015;233:54-70.
- Li Y, Yang MJ. Humidity sensitive properties of a novel soluble conjugated copolymer: ethynylbenzene-co-propargyl alcohol. *Sensors and Actuators B: Chemical*. 2002;85(1-2):73-8.
- Sakai Y, Sadaoka Y, Matsuguchi M. Humidity sensors based on polymer thin films. *Sensors and Actuators B: Chemical*. 1996;35(1):85-90.
- Dey KK, Bhatnagar D, Srivastava AK, Wan M, Singh S, Yadav RR, et al. VO₂ nanorods for efficient performance in thermal fluids and sensors. *Nanoscale*. 2015;7(14):6159-72.
- Kumar R, Yadav BC. Humidity sensing investigation on nanostructured polyaniline synthesized via chemical polymerization method. *Materials Letters*. 2016;167:300-2.
- Yang MJ, Casalbore-Miceli G, Camaioni N, Mari CM, Sun H, Li Y, et al. Characterization of capacitive humidity sensors based on doped poly(propargyl-alcohol). *Journal of Applied Electrochemistry*. 2000;30(6):753-6.
- Li D, Jiang Y, Li Y, Yang X, Lu L, Wang X. Fabrication of a prototype humidity-sensitive capacitor via layer-by-layer self-assembling technique. *Materials Science and Engineering: C*. 2000;11(2):117-9.
- Prabhu S, Poullose EK. Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. *International Nano Letters*. 2012;2(1):32.
- Krajewska B. Application of chitin- and chitosan-based materials for enzyme immobilizations: a review. *Enzyme and Microbial Technology*. 2004;35(2-3):126-39.
- Kumar MNV. A review of chitin and chitosan applications. *Reactive and Functional Polymers*. 2000;46(1):1-27.
- Yadav BC, Srivastava R, Dwivedi CD. Synthesis and Characterization of ZnO Nanorods by the Hydroxide Route and Their Application as Humidity Sensors. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*. 2007;37(6):417-23.
- Srivastava R, Yadav C. B. Nanostructured ZnO, ZnO-TiO₂ and ZnO-Nb₂O₅ as solid state humidity sensor. *Advanced Materials Letters*. 2012;3(3):197-203.

25. Yadav BC, Singh R, Singh S. Investigations on humidity sensing of nanostructured tin oxide synthesised via mechanochemical method. *Journal of Experimental Nanoscience*. 2013;8(5):670-83.
26. Kumar R, Yadav BC. Fabrication of Polyaniline (PANI)—Tungsten oxide (WO_3) Composite for Humidity Sensing Application. *Journal of Inorganic and Organometallic Polymers and Materials*. 2016;26(6):1421-7.
27. Fleming WJ. *A Physical Understanding of Solid State Humidity Sensors*. SAE International; 1981.