

HUMIDITY SENSING STUDY OF POLYANILINE/COPPER OXIDE NANOCOMPOSITES

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Abstract

In-situ polymerization of aniline was carried out with copper oxide, in the presence of oxidizing agent ammonium sulphate, to synthesize polyaniline/Copper oxide composites, by chemical oxidation method. The polyaniline/Copper oxide composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50wt. % of copper oxide in aniline. Fourier Transform Infra-Red Spectroscopy shows that the stretching frequencies are shifted towards higher frequency side. The surface morphologies of these composites studied using Scanning Electron Microscopy indicates that copper oxide particles were embedded in the polyaniline (PANI) chain. The conductivity studies reveal that the dimensions of copper oxide particles in the matrix have influence on both values. The electrical resistance of the polyaniline/copper oxide composites decreases with the increase in percentage relative humidity. The result reveals that the polyaniline/copper oxide nanocomposites can be used in the fabrication of humidity sensors.

Keywords: Polyaniline; Copper Oxide; Composite; Conductivity, Resistance; Humidity

Introduction

Humidity

The term humidity refers to the concentration of water vapour in air, where the water is in a gaseous phase. Humidity is defined as the amount of water vapour in an atmosphere of air or other gases. Humidity parameters are stated in diverse ways and the corresponding units are based on the measurement technique used. The most commonly used terms are —Relative Humidity (RH)‖, —Parts Per Million (PPM)‖ by weight or by volume and —Dew/Frost Point (D/F PT)‖, in which the two latter are subclasses of —Absolute Humidity (AB)‖. Absolute Humidity units are applicable for the primary measurement results in as much as one is able to directly measure the value of the water vapour content. In contrast, Relative Humidity is true for the secondary measurement results, since measurement of the water vapour values is mediated in some fashion.

Humidity Sensors

Humidity sensor is a device used to measure the percentage of relative humidity based on the electrical resistance of an object. Therefore, the relative humidity measurements have been extensively studied and a remarkable progress has been made [30]. Based on the changes in electrical or optical properties, different humidity sensors are popularly studied. Different types of polymers play an important role in optical sensors categorized as inorganic and organic [44] e.g. Polyaniline, Polyaniline/Copper Oxide poly(vinyl chloride) (PVC), poly(tetrafluoro ethylene) (PTFE), nafion, nylon, agarose, sol-gels, etc.

Types of Sensors

Humidity sensors have been organized into three groups, these are, Optical humidity sensors, Acoustic humidity sensors and Electronic humidity sensors. Electronic sensors are the most common type of sensors today. This technology has a very long history and follows the first generation of mechanical humidity sensors. These mechanical sensors were based mainly on change in the mechanical properties of some materials. These materials were frequently of animal origin, for example, horse or human hairs. These first mechanical sensors, which were slow and imprecise, were used throughout human history until the second half of twentieth century. At that time, practically simultaneously with the first electronic chips, the second generation of the humidity sensors has emerged. These were electronic humidity sensors. Today, humidity sensing based on electronic sensors is the dominant technology.

Importance of Humidity sensors

Humidity is a physical quantity that has significant importance in a number of areas ranging from life sciences [30,31] to building automation [32]. Hence humidity control, sensing and monitoring is important in a number of areas. Fast humidity sensors are required for the diagnosis of pulmonary diseases [33] and for mapping the human respiratory system [34] by monitoring the water vapor content of exhaled breath.

For meteorological applications [35] sensing of humidity is important as it indicates the likelihood of precipitation, dew or fog. In the semiconductor industry, the performance of photo-resist is critically dependent on the humidity. In the electronics industry, humidity monitoring is important as electronic items may malfunction due to high humidity. Furthermore, humidity control is essential in some buildings where humidity sensitive materials are stored such as museums, archives, warehouses.

For human comfort and to maintain the quality of a number of food products, it is important to control humidity levels inside buildings, cars, shops and other places. Many different types of humidity sensors are needed to cover all the previously mentioned applications. As a consequence, a wide range of sensor types, has been proposed for humidity measurements

Polymers

Conducting polymers have achieved more attention towards the humidity sensing application in present era due to its low weight, easy processing, and high absorption capability because of its porous nature [1]. Among the large variety of conducting polymers, polyaniline (PANI) has emerged as the most promising one because of its diverse properties like relatively inexpensive monomer, easy preparation, high yield of polymerization, environmental stability, and unique processability for device fabrication [2, 3]. The various techniques such as electrochemical polymerization, chemical oxidation, and electrochemical deposition and spin coating have been explored for the fabrication of polymer sensors [4]. Advantages with polymers as sensing materials are lightweight, flexible, low cost, and simple fabrication process.

Polyaniline has shown very promising results for sensing applications in comparison to other classical sensor materials employed in the fabrication of sensors [5, 6]. Various oxide doped polymer composite materials have been examined as the humidity sensor; for example, CuO, ZnO, and CdO, are reported to exhibit high sensitivity toward humidity [7, 8]. However, further improvements in the performance of the mixed-potential type polymer sensors are still needed in order to realize a commercially viable device of this type [9]. Basically, polymer metal oxide is used in humidity sensor applications and is prepared by conventional and advanced wet chemical processing methods at room temperature and is mainly developed to offer porous bodies. The advantage of an absorbent spongiform surface rather than a condensate is a greater permeability of water molecules, so water vapour molecules can easily pass through the pore openings and capillary condensation occurs in the capillary porous structures which are formed between the grain distributions in ceramic surface during the pore removal process.

Aims and Objectives

- To synthesize and characterize Polypyrrole/CuO nanocomposite humidity sensor.
- To study the humidity sensing properties of Polypyrrole/CuO nanocomposites.

Materials and methods

Experimentation

Synthesis of Copper Oxide (CuO)

For the synthesis of copper oxide nanoparticles, 10 g of copper sulphate was mixed with 20 ml distilled water, followed by addition of drops of Acetic acid. Ammonium hydroxide was added drop by drop till the reaction was completed and the solution was allowed to settle down for 24hrs. The precipitate of $\text{Cu}(\text{OH})_2$, was filtered off from the solution, then its dried in oven at 100°C for 3hrs and finally heated at 500°C in furnace for 3hrs. Copper Oxide nanoparticles were obtained after the heating which is black in colour.

Synthesis of Polyaniline

For the chemical polymerisation of Aniline, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used as an oxidant and anhydrous ethanol as solvent. 20 ml of aniline was added to 50 ml of ethanol and stirred for 10 minutes to obtain ethanol solution of aniline. To this solution, 0.1M of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added drop wise with continuous stirring. The suspension was stirred with the magnetic stirrer at 0°C for 3hrs and left for 24 hours for complete polymerization. Finally, the suspension was filtered and washed thoroughly with acetone and distilled water in order to remove the unreacted aniline and excess ammonium sulphate. A precipitate of polyaniline was obtained which was dried for 5hrs at 70°C in vacuum oven.

Synthesis of Polyaniline-CuO composites

4.5g of aniline was dissolved in 25ml ethanol, and stirred for 10mins, the ethanol solution of aniline was added to 0.5g of copper Oxide (CuO) (10%), 0.1M of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added drop wise to the ethanol solution of aniline/copper Oxide. This reaction mixture was stirred for 3hrs at 0°C with magnetic stirrer in order to disperse CuO in the polymer solution and left for 24 hours for polymerization. The obtained product was filtered and washed thoroughly with acetone and distilled water in order to remove the unreacted aniline and excess ammonium sulphate. The samples were vacuum dried for 5 hrs at 70°C . The experiment was repeated four times with the different grams of aniline and Copper oxide (CuO), as follows; 4.0g of aniline added to 1.0g of Copper oxide (20%), 3.5g of aniline added to 1.5g of CuO (30%), 3.0g of aniline added to 2.0g of Copper oxide (40%) and 2.5g of aniline added to 2.5g of Copper Oxide (50%) wt.

Table 1: Shows % composition of Polyaniline/Copper Oxide nanocomposites

S/No	PANI(g)	CuO(g)	Wt %
1	4.5	0.5	10
2	4.0	1.0	20
3	3.5	1.5	30
4	3.0	2.0	40
5	2.5	2.5	50

Note: The overall weight of each of PANI/CuO is 5grams.

Characterization

The above synthesized PANI-CuO composites are structurally and surface morphologically characterized by using different techniques like FTIR, DC Conductivity meter, scanning electron microscopy and humidity sensing chamber.

The FTIR spectra of pure polymer and copper oxide/polymer composite were recorded with the help of Perkin-Elmer FTIR spectrometer in the range $400\text{--}4000\text{cm}^{-1}$, in KBr medium at room temperature. For recording FTIR spectra, sample powders are mixed with KBr in the ratio of 1:25 by weight and grounded to ensure the uniform dispersion of samples in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of approximately 1mm thickness [10, 11].

The morphology of the pure PANI, PANI/CuO (wt 30%) nanocomposite and CuO were recorded using scanning electron microscope (SEM) machine, (Model: Zeiss EVO 18 Materials Analysis SEM). In order to prepare conducting surface, each sample was coated with gold through sputtering before taking the images. [12].

The electrical conductivity of pure PANI and PANI/CuO nanocomposites were recorded using, Hioki 3532-50 LCR Hitester electrometer. A typical experimental setup used for the measurement of dc conductivity consists of a sample holder securely locating the sample coated with silver paste in order to get better contact inserted from top aperture of the heating furnace. A potential difference is applied across the sample. The electrodes and thermocouple leads are taken out from top aperture and connected to Keithely 2100 electrometer to measure the change in current of the samples and temperature indicator, respectively. A heater placed at the bottom of the furnace is capable of giving a variable but linear rate of temperature increases over a broad range of temperatures. The DC conductivity of all the samples is obtained by measuring current flowing through a piece of the material and using the sample dimensions σ can be calculated using

$$\sigma = (d/AV) S \text{ cm}^{-1}$$

Where d (cm) is the sample thickness, A is its area (cm^2), V is the potential difference across the material, and I is the current flowing through the material.

Fabrication of Humidity Sensor Set Up:

Humidity sensor chamber is made up of side glass plates of size $250\text{mm} \times 250\text{mm}$ in dimension and 5mm thickness provided with top and bottom glass plates. The chamber is made airtight by rubber beading [13, 14]. The sample holder is then fixed at the central part of the chamber and dc fan at the left corner in order to distribute the humidity uniformly throughout the chamber. The vapors are allowed to pass through the bottom of the left side inlet which is controlled by using dimmer stat. The percentage of humidity in the chamber is monitored by using hygrometer and changes in the resistance of the samples are measured by Keithley meter. Thermal filament is inserted in right side of the bottom connected to the

temperature indicator. The right upper side is connected to vacuum pump to dehumidify the chamber for the next cycle/sample. The block diagram of the sensor setup is shown below:

Fig 1: Humidity sensing setup

Results and discussion

FTIR Analysis

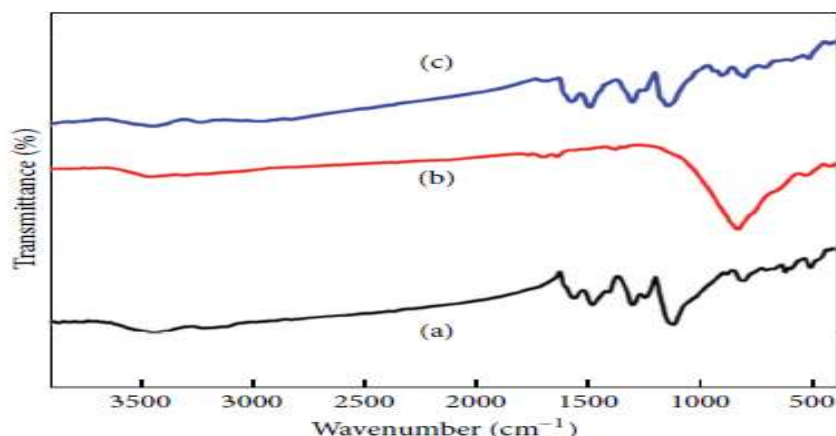


Fig 2: Infrared spectra of (a) PANI (b) CuO (c) PANI-CuO (30 wt%)

Figure 2(a, b, and c) shows FTIR spectra of the pure PANI, CuO, and PANI-CuO composite. Figure 2(a) represents the FTIR spectra of pure PANI. The strong peaks in wave number are in the range 1000–1600 cm^{-1} , attributed to the vibrational bands. The band at 504 cm^{-1} is due to CH out of plane bending vibration. The bands at 1561 and 1450 cm^{-1} are attributed to C=N and C=C stretching mode of vibration for the quinoid and benzenoid units of polyaniline. The bands at 1301 and 1421 cm^{-1} correspond to the characteristic of pure polyaniline. The FTIR spectra of the composite (Figure 2(c)) exhibit the characteristic peaks similar to that of pure PANI with a small shift in the characteristic peaks corresponding to that of the pure PANI. The characteristic peaks of CuO completely disappear in the IR spectra of composite which reveals the strong interaction between PANI backbone and CuO particles during the formation of composite.

SEM Analysis

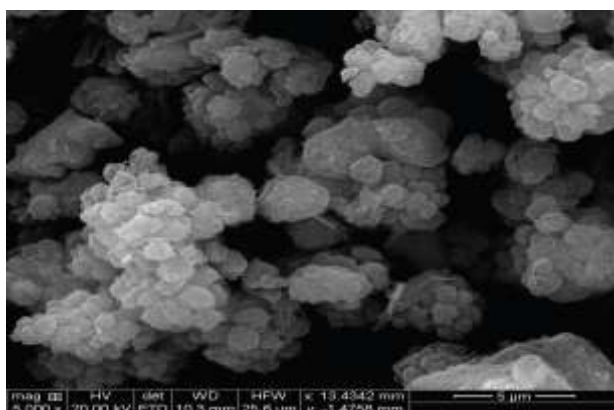


Fig. 3(a): SEM micrograph of pure PANI

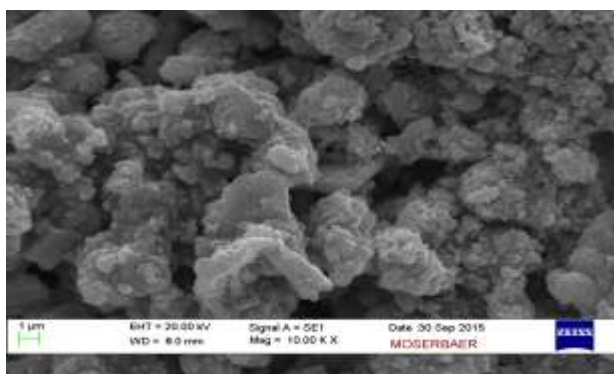


Fig. 3(b): SEM micrograph of CuO

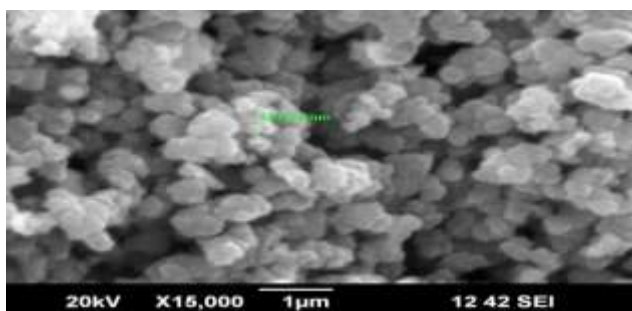


Fig. 3(c): SEM micrograph of PANI/CuO (30wt. %) nanocomposites

Figures 3(a), 3(b), and 3(c) show the surface morphology of pure PANI, CuO, and PANI-CuO composite (30 wt%) recorded using SEM. Figure 3(a) shows the SEM micrograph of pure PANI with smooth surface having micro pores. The SEM image of CuO in Figure 3(b) shows an agglomerated particle structure having uniform distribution. Figure 3(c) shows the SEM micrograph of PANI-CuO (30 wt%) composite. From the micrograph of composite, one can clearly observe the uniform distribution of CuO particles in PANI matrix with the formation of more capillary pores and a conducting network. These capillary pores facilitate the absorption of more water molecules leading to enhanced humidity sensitivity in the composite compared to pure PANI.

DC Conductivity analysis:

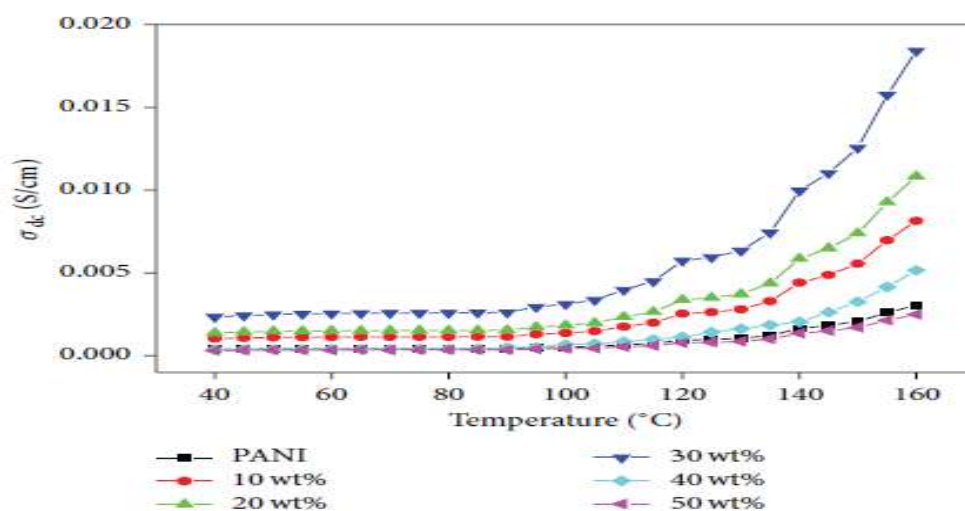


Fig. 4: conductivity vs temperature at different frequency of pure polyaniline, and different wt % of CuO.

D.C. Conductivity.

Figure 4 shows the variation of DC conductivity as a function of temperature for polyaniline and polyaniline-CuO composites for different weight percentages. It is observed that the conductivity of polymer composites increases with increase in temperature as well as increase in dopant percentages. The three-step conductivity is observed in the range of 30°C to 180°C. In first step, the temperature from 30°C to 60°C the conductivity of the pure polyaniline and it remains constant because insufficient activation energy fails in hopping of polaron from one island to other [15]. In second step from 60°C to 130°C, the conductivity increases gradually due to the hopping of polarons and bipolarons in short range order. Further, in third step from 130°C to 180°C the conductivity suddenly increases due to hopping of charge carriers in long range order. The three-step conductivity is characteristic property of amorphous semiconducting materials explained by Mott theory. Among all composites 30 weight percentage polyaniline-CuO Composite shows high conductivity due to the elongation of polymer chain in framed network favourable of hopping polarons in long range orders. The conductivity of other composites like 10, 20, 40, and 50 followed 30wt% and its conductivity is lower due to the partial blocking of polarons at the interface of two composite islands. However the expansion of composites is confirmed from thermal coefficient plot as shown in Figure 6. It is observed that the composite shows negative thermal coefficient (NTC) behaviour as a function of temperature. The NTC value decreases with increase in metal oxide percentage in polymer matrix due to decrease in the distance between two grains [16]. It is also known that the thermal expansion will cause significant stress in the matrix as the filler does not allow expansion or contraction, which increases the electron density at the junction, causing the blocking of charge carriers [10, 20].

RH (%)	PANI resistance (Ohm)	10% CuO/PANI (Ohm)	20% CuO/PANI (Ohm)	30% CuO/PANI (Ohm)	40% CuO/PANI (Ohm)	50% CuO/PANI (Ohm)
20	15	22	27	30	39	11
30	14	20	26	29	37	10
40	12	17	25	27	34	10
50	10	16	22	23	30	5
60	8	15	20	22	28	5
70	7	13	19	20	26	4
80	6	12	17	19	25	4
90	5	12	16	17	24	3

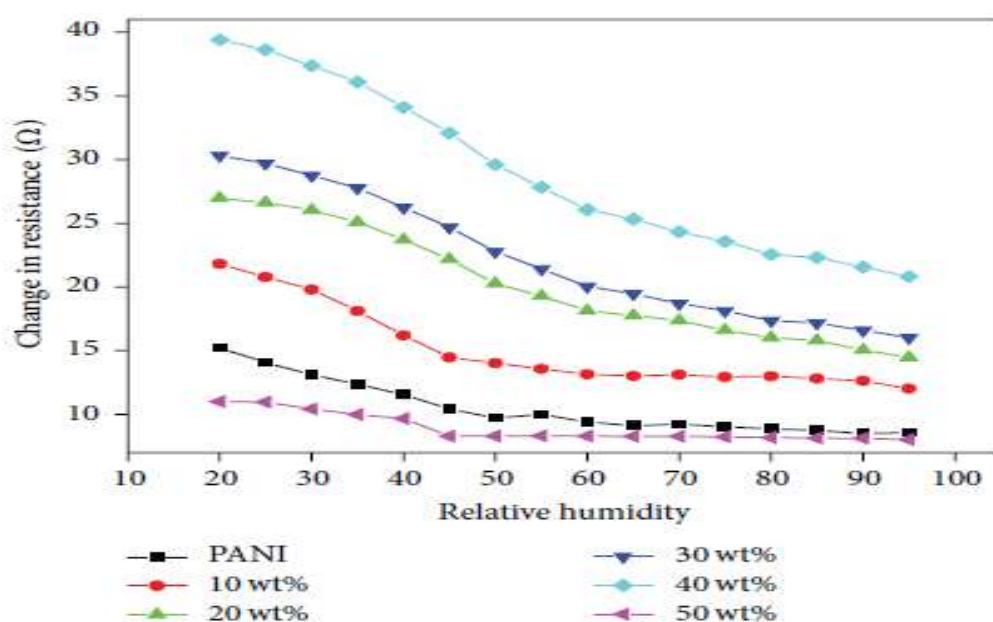


Fig. 5: Change in resistance as function of relative humidity of PANI and PANI-CuO composites.

Humidity Sensing Properties.

Figure 5, shows the change in resistance as a function of humidity from 15% RH to 95% RH at room temperature. It is found that the change in resistance increases with increase in percentage of relative humidity (% RH) due to the uncurling of polymer chain giving more favourable path for conduction of charge carriers. The proposed mechanism for change in resistance of these polymer composites is adsorption and desorption of humidity. In lower humidity level the change in the electrical resistance is slow due to the lower adsorption limit

(LAL), where uncurling process of the polymer is very slow leading to large distance of hopping sites. At higher humidity, composites absorb more vapour from a long conduction path as shown in Figure. Hence change in resistance decreases suddenly. It is important to note that the pure polymer shows large change in resistance but above 30% RH the polymer becomes unstable and starts degrading as results change in resistance almost constant. Among all composites, 30wt% of polyaniline-CuO composite shows linear decrease of change in resistance throughout the range indicating that these composites are more stable and help in holding the vapour molecules.

The sensitivity of detecting the humidity is defined by the percentage change in resistance per 10% change in the value of relative humidity. The variations in the resistivity as a function of relative humidity (RH) value for PANI/CuO composite in the form of pellets for five different weight percentages (10, 20, 30, 40, and 50wt%). The percentage of sensitivity for detection of humidity is defined as:

$$S = \frac{RH_2 - RH_1}{RH_1} \times 100,$$

Where RH_2 is the resistivity of the sample for humidity at level 2 (highest RH level) and RH_1 is the resistivity of the sample for humidity at level 1 (lowest RH level). Figure shows the sensitivity of polyaniline and polyaniline-CuO composites as a function of relative humidity for different weight percentages. The sensitivity is measured from RH 20% to RH 95% [17 18]. It is found that the sensitivity increases with increase in relative humidity. Among all composites 30wt% shows high sensitivity and more stability in long range of RH % followed by other composites which shows almost similar behaviour. These composites above 30wt% the absorption is good but as the polymer percentages is more than metal oxide fails to hold the water vapour for longer time as a results after some period of exposing with humidity starts saturating the surface; hence, sensitivity decreases. In case of pure polyaniline sensitivity even more than composites but the stability of the polyaniline loses above 50% RH and starts degradation of polymer. The vapour is removed from the humidity chamber by using vacuum pump but we cannot remove it completely from the samples. Therefore, once the humidity of chamber attends 40% RH, heating should be switched on till the electrical resistance comes to base level in order to start next cycle [19].

Conclusion

From the humidity sensing results, it has been observed that the resistance of the polyaniline and its copper oxide (CuO) nanocomposites decreases with the increase in humidity from 25 - 95% range and thus, implies its potential to serve as a humidity sensing materials in fabrication of electrochemical humidity sensors.

Recommendation:

Based on this research work, we recommended to the government, Pharmaceutical industries, food industries, semiconductor industries, electronics industries and meteorological industries that, Polyaniline/CuO nanocomposites can be used in fabrication of electrochemical humidity sensors.

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