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# Humidity sensing using polyaniline/polyvinyl alcohol nanocomposite blend

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**Abstract:** Studies on organic conducting polymers have gained attention in the past decade due to their simple, low cost fabrication processes, low temperature operation and ability to conform to various device shapes and geometries. This paper presents chemical oxidative synthesis of HCl doped polyaniline (PANI)/polyvinyl alcohol (PVA) nanocomposite using ammonium persulphate as oxidizing agent. PANI/PVA blends were prepared by adding 0.05mM, 0.1mM and 0.15mM concentrations of PVA into synthesized PANI in aqueous solvent. UV-Visible spectroscopy and FT-IR spectroscopy were used to investigate the analytical and functional groups present in the synthesized nanocomposites. The results indicated the formation of highly conducting PANI/PVA blends. Humidity sensors were prepared by casting thin films of as-prepared nanocomposites with varying concentrations of PVA onto interdigitated electrodes over PCB. On exposure to humidity, it was observed that the electrical resistance of the fabricated sensors reduced by 60-75% for 90% humidity. It may be concluded that the addition of appropriate amount of PVA to PANI enhanced the humidity sensitivity.

## 1. Introduction

Monitoring and control of ambient humidity is crucial for food processing and packaging, drug manufacturing and storage, semiconductor fabrication, preservation of antiques and paintings etc. [1,2]. Humidity sensors are composed of metal oxides, polymers and nanomaterials whose electrical resistance or capacitance changes with water ingress [3-5]. Among these, polymer thin film based humidity sensors have the advantages of large scale processability, easy synthesis at room temperature, and application over a wide range of substrate geometries. Conducting polymers such as polyaniline, polypyrrole, poly thiophene etc., exhibit unique electrical, electrochemical and optical properties [6,7]. Interestingly, these polymer properties can be precisely tailored to meet the needs of specific application by doping with suitable cations, anions and nanoparticles [8,9]. Polyaniline (PANI) is an intrinsically conducting organic polymer formed by oxidizing individual aniline monomers. It finds application as electrodes in rechargeable batteries, OLEDs, electromagnetic shielding, electrodes for flexible solar cells and conducting ink for 3D printing [10-13]. When the aniline monomer is oxidized, the hydrogen in the amine group is removed and attached to the neighboring phenyl group. This repetitive polymerization results in long chain polymer nano-fibers of PANI. The addition of protonic acid such as HCl, increases the electrical conductivity of PANI. Although fully cross-linked PANI nano-fibers are insoluble in water, their electrical resistance changes significantly with changes in external humidity conditions.



When exposed to humidity the effective resistance of PANI film changes due to the formation of H-bonds between water molecules and the nitrogen present in the amine group. Thus, the conductivity of PANI increases with increasing humidity due to continual proton exchange. This makes PANI based derivatives and composites attractive candidates for humidity sensing materials. Also, it was observed that the addition of certain non-conducting hygroscopic polymers such as polyvinyl alcohol (PVA) into the interpenetrated networks (IPN) of PANI fibers enhances its humidity sensitivity [14]. In addition, PVA has good adhesion to different substrates providing sufficient mechanical reinforcement for PANI/PVA nanocomposites. *Yang et al* report the fabrication of microsensor using PANI/PVA as humidity sensing material [4]. Although the sensitivity and response of reported sensor is excellent, its fabrication is somewhat tedious, requires clean room and lithography facilities. This paper aims at fabricating a simple low-cost humidity sensor using PANI/PVA films. The nanocomposites blends were prepared by chemical oxidation technique and doped with HCl for improved electrical conductivity. These composites were then characterized using UV-Visible spectroscopy and FT-IR. PANI/PVA films were used as sensing elements whose electrical resistance changes with humidity levels. The variation of electrical resistance for different weight ratios of PANI/PVA nanocomposite was evaluated. Finally, sensor response was obtained for relative humidity in the range 17% to 91% and compared with commercial sensor.

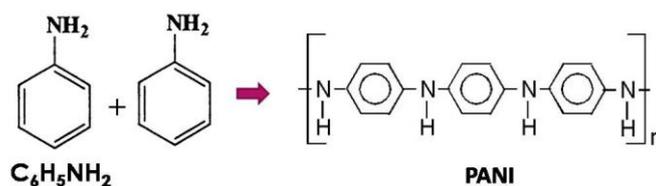
## 2. Experimental Procedure

### 2.1. Materials:

Aniline ( $C_6H_5NH_2$ ) (99.5 %), ammonium persulfate ( $(NH_4)_2S_2O_8$ ) (98 %), concentrated hydrochloric acid (HCl) (90%) and polyvinyl alcohol ( $(C_2H_4O)_x$ ) (99 %) used in this paper for the preparation of PANI/PVA composites were procured from S D Fine chemicals, Mumbai. All the chemicals used in this paper were of analytical grade and were used without further purification.

### 2.2. PANI/PVA Synthesis

In this paper, PANI/PVA blends were prepared by chemical oxidation method. Polyaniline was synthesized by oxidation of aniline monomer using ammonium persulphate (APS) as an oxidizing agent. During the oxidation process, the hydrogen in the amine group is replaced with a carbon bond from the orthoposition of the phenyl group. This process repeats itself till all the aniline is consumed and long chain polymer is formed. The addition of protonic acids to polyaniline during the polymerization process includes  $H^+$  ions into the lattices of the N-H bond, thus enhancing the conductivity of the PANI nano fibres (see figure 1). Studies indicate that addition of HCl to PANI provides highest electrical conductivity to the polymer compared to other protonic acids [8].



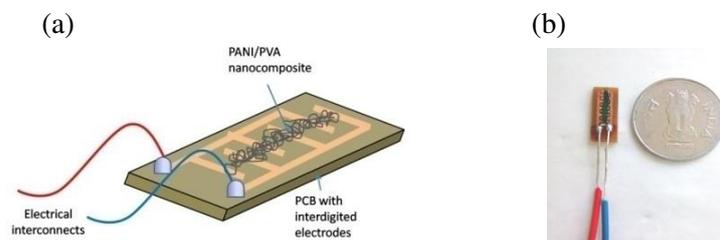
**Figure 1.** Scheme showing the formation of polyaniline

1 molar concentration of aniline was prepared by dissolving 9.3g of aniline in 100mL of distilled water. Further, 10mL of concentrated HCl was added to aniline solution and stirred vigorously to obtain a homogenous solution. Similarly, 22.8g of APS was dissolved in 100mL of distilled water to obtain 1 molar solution. 0.05mM concentration of PVA in aqueous solution was prepared by dissolving 50mg of PVA powder in 10mL of distilled water at 85°C. PANI/PVA blends were made by mixing equimolar concentration of aniline solution (1M), APS solution (1M) and PVA (0.05mM) in aqueous solvent. This

mixture was stirred continuously for about 8-10 hours at room temperature. At the end of the polymerization process, a dark green residue settles to the bottom of the beaker which can be filtered and used for humidity sensing applications. Different samples of PANI/PVA blends were made by varying the concentration of PVA in PANI. These samples are referred to as  $S_0$  for plain PANI,  $S_1$ ,  $S_2$  and  $S_3$  for PVA 0.05mM, 0.1mM and 0.15mM respectively.

### 2.3. Sensor Fabrication

Printed circuit board (PCB) made of thick FR4 polymer is used as the base material for sensor chips. The copper clad FR4 sheets are available commercially and an interdigitated electrode pattern was etched into it. This pattern ensures maximum electron collection efficiency at lower bias voltage [15]. The interdigitated electrodes used in this study consist of 6 fingers for each electrode which are interlaced as shown in figure 2 (a). The dimensions of the PCB chip, electrodes and sensing film in mentioned in Table below. The synthesized PANI/PVA nanocomposite films were applied over the electrodes and allowed to dry in room temperature. Wires were soldered to the contact pads of the PCB for electrical interconnection. figure 2 (b) shows the photograph of fully fabricated humidity sensor. In this paper, the humidity sensing response was evaluated for samples  $S_0$  to  $S_3$  corresponding to PANI/PVA blends with varying PVA concentration.



**Figure 2.** (a) Schematic diagram showing the components of fabricated humidity sensor  
(b) Photograph of fabricated humidity sensor chip

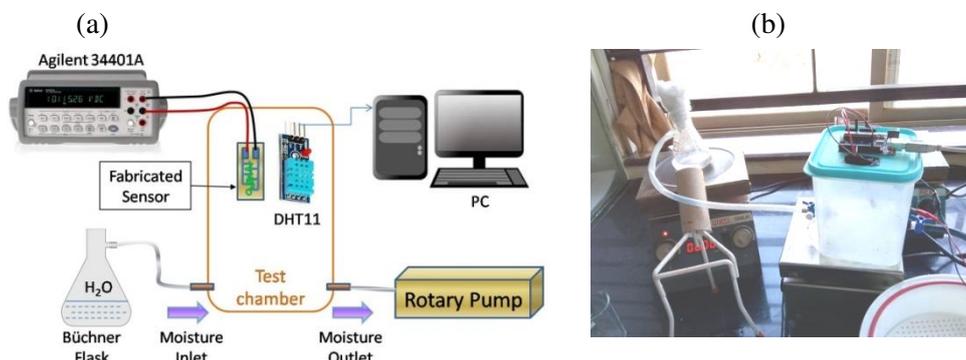
**Table 1:** Dimensions of the fabricated humidity sensor chip

Sensor elements	Parameters	Dimensions in mm
PCB sensor chip	Length, $L_c$	15
	Width, $w_c$	7
Electrode	Length, $L_e$	10
	Width, $w_e$	4
	Finger length, $L_f$	3
	Finger width, $w_f$	1
Sensing film (PANI/PVA)	Finger gap spacing	0.5
	Length, $L_s$	10
	Width, $w_s$	2
	Thickness, $t_s$	0.15

### 2.4. Humidity sensing set-up

Figure 3 (a) shows the schematic diagram of the humidity sensing test chamber. It was built using an air-tight plastic container with two openings at the bottom. One for inlet of moisture and the outlet is connected to a rotary pump for evacuation. The fabricated sensor is placed within the chamber along with a commercial humidity sensor (OLatus DHT11 Module Temperature and Humidity sensor). The commercial sensor was connected to a PC via Arduino Uno which provides a GUI display of the chamber temperature and relative humidity (RH%). It should be noted that the temperature within the test chamber was kept at 27°C throughout the experiment. The variation of electrical resistance in the fabricated sensor with respect to RH% was measured using Agilent 34401A digital multimeter. The

relative humidity (RH%) within the chamber was created by boiling distilled water in a Büchner flask as seen in figure 3 (b). The resistance of the sensor was measured for humidity variation from 17% to 91% for 4 different PANI/PVA blend samples  $S_0$  to  $S_3$ .



**Figure 3.** (a) Schematic diagram showing humidity sensing test chamber (b) Photograph of the test chamber

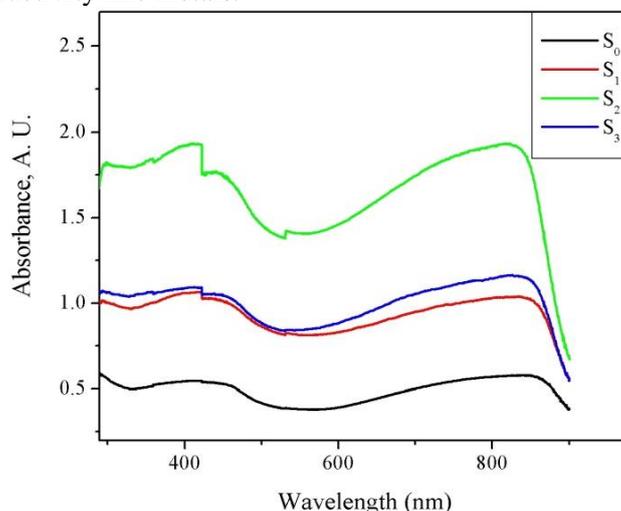
### 3. Results and discussion

#### 3.1. Characterization of PANI/PVA nanocomposites

The as-prepared PANI/PVA nanocomposites were characterized using UV-Visible spectroscopy and FT-IR spectroscopy to investigate the electronic transition and functional groups present.

##### 3.1.1 UV-Visible spectroscopy

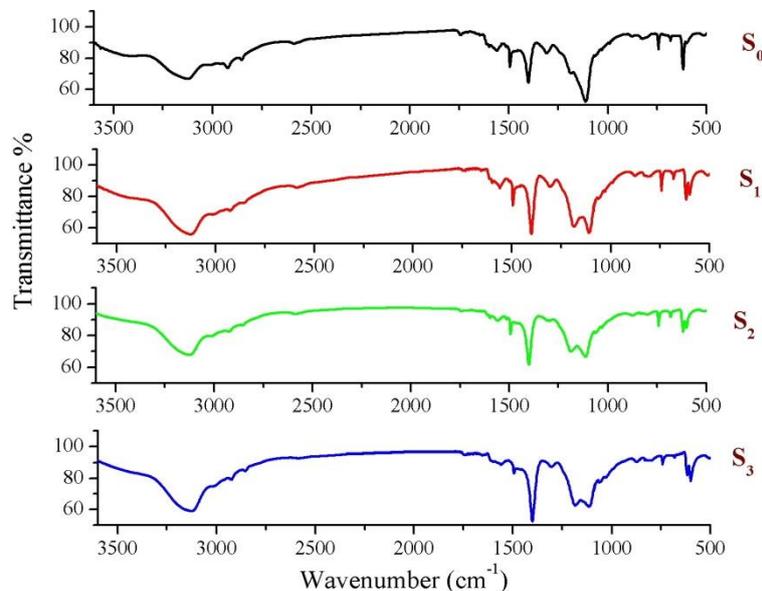
Figure 4 shows the UV-VIS absorption spectra of the HCl doped PANI/PVA nanocomposites in aqueous solution. Samples  $S_0$  refers to plain PANI. Sample  $S_1$  to  $S_3$  refers to PANI/PVA blends with varying concentration of PVA (0.05mM, 0.1mM and 0.15mM). All the samples show absorption peak at 300 nm corresponding to the  $\pi - \pi^*$  transition of the benzoid rings which is widely observed in HCl doped PANI composites [17]. The broad absorption bands in 420-460 nm comes from the hydrogen bonding due to polaron/bipolaron transition [13]. Maximum peak at 840 nm is due to extended coil conformations in conducting phase of the emeraldine salt in PANI [14]. This peak gradually decreases into the IR wavelength which is attributed to free-carriers and is characteristic of conducting polymers with high electrical conductivity like metals.



**Figure 4.** UV-Visible absorption spectra of PANI/PVA nanocomposites

### 3.1.2 FT-IR spectroscopy:

Figure 5 shows the FT-IR spectra of HCl doped PANI/PVA nanocomposites in aqueous solution. The medium peak at  $3445\text{ cm}^{-1}$  arises due to the free N-H stretching vibrations of primary amine in aniline [17]. The broad band from  $3300\text{--}3100\text{ cm}^{-1}$  corresponds to the  $\text{--OH}$  stretching bend. The intensity of this band gradually increases with higher concentration of PVA which contains  $\text{--OH}$  functional group. This confirms the increasing weight percentage of PVA in the composite. The peaks from  $2863\text{--}2932\text{ cm}^{-1}$  correspond to ring C-H vibrations [16]. The strong peak at  $1563\text{ cm}^{-1}$  is due to the presence of benzenoid ring and the peak at  $1494\text{ cm}^{-1}$  comes from the quinoid ring respectively [14]. The peak at  $1306\text{ cm}^{-1}$  is due to the  $\text{--CN--}$  stretching mode of the of the aromatic amines. The strong peak at  $1191\text{ cm}^{-1}$  corresponds to C-O stretching and its intensity increases with PVA concentration. Also, the peak at  $1112\text{ cm}^{-1}$  is due to C-N stretch of the aliphatic amine which tends to decrease intensity with increasing PVA concentration. The peak at  $754\text{ cm}^{-1}$  is pertaining to the  $\text{--NH}$  wag of the primary amine in PANI. The peaks from  $719\text{--}889\text{ cm}^{-1}$  corresponds to the bending of aromatic C-H [9].



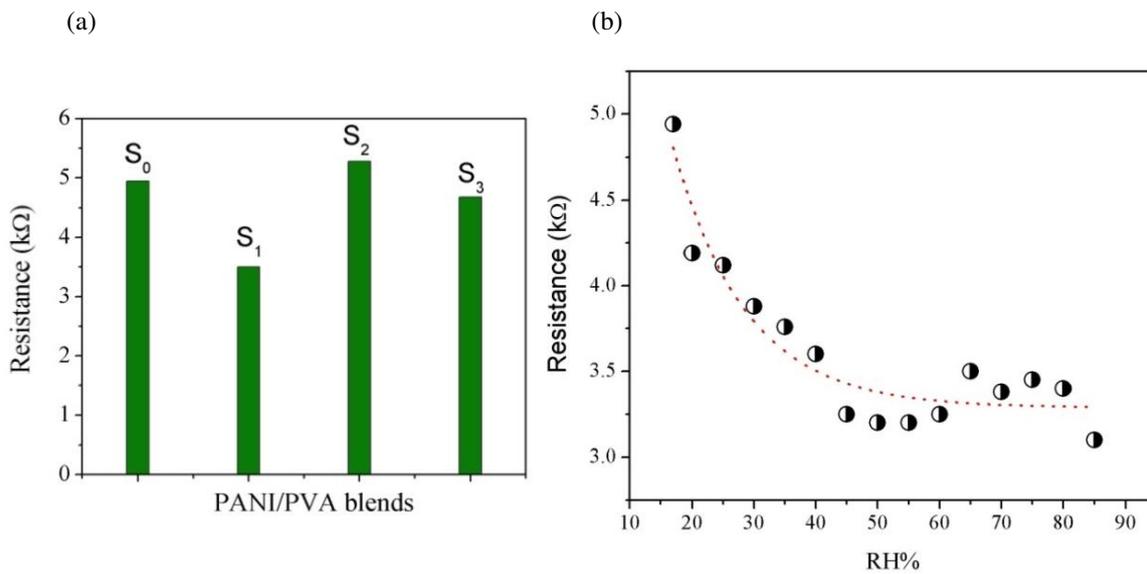
**Figure 5.** FT-IR Spectrum of PANI/PVA nanocomposites

### 3.2. Sensor response to humidity

Figure 6 shows the base resistance of the humidity sensors measured at 17% relative humidity in ambience. HCl doped PANI is highly conducting, however addition of PVA decreases its electrical conductivity [16]. It may be noted that the resistance of PANI film was measured to be  $4.94\text{ k}\Omega$  and this value decreases with increasing concentration of PVA in the nanocomposite which is attributed to the increased percentage of IPN networks [14]. The fabricated sensor resistance depends on the conductivity of the PANI/PVA blends as well as the geometry of the deposited nanocomposite film. In this study, nanocomposite films were cast over PCB strips using a paint brush. This method doesn't ensure deposition of PANI/PVA films with uniform thickness and this aspect significantly affects the sensitivity of the humidity sensor. However, care was taken to maintain a uniform thickness for all the samples throughout this study. The humidity sensing response was evaluated experimentally for each of the fabricated PANI/PVA coated sensors ( $S_0$  to  $S_3$ ) for different relative humidity from 17% to 91% (refer subsection 2.4) Figure 7. As per reported literature the resistance of PANI film decreases with

increasing levels of humidity [18]. When water molecules interact with the nitrogen center present in the amine group of the polymer backbone, under certain pH conditions, water molecules dissociate to form H<sup>+</sup> ions. There are plenty of charged sites which can accept H<sup>+</sup> ions in emeraldine salt of PANI such as the –NH– group. The presence of H<sup>+</sup> ions near these charged sites increases the doping concentration of PANI film which in turn reduces its resistance at higher humidity levels [16]. Figure 6 (b) shows a non-linear response of the PANI humidity sensor and the variation of resistance at different RH% is given by equation (1)

$$R = 3.28 + 6.41 \exp(-RH\%/11.78) \text{ in } k\Omega \quad \dots(1)$$



**Figure 6.** (a) Variation of base resistance for various concentrations of PVA (b) Response of PANI films to humidity

*3.2.1 Sensitivity:*

The sensitivity of the fabricated sensor to changes in relative humidity in the test chamber at room temperature is given by equation (2).

$$\frac{\Delta R}{R} \% = \frac{R_0 - R_{RH}}{R_0} \times 100 \quad \dots(2)$$

Where, R<sub>0</sub> refers to the base resistance at ambient humidity and R<sub>RH</sub> measured at particular relative humidity in the test chamber. Figure 7 shows the sensitivity of the fabricated sensors with various PANI/PVA concentrations from S<sub>0</sub> to S<sub>3</sub> for relative humidity between 17% to 91%. It may be observed that addition of PVA to PANI increases the change in resistance significantly. This corresponds to the affinity of PVA molecules to absorb and retain water molecules in the IPN networks thereby increasing the sensitivity of PANI to humidity changes. As seen in figure 7, the sensitivity of fabricated sensor is highest for 0.1mM concentration of PVA (S<sub>2</sub>) which is 40% more than plain PANI (S<sub>0</sub>) films. This is possible due to the maximum interpenetration limit of PVA into PANI nano-fibers.

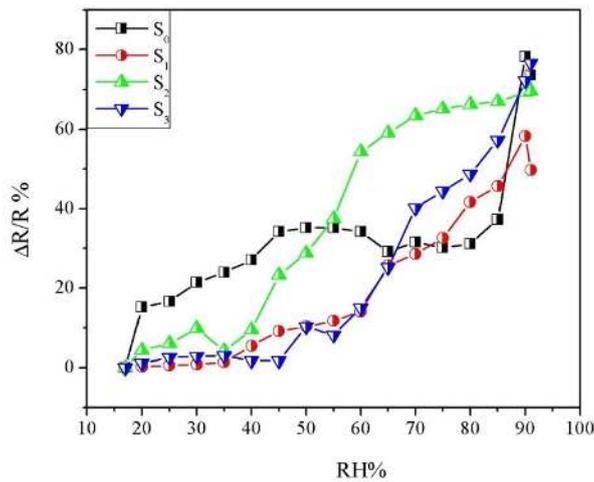


Figure 7. Response of the fabricated humidity sensor for varying RH%

3.2.2 Hysteresis:

After humidity levels were increased and corresponding resistance changes were obtained. The humidity was brought back to ambience and the corresponding change in resistance was recorded for decreasing humidity for PANI and PANI/PVA blend. In both cases the hysteresis was huge which attributed to room temperature measurements as seen in figure 8. However, by heating the sensor after humidity sensing the hysteresis effects may be reduce significantly.

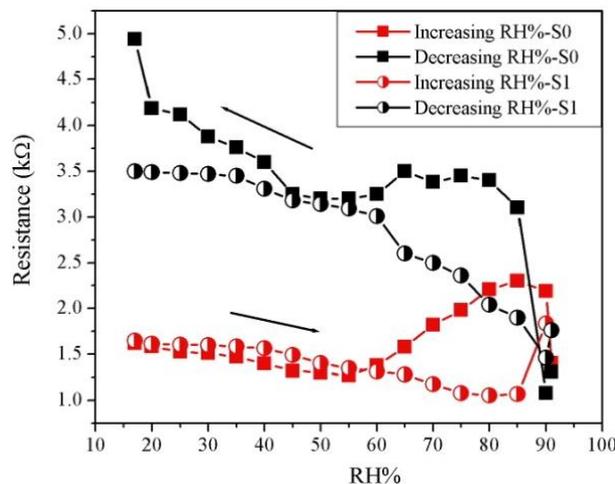


Figure 8. Hysteresis of humidity sensors with PANI (S<sub>0</sub>) and PANI/PVA nanocomposite (S<sub>1</sub>) films.

4. Conclusion

PANI/PVA nanocomposite blends were prepared in aqueous solution by chemical oxidation technique and doped with HCl for increased conductivity. In this study, 0.05mM, 0.1mM and 0.15mM concentration of PVA was incorporated into PANI and their corresponding sensitivities for humidity changes were recorded. UV-Visible spectrum results show the presence of sharp peak at 800nm indicating highly conducting PANI nanocomposites. FT-IR spectrum showed sharp peaks indicating the presence of PVA and PANI. Humidity sensor was calibrated using a commercial sensor and its resistance was measured with respect to increasing humidity. 0.1mM concentration showed the best response at room temperature. The electrical resistance of the fabricated sensors reduced by 60-75% from its base resistance for 90% RH. It may be concluded that the addition of PVA to PANI increased the humidity sensitivity significantly.

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