Synthesis and characterization of highly crystalline polyaniline film promising for humid sensor

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ABSTRACT

Polyaniline (PANI) was prepared in emeraldine via chemical oxidation method using $CuSO_4$ as initiating agent. The chemical characterizations were made using UV-vis (ultraviolet-visible spectrophotometry), FT-IR (Fourier transform spectroscopy), TG-DTA (thermo-gravimetric/differential thermal analysis), ESI-MS (electrospray ionization mass spectrometry), XRD (X-ray diffraction), SEM (scanning electron microscopy) techniques. The results revealed the formation of homogeneous, crystalline PANI with sub-micron size particles. The PANI thin film of 0.5 µm thickness has been fabricated using spin coating technique. The resulting PANI film was exposed to controlled humid condition and change in resistance has been recorded. The resistance was continuously decreased from 13.5 to 3.75 MΩ with a linear change in humidity ranging from 3 to 95%. The result was reproducible and checked by repeating observation. Copyright © 2010 VBRI press.

Keywords: Polyaniline, crystallinity, resistance, humidity sensor

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Introduction

Designing and developing humidity sensor and humidity sensitive materials is an area of current interest because their importance in the environmental monitoring and evaluation of hermeticity of micro packaging [1-3]. The materials used for humidity sensing purpose are reported viz. different oxides, modified polymeric resins and conducting polymers [4-7]. These materials change their properties including resistance, impedance, mass and refractive index as the function of relative humidity. This is the basis for development of different types of humidity sensors such as resistive, optical, quartz crystal microbalance [8-10].

In this context, the organic polymers are observed to be fairly fit for sensing purposes due to moderate resistance, wide spectrum of structural variability and their changes in erratic atmosphere [11]. Among conducting polymers, polyaniline (PANI) has been reported as a promising candidate with great potential for practical uses such as light emitting diodes, transparent electrodes, electromagnetic radiation shielding, corrosion protection of metals, battery, gas and humidity sensing purposes [12-13]. Vijayan et al. has established co-doped PANI for humidity sensing applications and monitored its optical properties with limited range and sensing parameters [14]. Typically, the electrical property of PANI quite differs due to its different phase, structures and employed synthetic routes. Further, PANI is also reported as highly biocompatible because of its accommodating surface behavior [15]. Various methods were used for PANI synthesis viz. electropolymerization [16], chemical polymerization [17], copolymerization, [18] and plasma polymerization [19]. However, the chemical route is used with different polymerizing agents such as HNO_3, ammonium persulphate, etc. with less rigorous synthetic condition. The wide spectrum properties of PANI are reported due to change in polymerizing agents and solvents.

The humidity sensitive materials should not be highly conducting, since the water molecule is also having high resistance. Thus the synthesis of PANI by different routes and its use in sensing sciences seems an important scientific investigation. The present manuscript describes the synthesis and characterization of emeraldine form PANI by chemical oxidation route employing $CuSO_4$. Further the resistance of PANI was monitored as function of relative humidity in the 3 to 95 % RH range to explore its use for humidity sensing.

Experimental

Materials and methods

Aniline (99.5%), hydrated copper sulphate ($CuSO_4.5H_2O$, 99.5%) and glacial acetic were procured from E. Merck, Germany. All supplementary chemicals were of analytical grade and solutions were prepared with mili-Q water.

UV-vis study was carried out on a UV2501PC, Shimadzu spectrophotometer. FT-IR characterization was done using a RK1310, Perkin Elmer, FTIR spectrometer via making pellet with dehydrated KBr at 10 ton pressure. The thermal analysis was observed with a PTC10A, Rigaku Thermoflex thermal analyzer at 10 ^{o}C min^{-1} heating rate. ESI-MS analysis was obtained from ESI-MS KC455, Micromass, Water Ltd. The crystallinity of the PANI was studied by RAD/Max200B, Rigaku Rotaflex, XRD spectrometer using 1° min^{-1} scanning speed. The SEM images were taken with a JEOL-840 scanning electron microscope, JEOL Corporation operated at 15 kV. The films were sputter-coated with a thin layer of gold (~20 nm) prior to the SEM examination. The electrical resistance of film was monitored as function of relative humidity by using RISH max laboratory digital multimeter (measuring range up to 40 MΩ).

PANI synthesis, film preparation and humidity sensing

Aniline (5 mL) was added in a 25 mL reaction tube containing 15 mL of methanol. The solution was stirred on a magnetic stirrer for 45 min to make a homogenous solution. The temperature was maintained at 40 ±0.2^{o}C. To this solution, 5 mL of 0.05 M aqueous copper sulphate

solution was added drop by drop with constant stirring on magnetic stirrer at 40 ±0.2 °C temperature. The color was observed during reaction and information is listed in **Table 1**. At the end of reaction, the green color particles were yielded. Typically, PANI was separated from oligo-aniline unreacted styrene monomer and polystyrene homopolymer by pouring the viscous solution into a large quantity of toluene. The copolymer was separated from polyacryamide and acrylamide by precipitating the resulting solution with methanol and water (7:3, v/v) mixture. Finally, a white, fluffy solid of PSA was obtained after vacuum-drying at room temperature. PANI yield (%) = 85.5; M_w (DMF with 10 mM LiCl) = 59 kDa. Next, the reaction mixture was allowed to keep over night and then material was recovered by centrifugation and dried under vacuum oven at 60 °C. A schematic of the polymerization reactions is shown in **Fig. 1**.
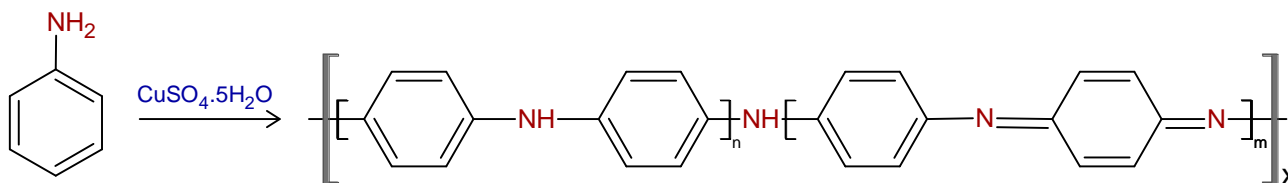

Fig. 1. Schematic illustration of PANI synthesis

Table 1. Colour change as observed during polymerization.

Time (w.r.t. the addition of copper sulfate solution to the reaction mixture)	Color change in the reaction mixture (solution of aniline and methanol + aqueous solution of $CuSO_4$)
0 min	Transparent colorless
30 min	Opaque blue
45 min	Greenish
1 h 30 min	Dark green

The PANI thin film was prepared by spin-coating method. Typically, PANI (200 mg, green product) was dissolved in glacial acetic acid (50 mL). The solution was used as a precursor solution to cast the film at 2000 rpm. For the humidity sensing, the PANI coated film was fixed inside the wall of an air-tight glass chamber (4 cm × 7 cm) via holder at a fixed %RH. The relative resistance change of PANI film before and after exposure at various %RH points has been monitored using laboratory digital multimeter. The saturated solution of KOH was used to control %HR of the glass chamber and also monitored by a reference hygrometer. During our experimental observations set up, the relative humidity inside the sensing chamber was variably controlled up to 90%. A thermometer with least count of 0.1 °C was also positioned together for monitoring the temperature inside the chamber. All experiments were conducted at 45 °C, with the same sensor used for each set of measurements. Prior to each measurement the sensor was heated under vacuum at 60-75 °C for 10 h to completely remove the adsorbed moisture over the PANI film surface. All sensing measurements were carried out at 45 °C.

Results and discussion

Polymerization of aniline monomer can be found in one of three idealized oxidation states: leucoemeraldine-white/clear, emeraldine- green or blue pernigraniline-blue/violet. These three colors represent different degree and nature of polymerization (**Table 1**). The emeraldine form of PANI is most symmetric, often referred to as emeraldine base (EB), and is either neutral or doped, with the imine nitrogens protonated by an acid. Emeraldine base is also regarded as the most useful form of PANI due to its high stability and the fact that electrically properties of PANI can be optimized by doping the emeraldine form. The prepared PANI seems emeraldine based on green color of synthesized precipitate.

UV-vis and FTIR spectra

The emraldine form of PANI shows strong peaks at ~320 nm for exciton transition of $\pi \rightarrow \pi^*$ and at ~660 nm for transition between benzenoid → Quinoid ring. Normally, the change of second peak is due to the change in degree of polymerization, while the change in position of first peak is due to degree of oxidization. For example BB → B → BB absorbs at 333 nm while BB → Q → BB at 310 nm [**20**]. Comparing the obtained results from **Fig. 2a** and **Table 2**, it is found that both the transitions are observed at 292 nm and 663 nm with shifts in the peak positions. This will be probably due to unique chemical structure and degree of ionization.

The FTIR spectrum of PANI is shown in **Fig. 2b** and peak positions are tabulated in **Table 3** along with its group frequencies. The result is showing all the expected peaks of PANI e.g., NH-hydrogen bonding, C-N stretching, C-H-bonding, aromatic ring, benzenoid and quinoid ring deformations [**21**]; however, some shifting in position is observed, which might be due to different polymeric matrix of the synthesized PANI.

Thermal and ESI-MS analysis

In order to understand thermal stability of the material and specially to find application at high temperature, the TG-DTA analysis has been carried out .Thermal behavior of PANI was found different than earlier reported results [**22**]. The TG-DTA result is shown in **Fig 3a**, the result indicates the stability of PANI up to 202.95 °C since neither weight loss nor DTA peaks is observed till this temperature. After that a strong endothermic peak at 242.41 °C was observed with energy consumption of -2.39 KJ g^{-1}. Also, the TGA curve shows a sharp weight loss of 46.681 % in the temperature range of 202.95-317.92 °C.

Table 2. Data of UV-vis spectra of PANI.

Peak position (nm)	Absorbance	Nature
663.50	0.2159	broad
292.5	2.7758	Sharp
282.00	1.7156	Sharp
270.00	1.2809	Sharp
259.50	1.5804	Sharp

This may be due to the melting and followed by decomposition of PANI. The result has been compared with previous reported data, which shows early weight loss and endothermic peaks at 115, 260, 520, 92 and 530 ^{o}C in case of emeraldine and its salt respectively. Our result indicates that the prepared PANI is having better thermal stability due homogenous single phase matrix.

Table 3. FTIR data of PANI

Observed peaks position (cm^{-1})	Expected vibrations
3444.27	OH stretching
2924.39	NH with H bonding
1605	Benzenoid ring stretching
1494.93	C-C stretching
1465.00	C-N stretching
1166.37	C=N=C stretching
1112.94	Benzenoid ring deformation
1024.08	Aromatic ring deformation
956.27	Quinoid ring plane deformation
752.70	C-H out of plane bending
691.31	Aromatic ring

The ESI-MS spectrum plays an important role in direct detection of polymerised matrices [23-25]. ESI-MS spectra yield multiple ion peaks for polymers self-assembled species or macromolecules [25]. The graph (**Fig. 3b**) shows a protonated ion peaks (i.e., in 3:2 of CH$_2$-Cl$_2$:CH$_3$-CN) centered at m/z 878 Da with a regular fragmentation pattern associated with loss and gain of monomeric or branched chain unit [25]. The graphs infer the presence of polymerized matrix with regular homogenous structure not associated aggregates.

SEM study

The SEM photographs of PANI before and after exposure with humidity are shown in **Fig. 4**. It confirms the homogenous brush like structure with crystallite size approximately 250 nm before exposure (with moist) (**Fig.**

4a). After exposure (with moist) the brush surface slightly flattened over the surface (**Fig. 4b**). The found structure is not identical to earlier results; however it appears to be identical to the one reported by Laska *et al.* with some variation in size and distribution [**21**].
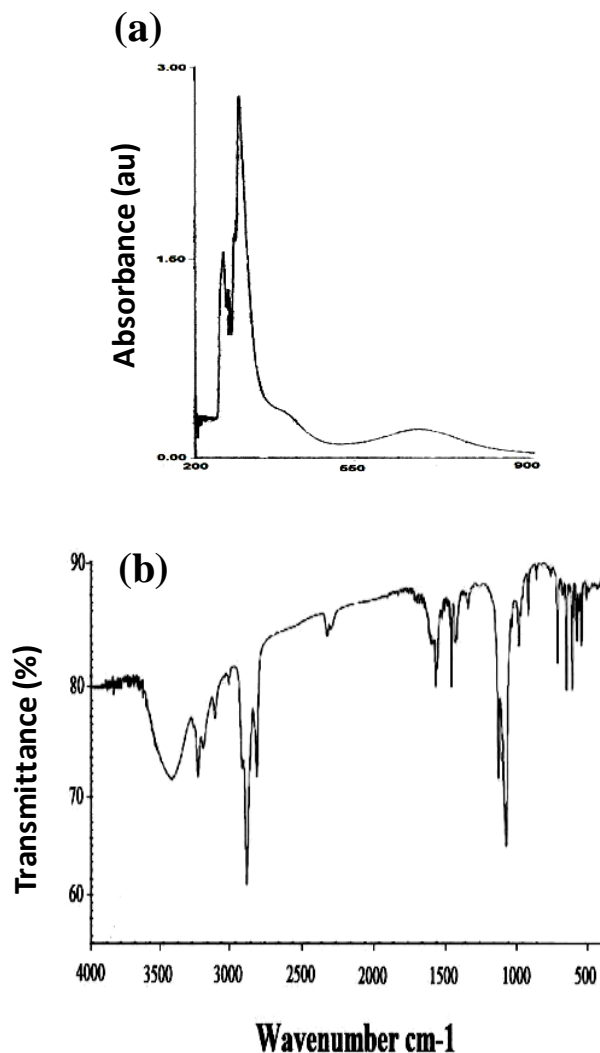
Fig. 2. Spectra of PANI (a) UV-vis spectra and (b) FTIR.

XRD measurements

The XRD pattern of polymer generally differs because of uncertainty in polymeric chains. It depends on the synthetic routes, solvent and ionized state. For example, the XRD pattern of PANI prepared by different methods has been reported to have amorphous to crystalline nature with different percentage [**21**]. The XRD of emeraldine form of PANI prepared by using methanol has peaks at $2\theta = 15, 20$, and 24°. The XRD spectra of PANI synthesized in this study is shown in **Fig. 5** and the values are tabulated in **Table 4**. All the three peaks are observed at 13.360, 20.020 and 26.775^{o} 2θ values along with other prominent peaks. The shifting in position is due to different crystalline behavior and structure on PANI. However, result reveals the strong crystalline nature of synthesized PANI.

Humidity sensing

The humidity sensing behaviors of PANI film (thickness of film ~ 500 nm) were evaluated by measuring the resistivity in closed chamber. The change in the resistivity of the sensing probe, a flat -shaped glass coated with crystalline PANI film as a function of %RH and time was recorded in a closed chamber at 45 °C. **Fig. 6** shows the variation of output resistivity versus %RH profile of PANI film with varying %RH .The resistivity decreases with an increase in %RH ranging from 3 to 95. In general, the observed electrical permeability of probe increases with increase in %RH and exhibits the sensitivity of 0.81 (i.e., ratio of change in resistance to % RH change and %RH range 3-95).
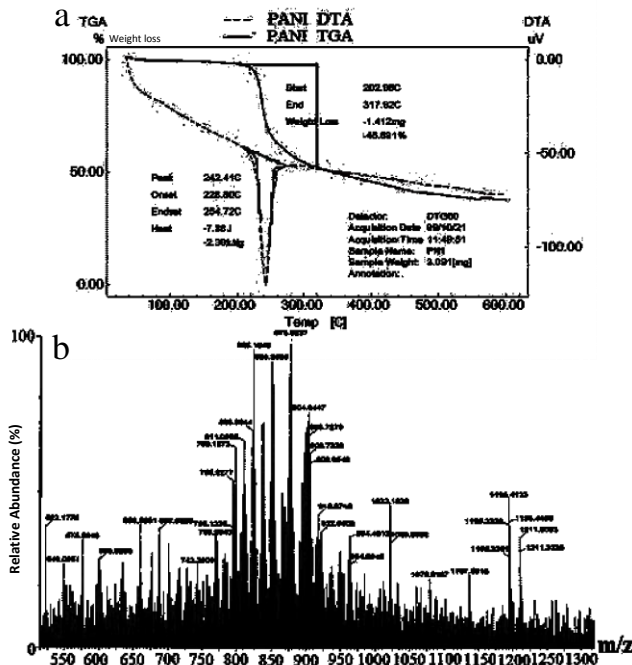

Fig. 4. SEM photograph of PANI (a) before and (b) after exposure with humidity.

Fig. 3. Spectra of PANI (a) TG-DTA graph and (b) ESI-MS.

Fig. 5. XRD spectra of PANI.

The change in resistivity is in agreement with reported trend of the resistivity of PANI and depends on its moisture content. The wet polymer with a small degree of protonation is apparently sufficient to cause a decrease in resistivity of more than six orders of magnitude [**26**]. It supports the observed trend in electrical resistance in this paper. The effect of interferents (methanol and ethanol) was studied on the output responses of the probe. The volatile methanol and ethanol were added into the sensing chamber. It was found that the presence of interferents had a negligible effect at %RH ranging from 5 to 60 but after that, response was obtained about 2-5% higher than those obtained from the standard method; therefore, using this probe, %RH can be detected with negligible interference. The change in resistivity with the time was recorded at 65 % RH. The resistance change of PANI ~80 % found in 30 sec. The desorption process completed after 1 min 20 sec and the material found stable for more than 90 days.
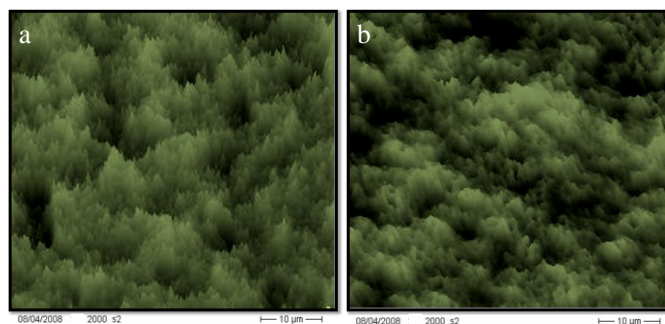
Table 4. Data of XRD spectra of PANI.

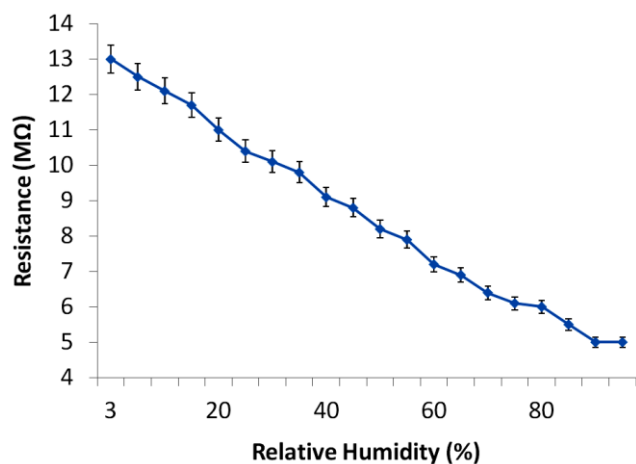| 2θ angle	d-values A°	(α1) Peak intensity
13.360	6.6260	750
20.020	4.4315	1190
26.775	3.3268	102
33.630	2.6627	108
34.460	2.6069	08
55.110	1.6651	20
59.885	1.5432	03
62.710	1.4803	06

Fig. 6. Humidity sensing behavior of PANI.

Conclusion

The emeraldine form of PANI was synthesized by chemical polymerization route. The material was characterized by using various analytical techniques. Further it was used to sense humidity of closed chamber by monitoring resistance as a function of humidity of a closed chamber. The results revealed its suitability to monitor humidity in the range of 3 to 95% with appreciable parameters.

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