

## Nanostructures of Polyaniline with Organic and Inorganic Dopants for Sensing of Ammonia

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Nanostructured samples of polyaniline (PANI) doped with different dopants (organic and inorganic) have been synthesized employing polymerization and electrodeposition. The influence of nature of dopants (organic and inorganic) and process variation on the room temperature electrical conductivity and on ammonia vapour sensing performance (response percentage and response time) has been investigated. The synthesized samples have been structurally characterized by transmission electron microscopy (TEM) and fourier transform infrared (FTIR) spectra. Regardless of type of dopants, polymerization produces nanospheres of PANI and electrodeposition leads to formation of nanorod-like structures. Among all the synthesized samples, the organic doped electrodeposited sample exhibits highest conductivity. The conductivity of the prepared samples were measured as a function of time after exposure to ammonia indicating that the polymerized samples (both for organic and inorganic dopants) exhibit fastest response (least response time), while the electrodeposited samples show sluggish response. Thus response percentages of different samples are found to depend on the nanostructures which vary with the nature of dopants and process of preparation.

**Keywords:** Polyaniline, Sulfosalicylic acid, Bismuth nitrate, Nanostructure, Ammonia sensing, Response percentage, Polymerization, Electrodeposition.

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## 1. INTRODUCTION

The discovery and the progress in the synthesis of electrically conducting or conjugated polymers (CP) opens up a new direction of research and have attracted considerable attention as important polymer materials now a day. These polymers made a significant impact and provide a vast field for a number of growing new technologies such as electromagnetic interface shielding (EMI) [1,2], energy storage devices [3,4], displays [5], micro-electronics devices [6], sensors and actuators [7] etc. The importance of environmental protection is well recognized which led to give a spot light in the development of suitable conducting polymer based gas sensors. Polypyrrole, polyaniline etc are some of the CPs which has been studied for the same as these polymers possess several attractive features for the use as gas sensors. The advantages of conducting polymers over inorganic components used are their diversity, intrinsic conductivity, fast response, easy synthesis, stability in air and particularly sensitivity at room temperature [8,9].

Polyaniline (PANI) gained its importance as a potential candidate to be used in gas sensors due to its ease of processing, high environmental stability, simple and reversible doping/dedoping chemistry, mechanical flexibility and modifiable electrical conductivity [10]. PANI in its base or salt form has been used as a sensing material for different vapours like hydrogen, ammonia etc. [11, 12].

Nano conducting polymers being one of the recently focused areas of research, sensors based on such polymers are considered to be effective for monitoring hazardous gases in the environment. Investigations of

sensing properties of conducting polymer reveal that PANI especially in its nanoform has been deemed to be one of the potential candidates to be used as gas sensors [13-16]. Micro and nanostructural polyanilines shows a great promise as good sensing materials because of their high surface to volume ratio which facilitates the diffusion of gas molecules [17, 18].

The present work is emphasized on the comparison of performance of PANI for sensing aqueous ammonia by the use of (i) sulfosalicylic acid as organic dopant and (ii) bismuth nitrate as inorganic dopant for the synthesis of PANI. Under each condition the materials were prepared by (a) polymerization and (b) electrodeposition method. Nanostructures of various sizes were obtained in the four cases mentioned above. The synthesized materials were structurally characterized and their electrical conductivity has been investigated as a function of time when exposed to aqueous ammonia. The response behavior is found to vary with the nanostructures which in turn depend on the nature of the dopants as well as synthesis procedures.

## 2. EXPERIMENTAL

### 2.1 Materials used

Aniline (99 percentage), Ammonium persulfate (APS), Sulfosalicylic acid (SSA), Bismuth Nitrate penta hydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), Dimethyl formamide (DMF), Ethanol and Ammonia (25 percentage) were obtained from Merck specialties and filter paper was purchased from Whatman. Water was purchased from hydro lab. All the chemicals were analytically pure grade and used as received without further purification.

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## 2.2 Synthesis of PANI

### 2.2.1 Polymerization of SSA doped PANI

In a typical procedure for preparing nanostructured PANI doped with SSA, 2.0 ml of aniline was dissolved in 190 ml of aqueous solution containing 1.4 g of SSA. It was stirred with magnetic stirrer and heated to boiling and then cooled to room temperature yielding a clear solution. A pre-cooled aqueous solution of APS used as oxidant, prepared by dissolving 5.02 g of APS in 100 ml of water, was mixed to the aqueous solution of the aniline monomer drop wise to start the oxidation and the reaction mixture was stirred for 6 h. The temperature of the reaction mixture was kept between 0 – 5 °C throughout the reaction time. A dark green precipitate was formed indicating PANI emeraldine salt (doped with SSA) which was recovered from the reaction vessel by filtration. The precipitate was washed with water and ethanol for several times to remove any of the oxidant present till the filtered water becomes colourless. It was then rinsed with  $5 \times 10^{-3}$  M SSA to compensate the loss of dopant and again washed with water. Finally the prepared sample was vacuum dried at 60°C for 24 h. A part of the synthesized sample was made in pellet form which was further used for the detection of ammonia.

### 2.2.2 Polymerization of Bi(NO<sub>3</sub>)<sub>3</sub> doped PANI

For preparation of nanostructured PANI doped with Bi(NO<sub>3</sub>)<sub>3</sub>, 2.0 ml of aniline was dissolved in 190 ml of aqueous solution containing 2.7 g of Bi(NO<sub>3</sub>)<sub>3</sub>. It was stirred with magnetic stirrer and heated to boiling and then cooled to room temperature yielding a whitish solution. The remaining is followed as above.

## 2.3 Electrodeposition of SSA and Bi(NO<sub>3</sub>)<sub>3</sub> doped PANI

A 60 ml solution of PANI emeraldine salt was prepared by dissolving the synthesized samples separately in dimethyl formamide in the ratio 2 mg of synthesized PANI in 1ml of DMF. The solutions are then sonicated for 4 h. These solutions were then transferred to a standard electrochemical cell of volume 80 ml for deposition of PANI on cathode. Graphite was used as anode. Indium Tin Oxide (ITO) coated glasses were washed with water as well as methanol and were used as cathode. A voltage of 20 volts was applied across the electrodes. The deposited PANI (Bi(NO<sub>3</sub>)<sub>3</sub> and SSA doped) on ITO were then dried in vacuum oven for 2 h at 60°C.

## 2.4 Structural Characterization

The Fourier transform infrared (FTIR) spectrum of the polymerized sample was recorded on a Shimadzu Spectrophotometer within the wave number range of 500 to 4000 cm<sup>-1</sup>. Transmission electron microscopy (TEM) was performed to understand the structural morphology of the synthesized samples. The conductivity at room temperature was measured using an electrometer (Keithley model no 6517 A) and microvoltmeter (Keithley 177 Microvolt DMM).

## 2.5 Gas-sensitivity Characterization

For sensing properties a simple set up was used. The sample was fixed to a holder and placed in the mouth of a bottle containing 25 percentage aqueous ammonia solutions and covered up. The whole experiment was performed in a hood. Ammonia vapour comes in contact with the samples as they are released from the solutions. The dc electrical resistances of the samples exposed to the vapour were determined using a four probe configuration. The electrical contacts on the sample surfaces were made by copper wires and silver paste. The resistances of the samples were measured as a function of time with electrometer and micro voltmeter. Thus from the dimension the conductivity was found out as a function of time.

## 3. RESULTS AND DISCUSSIONS

### 3.1 FTIR Analysis

Figure 1 (a, b) shows the FTIR spectrum of the SSA and Bi(NO<sub>3</sub>)<sub>3</sub> doped polymerized samples, in the range 500 to 3500 cm<sup>-1</sup>, before and after exposure to ammonia.

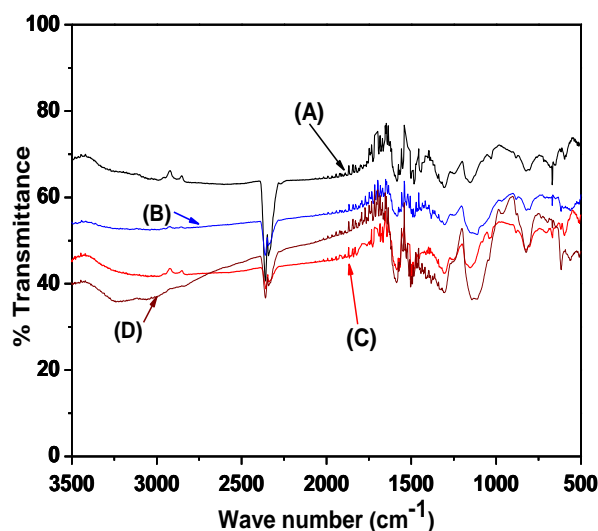


Fig. 1 – FTIR spectra of (A) SSA doped and (B) Bi(NO<sub>3</sub>)<sub>3</sub> doped PANI before exposure to aqueous ammonia, (C) SSA doped and (D) Bi(NO<sub>3</sub>)<sub>3</sub> doped PANI after exposure to aqueous ammonia

The characteristic peaks of SSA doped PANI as observed from the figure are at 823 cm<sup>-1</sup> associated with the aromatic C-H bending out of the plane for 1,4 disubstituted benzene ring [19], 1151 cm<sup>-1</sup> due to B-NH<sup>+</sup> = Q stretching, 1247 cm<sup>-1</sup> owing to C-N<sup>+</sup> stretching, 1303 cm<sup>-1</sup> due to C-N stretching of secondary aromatic amine and at around ~1484 cm<sup>-1</sup> for benzenoid (B) ring stretching.

The corresponding peaks of Bi(NO<sub>3</sub>)<sub>3</sub> doped PANI are observed at 821cm<sup>-1</sup>, 1143 cm<sup>-1</sup>, 1238 cm<sup>-1</sup> 1303 cm<sup>-1</sup> and 1483 cm<sup>-1</sup> respectively. Peaks at 1566 and 1585 cm<sup>-1</sup> for SSA doped PANI are attributed to C = C quinonoid (Q) ring stretching in emeraldine salt and base respectively [13]. Same peaks are observed at 1560 cm<sup>-1</sup> and 1583 cm<sup>-1</sup> for Bi(NO<sub>3</sub>)<sub>3</sub> doped

PANI. Structural modifications were introduced when exposed to aqueous ammonia as observed from the FTIR spectra. There is a decrease in the peak intensities assigned to quinonoid and benzenoid ring stretching in both the cases. This observation confirms the process of dedoping [20] when exposed to ammonia. Also a shift of the peaks towards left has been observed. This shift towards higher wave number [21] suggest dedoping which lowers the value of electrical conductivity when exposed to aqueous ammonia as has been observed in the present case.

### 3.2 TEM analysis

Nanospheres were obtained employing polymerization regardless of the type of dopants. For  $\text{Bi}(\text{NO}_3)_3$  doped PANI the nanospheres have an average 6 nm diameter as shown in Fig. 2 (a). But the nanospheres for SSA doped PANI have an average of 10 nm diameter (not shown). However it is observed that the method of electrodeposition yielded nanorods for both the dopants indicating that the nanostructures are process dependent. Figure 2 (b) shows the TEM image of the electrodeposited SSA doped PANI with an average diameter of 50 nm and 350 nm in length. But for  $\text{Bi}(\text{NO}_3)_3$  doped electrodeposited PANI the average diameter and length are 25 nm and 250 nm respectively. It is worth mentioning that the nanospheres and the nanorods are of different dimensions.

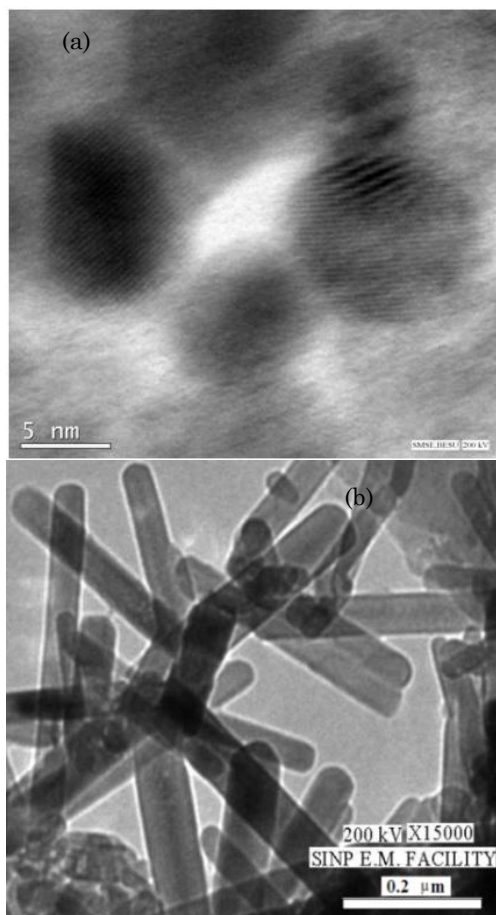


Fig. 2 – TEM images of (a)  $\text{Bi}(\text{NO}_3)_3$  doped Polymerized PANI and (b) SSA doped Electrodeposited PANI

### 3.3 Room temperature conductivities

The room temperature electrical conductivities of the prepared samples were measured and tabulated. It is observed that  $\text{Bi}(\text{NO}_3)_3$  doped PANI have less conductivity values than SSA doped PANI for both the synthesizing procedures. This is probably due to the multiple doping effects of  $\text{Bi}^{3+}$  ions which distort the polymer chain reducing the conductivity values. Maximum conductivity is obtained for SSA doped electrodeposited sample ( $34.827 \text{ Scm}^{-1}$ ) and the minimum conductivity is obtained for  $\text{Bi}(\text{NO}_3)_3$  doped polymerized sample ( $0.0967 \text{ Scm}^{-1}$ ). Further the samples prepared by polymerization were in powder form and due to pelletization for measuring electrical conductivity, random orientations have been introduced leading to diminish the values.

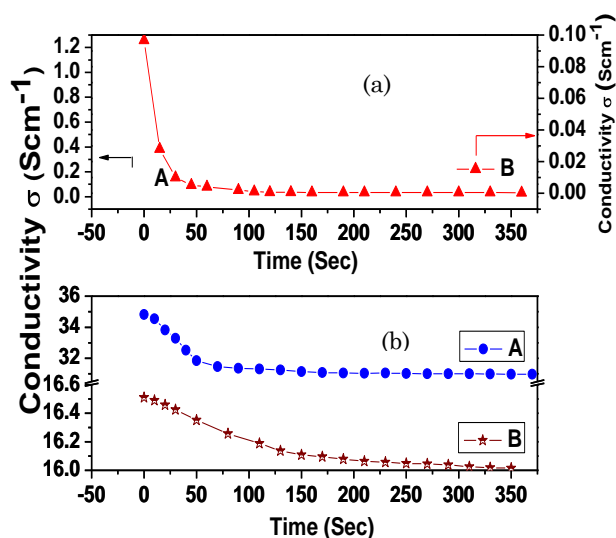


Fig. 3 – Conductivity of (a) -■- (A) SSA doped and -▲- (B)  $\text{Bi}(\text{NO}_3)_3$  doped polymerized samples and (b) -●- (A) SSA doped and -\*- (B)  $\text{Bi}(\text{NO}_3)_3$  doped electrodeposited samples

### 3.4 Dynamic response of organic and inorganic doped PANI in the presence of ammonia vapour

The variation of electrical conductivity was observed as a function of time for all the samples when exposed to ammonia and is shown in Fig. 3 (a & b). An exposure to ammonia vapour reduces the conductivity values of all the samples. A sudden initial decrease in conductivity is detected for both the polymerized samples. Among the electrodeposited samples, the initial rate of decrease in conductivity of SSA doped PANI is more than that of  $\text{Bi}(\text{NO}_3)_3$  doped PANI. The variation of response value, defined as  $(\sigma_0 - \sigma_t) / \sigma_0$ , where  $\sigma_0$  is the initial conductivity and  $\sigma_t$  is the final conductivity, with time is plotted in Fig. 4. It is observed from the figure that the response increases with time and attains saturation.

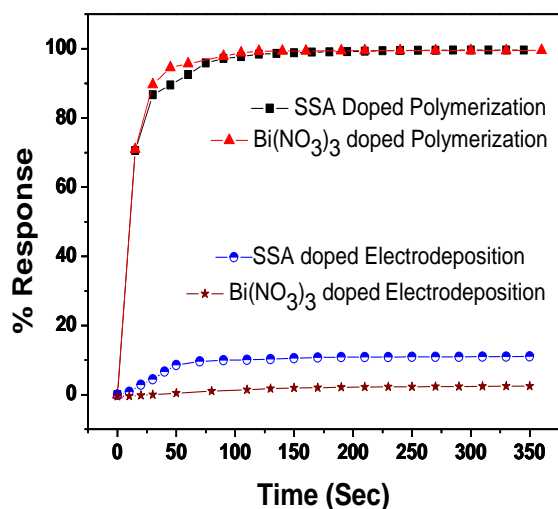


Fig. 4 – (a) Percentage response with time of SSA doped and  $\text{Bi}(\text{NO}_3)_3$  doped PANI synthesized by different method

This is due to the deprotonation of PANI emeraldine salt and formation of emeraldine base with time. Response percentage and response time (time corresponding to maximum response,  $t_r$ ) of the samples are presented in Table 1.

Table 1 – Measured parameters of the samples

| Process of Synthesis | Dopant                     | $\sigma$ ( $\text{Scm}^{-1}$ ) | $(\sigma_0 - \sigma_f)/\sigma_0$ % | $t_r$ (Sec) |
|----------------------|----------------------------|--------------------------------|------------------------------------|-------------|
| Polymerization       | SSA                        | 1.1305                         | 99.62                              | 50          |
| Polymerization       | $\text{Bi}(\text{NO}_3)_3$ | 0.0967                         | 99.36                              | 45          |
| Electro Deposition   | SSA                        | 34.827                         | 11.05                              | 150         |
| Electro Deposition   | $\text{Bi}(\text{NO}_3)_3$ | 16.425                         | 2.49                               | 130         |

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Interestingly, it is noticed that response is the maximum for the polymerized samples having response time 50 s for SSA doped and 45 s for  $\text{Bi}(\text{NO}_3)_3$  doped PANI. Both these values are comparable with the earlier reported response time of PANI doped with CSA (52 s) [14]. These values are low compared to response time of PANI doped with acrylic acid (60 s) [13], and with PTSA (60 s) [14], and are much lower compared to the response time of PANI doped with perfluorooctanoic acid (2 mins) [14] and composite (~5 mins) [22].

## 4. CONCLUSIONS

Polymerization and electrochemical deposition were carried out to synthesize PANI doped with organic and inorganic dopants. For the structural characterization FTIR and TEM investigations has been analyzed. The FTIR studies indicate the process of deprotonation or dedoping when the samples were exposed to ammonia which is in good agreement with the results of electrical conductivity that decreases with time on exposure to ammonia. Also conductivity is found to vary with the dopants as well as methods. TEM images indicate the formation of nanospheres and nanorods of PANI but of different dimensions. Maximum conductivity is obtained for SSA doped electrodeposited sample ( $34.827 \text{ Scm}^{-1}$ ). The variation of response with time indicates that the response increases for all the samples and attains a saturation value. Moreover response for the polymerized samples is higher for both the dopants as compared to other samples.

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