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# Growth, characterization and gas sensing properties of polyaniline thin films

S.G.Pawar, S.L.Patil, A.T.Mane, B.T.Raut, V.B.Patil\*

*Materials Research Laboratory, School of Physical Sciences, Solapur University, Solapur, Maharashtra, India*

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## Abstract

Polyaniline synthesized by chemical polymerization method and thin films were prepared by spin coating method. Room temperature sensing properties of polyaniline thin films were studied for various oxidizing (NO and Cl<sub>2</sub>) as well as reducing (NH<sub>3</sub> and H<sub>2</sub>S) gases. It has been observed that a polyaniline film possesses high sensitivity and fast response time for ammonia gas. Fourier transform infrared spectroscopy revealed formation of polyaniline. The morphological study showed that formation of uniform granular structure with average grain size of 60nm.

**Keywords:** Ammonia Sensor, Polyaniline, chemical polymerization, Fourier transform infrared spectroscopy

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## Introduction

The use of conducting polymers as sensing elements in chemical sensors is attracting attention due to their high sensitivity in changes of the electrical and optical properties when exposed to different types of gases or liquids [1-5]. The ease in synthesis of these polymers and sensitivity at room temperature add to the sensor's advantages. This can be of importance particularly as ammonia gas sensors that are used in different applications such as industrial process, fertilizers, food technology, clinical diagnosis, farms and environmental pollution monitoring. Conducting polymers that have been investigated for chemical sensors are polypyrrole, polyacetylene, polyaniline (PANi), polythiophene, porphyrin and *N*-vinylcarbazole. Among these conducting polymers, polypyrrole and polyaniline are widely investigated for NH<sub>3</sub> sensing. Polypyrrole was the first polymer used for NH<sub>3</sub> detection; however, its sensitivity was quite low and response was also irreversible. Polypyrrole films are not easily processible whereas polyaniline is soluble in

common organic solvents from which free standing films can be cast. Polyaniline is also considered to be one of the most technologically promising conducting polymers because of its easy preparation, low cost, and relatively stable electrical conductivity in air. Polyaniline has also been used in different applications such as displays, sensors, electrodes for batteries and photovoltaic cells. Electronic properties of Polyaniline depend on the degree of protonation and the method of synthesis [6-11].

In this paper, we report on the spin coated Polyaniline thin film having novel microstructure at the surface for NH<sub>3</sub> detection at room temperature with better response and recovery times.

## Materials and Methods

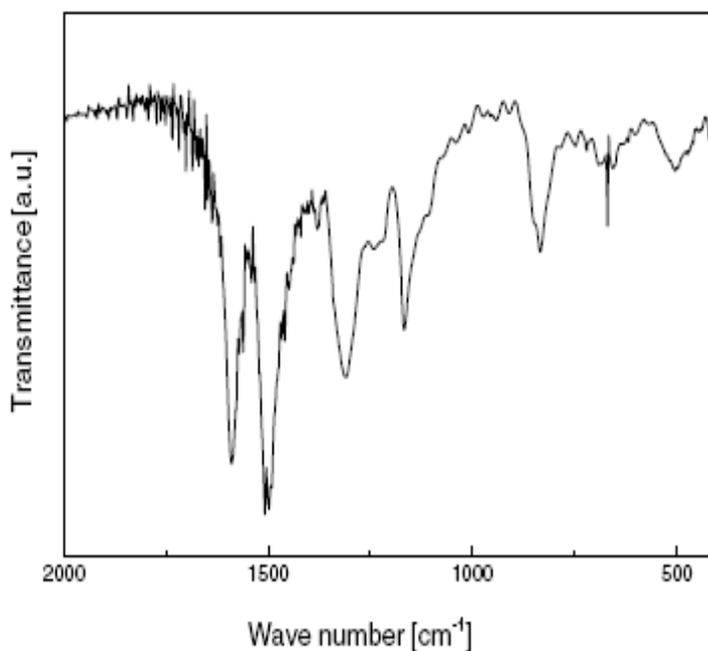
Polyaniline was chemically synthesized by oxidation method at ~0 °C. The precipitate was collected, washed repeatedly with 1M HCl and dried under vacuum for 48 h. The PANi powder so obtained is in the HCl doped state (PANi -HCl). For preparation of emeraldine-base PANi, the PANi -HCl powder was put in a 0.1M ammonia solution and stirred for 3h at room temperature. The precipitate was filtered, washed with deionized water until the water became neutral and then dried in vacuum for 48 h to obtain emeraldine PANi. PANi (0.2 gm) was dissolved in 30ml of *m*-cresol to prepare the solution. The solution preparation required 3–4 days of stirring with an initial heating at 50 °C for 40 min to make the solution homogenous. A thin film of Polyaniline was deposited on glass substrates using spin coating technique at a speed of 3000 rpm. The film was dried in air for 30min [12, 13]. The thickness of the film was ~140 nm as measured using Tencor Alpha step 100. Fourier-transform infrared (FTIR) spectroscopy was done in a reflectance mode using PerkinElmer Spectrum BX2. Surface morphological studies were carried out using scanning electron microscopy, Quanta-2000, Holland using acceleration voltage of 25kV. For this purpose thin layer of gold (50Å) was deposited on the film using physical vapour deposition and Atomic force microscopy (AFM) using (Digital Instruments) Nanoscope IIIa. Roughness of the film was determined from the AFM images. Absorption study was carried out with a PerkinElmer Lambda 900 UV/VIS/NIR spectrometer.

In order to measure the gas response, the resistance of the films was measured in air ambient and in gas atmosphere. For resistance measurement, two gold electrodes, separated by 1mm, were deposited on polyaniline film and silver wires were attached using silver paint. The resistance was measured using Rigol 6½ digit DMM. For monitoring the response of the films to various gases, the films were mounted in 250cc air tight container and the known gas (NH<sub>3</sub>, H<sub>2</sub>S, Cl<sub>2</sub> or NO) of particular concentration was injected through a syringe. All the gas sensitivity measurements were carried out at room temperature.

## Results and Discussion

### *Fourier transform infrared measurement*

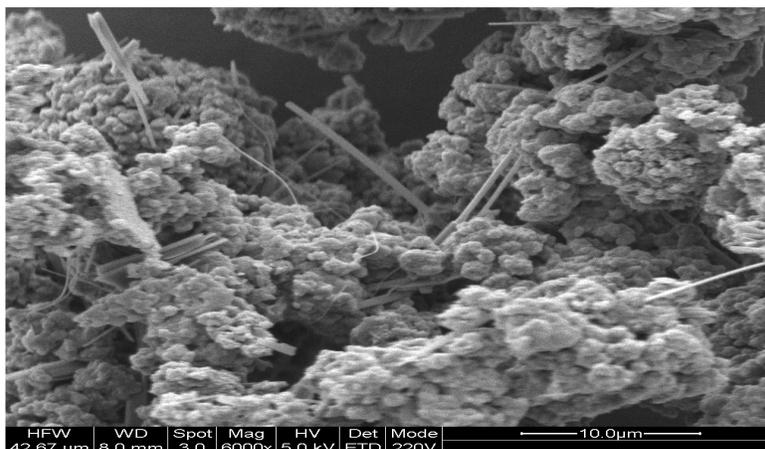
Proper formation of the Polyaniline film in a conducting form was established by FTIR measurement (Fig. 1). The peaks at 1,591 and 1,497 cm<sup>-1</sup> originate from aromatic C-C stretching vibrations whereas those at 1,307 and 1,167 cm<sup>-1</sup> are due to aromatic amine stretching. The peak at 832 cm<sup>-1</sup> comes from the out of plane hydrogen deformation of aromatic rings in PANi unit sequences [12-14].



**Fig.1. FTIR spectrum of a Polyaniline film**

#### *Surface morphology*

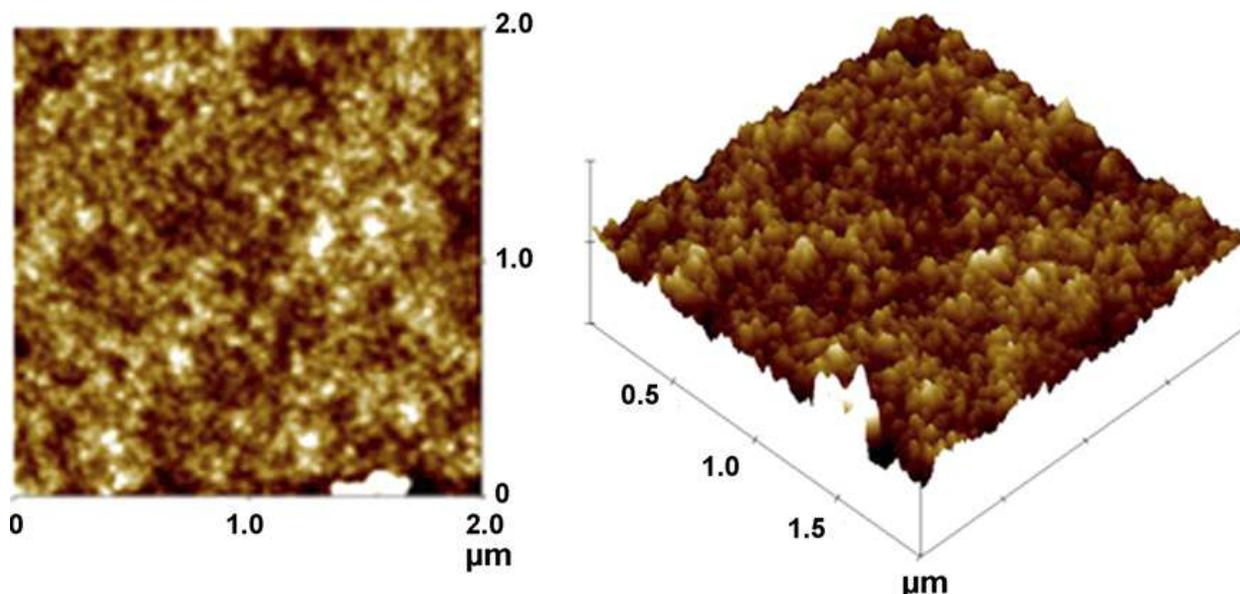
The microstructure of a polyaniline thin film is shown in Figure 2. The film has honeycomb morphology with an interlocking arrangement of globular particles and the average grain size is approximately 50 nm to 100 nm [12-14].



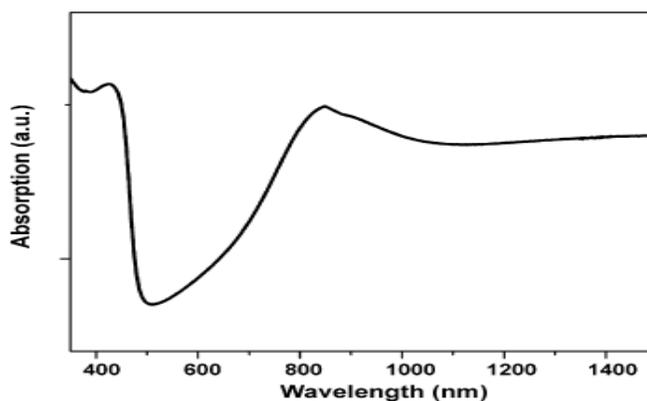
**Fig.2. SEM of a Polyaniline film**

AFM micrographs of the Polyaniline thin film (Figure 3) show the less aggregation of the polymer with a surface roughness of ~7 nm and confirm the extended coil conformation. This is supported by the free carrier tail in the absorption spectrum shown in Figure 4. The Polyaniline

film exhibits the absorption edge at  $\sim 470$  nm (benzene  $\pi$ - $\pi^*$  transition). This behavior is consistent with a delocalized polaron band structure. A steadily increasing free carrier tail, starting from  $\sim 850$ nm to the near IR region confirms the extended coil conformation of the Polyaniline [12-14].



**Fig. 3. Atomic force micrographs of a Polyaniline film**



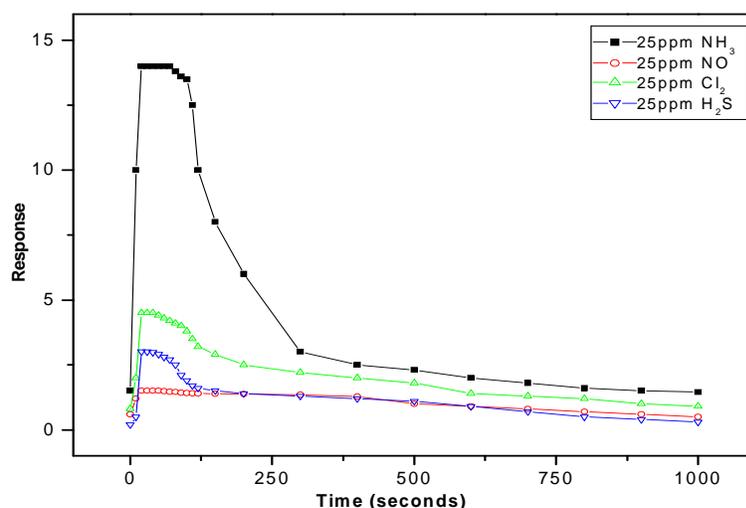
**Fig. 4. An absorption spectrum of a Polyaniline film**

#### *Gas sensing properties*

The gas sensing studies were carried out for  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}_2$  and  $\text{NO}$  gases. All the measurements were carried out at room temperature. For reducing gases like  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  the resistance of the films increases on exposure to the gas and for oxidizing gas like  $\text{Cl}_2$ ,  $\text{NO}$  the resistance of film decreases. Typical gas response curves of polyaniline films for 25 ppm concentrations of  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}_2$  and  $\text{NO}$  are shown in Fig.5. The response of the sensor is defined as

$$\text{Response} = |(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}| \times 100$$

It is seen that the response values for NH<sub>3</sub> (25 ppm), H<sub>2</sub>S (25 ppm), Cl<sub>2</sub> (25 ppm) and NO (25 ppm) are respectively 14, 1.5, 4.5 and 3.0. The response for NH<sub>3</sub> is better by a factor of ~ 10 and also faster than other gases. A high response for ammonia indicates that the polyaniline films are selective for this gas. The higher response towards NH<sub>3</sub> than NO, Cl<sub>2</sub> and H<sub>2</sub>S can be explained on the basis of different interactions between sensing film and adsorbed gas. Polyaniline is a p-type material and when it interacts with NH<sub>3</sub>, there is reduction in charge carrier density. Since the majority carriers (holes) density gets decreased due to electron donating nature of NH<sub>3</sub> gas. This results in decreasing the conductivity of material and film resistance increases. In case of oxidizing gas like NO there is an increase in charge carrier concentration, since NO gas is electron accepting in nature [15-17]. Hence it increases the conductivity of the material. The interaction of NO, H<sub>2</sub>S, Cl<sub>2</sub> with polyaniline film is very less as compared to NH<sub>3</sub>, hence it shows very less and sluggish response.



**Fig. 5. Gas response curves of a polyaniline film**

## Conclusion

Proper formation of the Polyaniline film in a conducting form was established by FTIR measurement. The microstructure of polyaniline thin film shows honeycomb morphology with an interlocking arrangement of globular particles and the average grain size is approximately 50 nm to 100 nm. AFM micrographs of the Polyaniline thin film shows the less aggregation of the polymer with a surface roughness of ~7 nm and confirms the extended coil conformation. The Polyaniline film exhibits the absorption edge at ~470 nm. Gas sensing characteristics shows high response for NH<sub>3</sub> is better by a factor of ~ 10 and also faster than other gases. A high response for ammonia indicates that the polyaniline films are selective for this gas.

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