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Preparation, Characterization and Chemical Sensing Properties of Polyaniline Thin Films

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Abstract: Novel chemical sensor was fabricated by forming the thin films of conducting polyaniline on glass substrates using spin coating technique. Structural and morphological characterizations of spin coated polyaniline (PANI) thin film were carried out using X-Ray Diffractometer (XRD) and Field Emission Scanning Electron Microscope (FE-SEM), respectively. The functional group present in the polyaniline thin film was confirmed using FTIR spectrometer. Sensing performance of the prepared film was studied. The resistance of the polyaniline thin film was reduced from 10^9-10^7 ohms towards the 25 ppm concentration level of ammonia at room temperature.

Key words: Ammonia gas sensor, conducting polymer, polyaniline, sol-gel, spin coating

INTRODUCTION

It is important to analyze the presence of ammonia gas at low ppm level itself for controlling environmental pollution. Moreover, in clinical diagnosis, sensing ammonia gas at nanolevel is a critical issue especially in diagnosing Hepatic Encephalopathy (HE) at earlier stage (Butterworth, 2003). And also ammonia gas plays vital role in industrial process, fertilizers, food technology and farms (Pawar *et al*., 2009). Hence, it is very important to develop a gas sensor for detection of ammonia gas.

In conventional gas sensors, metal oxides are used to fabricate gas sensors (Sivalingam *et al*., 2012) to sense ammonia for better sensitivity. But metal oxides can be operated only at high temperatures and also it consumes more power. The electrically conducting polymer polyaniline (PANI) has high sensitivity like a metal oxides and it can be operated at room temperature itself (Pant *et al*., 2007; Abraham *et al*., 2004). In addition, this sensor can be easily prepared and fabricated at low cost along with high stability.

Basically leucoemeraldine and pernigraniline form of polyaniline (Fig. 1) is poor in conductivity ant it can be made as excellent conductive material by doping with acids such as hydrochloric acid (HCl) (Scheme 1) or Camphor Sulphonic Acid (CSA) (Veluru *et al*., 2007; Chiang and MacDiarmid, 1986). The acid-doped polyaniline (n = m = 0.5) is called as emeraldine.

Spin coating technique is very convenient for forming polymer thin films. It is fast and controlling uniform coating polymer thin film on glass substrate (Ismail *et al*., 2011; Bodas *et al*., 2005).

Pawar *et al*. (2009) reported the increase in resistivity of the polyaniline thin film when ammonia was exposed and resistivity of the film was decreased with NO gas. Chubakswar *et al*. (2001) characterized gas sensing characteristics of polyaniline thin film with ammonia gas towards the concentration from 1-600 ppm and reported the ΔR was increased up to 58 ppm and above which it was saturated.

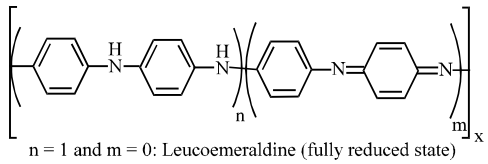
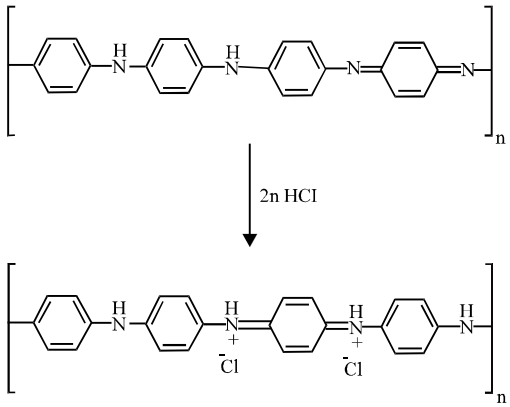


Fig. 1: Structure of polyaniline



Scheme 1: HCl doping of polyaniline for protonation

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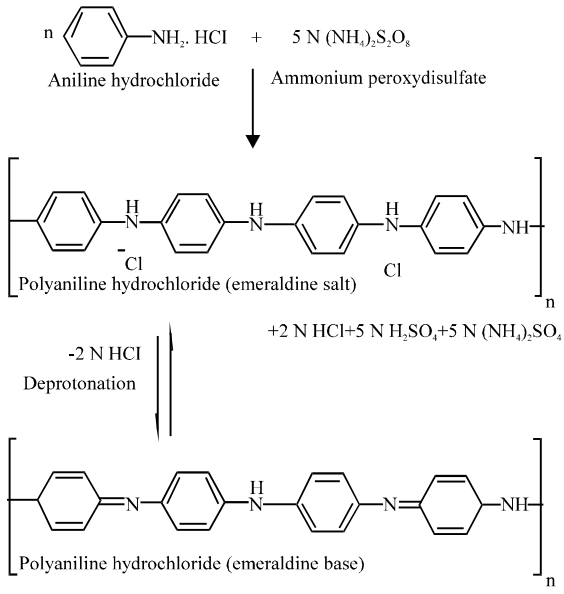

Scheme 2: Synthesis of emeraldine base polyaniline

In the present study, the emeraldine-base polyaniline was chemically synthesized by oxidative polymerization (Scheme 2) method at 0°C from the aqueous solution aniline hydrochloride and ammonium peroxydisulfate. Polyaniline thin film was coated on the glass substrate using sol-gel spin coating technique. Structural and morphological characterizations of spin coated polyaniline thin film were carried out using XRD and FE-SEM, respectively. The elemental composition of polyaniline thin film was confirmed using FTIR spectrometer. Sensing performance of the prepared film was studied with exposure of 25 ppm of ammonia gas.

MATERIALS AND METHODS

The aniline hydrochloride was obtained from SD Chemicals Limited, India and ammonium peroxydisulfate, HCL, ammonia solution were obtained from Merck, India.

Conducting polyaniline thin film was synthesized by suitably modifying the available method in literature (Stejskal and Gilbert, 2002). Polyaniline (PANI) was chemically synthesized by oxidative polymerization method at 0°C. 0.2 M of aniline hydrochloride was dissolved in 50 mL of deionized water. The 0.25 M of ammonium peroxydisulfate was dissolved in 50 mL of deionized water separately. Both solutions were stirred separately in 0°C for 1 h. After 1 h both solutions were mixed and solution was briefly stirred and left to rest for polymerization in 0°C. After 24 h the solution was filtered and precipitated PANI powder was collected.

For protonation, the PANI powder was washed repeatedly with 1 M of HCL and then dried. In order to prepare the emeraldine-base, 0.1 M of ammonia was mixed with HCL doped PANI and the solution was stirred for 3 h at room temperature. Then the solution was filtered and the emeraldine-base PANI (EB-PANI) powder was collected (Pawar *et al*., 2009).

Fifteen milligram of EB-PANI was dissolved in 20 mL of m-cresol and vigorously stirred for 5 days to prepare sol-gel. A layer by layer of polyaniline thin film was coated by using spin coating technique (model HO-TH-05, HOLMARC SPIN COATER, India) at a speed of 3000 rpm for 60 sec followed by drying at 60°C for 5 min. Polyaniline thin film samples were prepared by coating 4 layers.

Structural and morphological characterizations of spin coated polyaniline thin film were carried out using XRD (D8 Focus, Bruker, Germany) and FE-SEM (JSM 6701F, JEOL, Japan), respectively. The functional group present in the polyaniline thin film have been confirmed using FTIR spectrometer (Spectrum 100, Perklin Elmer, USA).

RESULTS AND DISCUSSION

Structural studies: Figure 2 shows the XRD pattern of polyaniline thin film. The XRD peaks confirmed the semi crystalline nature of synthesized thin film (Fattuom *et al*., 2008; Pelster *et al*., 1994).

Morphological studies: Figure 3 shows the FE-SEM image of polyaniline thin film. The highly porous nature of the material and the clumped spherical morphology was confirmed with FE-SEM.

Figure 4 shows the FTIR spectrum of polyaniline thin film. The functional group present in the synthesized polyaniline film was confirmed using FTIR spectrometer. The bands at 3436.81, 2924.36, 1637.20 and 1457.25 are corresponding to N-H stretching vibrations, CH stretch, C-C stretch and CN stretch, respectively confirmed the formation of EB-PANI film (Yadav *et al*., 2008; Levon *et al*., 1995).

Gas sensing characteristics: The conducting polymers are the better candidates for sensing organic vapours (Ding *et al*., 2009) at the room temperature. The charge carriers present in the conducting polymer chains participating in the sensing mechanism. The change in surface resistance of the thin film was recorded using electrometer (model 6517A, Keithley, Germany) in the

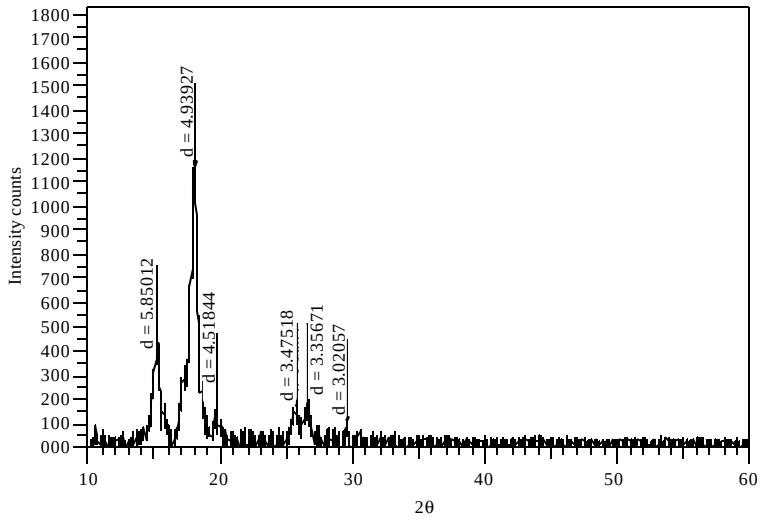

Fig. 2: XRD of polyaniline thin film

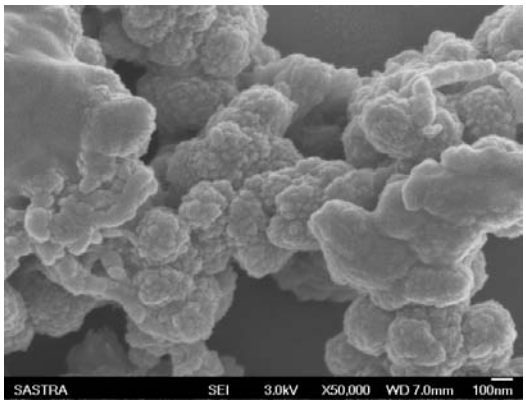

Fig. 3: FE-SEM image of polyaniline thin film

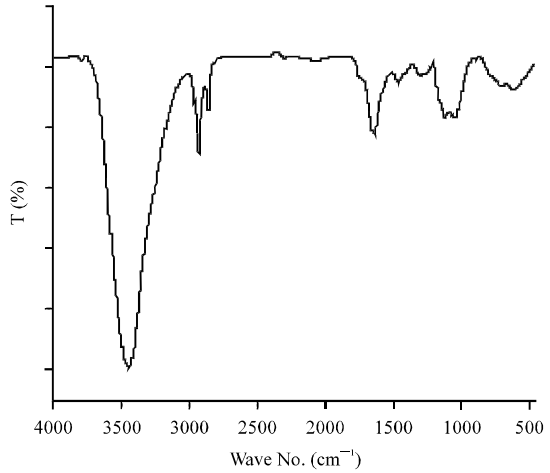

Fig. 4: FTIR spectrum of polyaniline

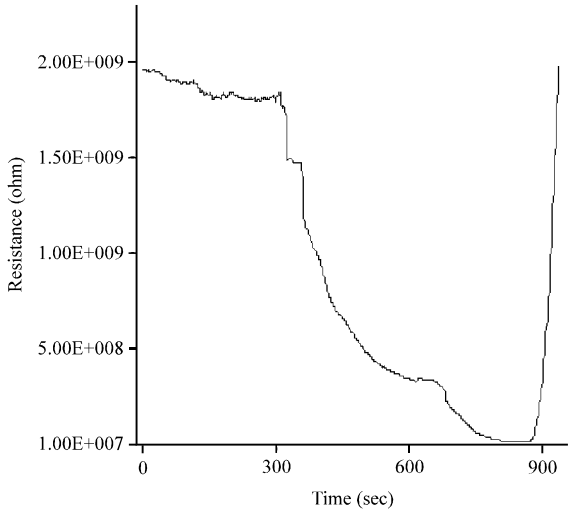

Fig. 5: Response of PANI thin film towards NH_3 (25 ppm)

presence of 25 ppm of ammonia and is shown in Fig. 5. The resistance of the polyaniline thin film was reduced from 10^9-10^7 ohms at room temperature. This response is found to be contrast and much better than the available results (Pawar *et al*., 2009). The sensitivity (S) is found to be 200 using the Eq. 1:

$$S = \frac{(R_o - R_g)}{R_g} \quad (1)$$

where, R_o is the electrical resistance of the PANI thin film in the absence of ammonia vapour and R_g is the electrical resistance of the PANI thin film in the presence of ammonia vapour. Response and recovery time of the polyaniline thin film was 480 and 183 sec, respectively.

CONCLUSION

Polyaniline thin film was coated on the glass substrate using spin coating technique. Structural and morphological characterizations of spin coated polyaniline thin film were carried out using XRD and FE-SEM, respectively and the functional group present in the polyaniline thin film was confirmed using FTIR spectrometer. Sensing performance of the prepared film was studied with exposure of 25 ppm of ammonia gas at room temperature. The response is found to be 200.

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