Ammonia Gas Sensor based on Nanostructured Thin Film of PANI-DBSA

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Abstract- **This paper presents the fabrication of ammonia gas sensor using nanostructured thin film of PANI-DBSA. First, the interdigitated electrodes (IDEs) of platinum (Pt) were patterned on the glass substrate by depositing Pt thin film of 80 nm thickness by RF sputtering technique in 100% Ar ambient using a 3-inch diameter Pt metal (99.999% pure) target, and, subsequently IDEs were patterned using conventional photolithography technique. The DBSA doped PANI has been synthesized by direct one step emulsion polymerization using aniline as a monomer and characterization is done using XRD, UV-Visible Spectroscopy, and SEM. The synthesized PANI-DBSA nanoparticles were deposited on IDEs patterned glass substrate to realize a nanostructured film using a spin coater at 1500 rpm. Gas sensing has been done for ammonia gas at different concentration levels in the form of relative response, response time, recovery time and repeatability. The fabricated sensor detects ammonia at 1ppm level quantitatively and reversibly at room temperature operation. The fabricated PANI-DBSA thin film gas sensor exhibits good sensitivity and response time at various ppm levels of ammonia.**

I. INTRODUCTION

Ammonia gas, irritating and corrosive in nature, is one of the most commonly produced industrially hazardous chemical gases. Therefore, it becomes imperative to detect the presence of ammonia gases in environment. In the recent past, different gas sensor technologies have been used for ammonia gas detection including semiconductor gas sensors, catalytic gas sensors, and electrochemical gas sensors. Chemiresistor, a MEMS-based gas sensors, using conducting polymers as sensing layer has been gaining popularity for ammonia gas detection due to its simple configuration, easy fabrication, cost-effectiveness, miniaturization, and most importantly room temperature operation [1].

In this present work, we report complete fabrication and characterization of MEMS-based ammonia gas sensor using nanostructured thin film of PANI-DBSA conducting polymer. Use of PANI-DBSA provides improved sensitivity as compared to other conducting polymers due it increased surface area/volume ratio of DBSA doped PANI in Nanoregime [2].

II. MATERIAL SYNTHESIS & CHARACTERIZATION

A. *PANI-DBSA Synthesis*

All chemicals used in this study were chemically pure. Aniline (LobaChemie) as monomer was freshly double distilled before use. Ammonium persulfate as oxidant [APS, (NH4)2S2O8], and dodecyl benzene sulfonic acid (DBSA) as a surfactant were purchased from Merck. Isopropyl alcohol (IPA), N-methyl pyrrolidone (NMP) and Chloroform (CHCl3) were also purchased from Merck and used as received. De-ionized water (resistivity >18 MΩ-cm) was used for synthesis.

DBSA and water (0.3 M aqueous DBSA solution) was stirred to form an emulsion at 0°C followed by adding monomer (0.1 mol aniline). In the emulsion, the polymerization was initiated by the dropwise addition of an aqueous solution of ammonium persulfate (0.1 mol in 100 mL de-ionized water) to maintaining reaction mixture at 0°C under continuous stirring. After completion of polymerization, the formed dark green emulsion of DBSA doped PANI was de-emulsified using propanol. The resultant mixture was filtered through sintered glass crucible and the precipitate so obtained was washed repeatedly until the pH of the filtrate became neutral. Subsequently, the filtered cake was dried and crushed to obtain PANI-DBSA nanoparticles.

B. *Characterization Results*

The characterizations of DBSA doped PANI nanoparticles were done with various characterization techniques. The optical spectrum of the chloroform dispersion of PANI-DBSA was recorded using UV-Visible spectrophotometer (Perkin Elmer lambda 25) in the wavelength range of 250–1000 nm. X-ray diffraction (XRD) pattern was recorded using Bruker Advanced D8 system in the diffraction (2θ) range of 10-80° using CuKα (λ= 1.540598Å) as the radiation source. The scanning electron microscope (SEM, Leo-440, Carl-Zeiss, UK, accelerating potential 10.0 kV) was used to investigate the surface morphology of PANI-DBSA powder.

Fig. 1(a) represents the XRD pattern of PANI–DBSA powder. The XRD pattern display three distinguished peaks at 2 θ values of 20.5° (d=4.32Å), 25.2° (d=3.52Å) and 26.9° (3.31Å). The two peaks at 2θ of ~20° and ~25°peaks confirm the formation of PANI and represent the periodicity in parallel and perpendicular to chain axis respectively. The third one and the relative prominence of 25° peak confirm the doping in PANI.

UV-Visible absorption spectra of PANI-DBSA dispersion in chloroform is shown in Fig. 1(b). The spectrum consists of three distinguished transitions peaks at 346 nm, 431 nm and 732 nm wavelengths which correspond to $\pi \rightarrow \pi^*$ transition of the benzenoid rings, polaron$\rightarrow\pi^*$ transitions, and $\pi^* \rightarrow$polaronic transitions respectively. The prominence of peak at 732

nm compared to the peak at 346 nm shows that the sufficient doping level present in the polymer (as an emeraldine salt form).

The morphology of synthesized PANI-DBSA nanoparticles is investigated by SEM image, shown in Fig. 1(c).

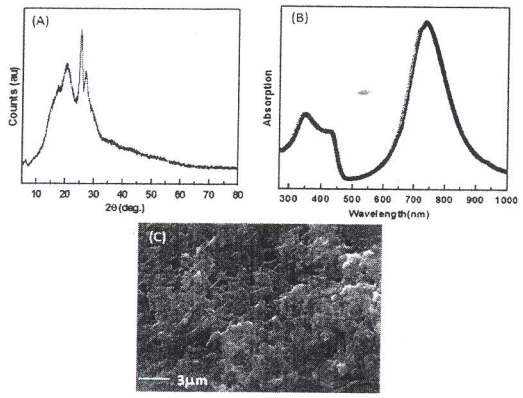

Fig. 1. (a) XRD pattern of PANI-DBSA powder, (b) UV-Visible spectra of PANI-DBSA dispersion in chloroform, and (c) SEM image of PANI-DBSA powder

III. SENSOR FABRICATION & GAS SENSING

A. Sensor Fabrication

A calculated amount (100 mg) of PANI-DBSA nanoparticles was suspended in chloroform (10 ml) under sonication for 3 hours followed by filtration through Whatman 41 filter paper. The obtained viscous solution of PANI-DBSA nanoparticles was spin coated at 1500 rpm on a glass substrate. The interdigitated electrodes (IDEs) of platinum (Pt) were patterned on the glass substrate prior to deposition of PANI-DBSA thin film to make the gas sensor. The Pt thin film of 80 nm thickness was deposited on glass substrate by RF sputtering technique in 100% Ar ambient using a 3 inch diameter Pt metal (99.999% pure) target and IDEs were patterned using conventional photolithography technique. The thin film of undoped PANI (EB) has also been prepared for comparison with PANI-DBSA film.

B. Gas Sensing Results

The sensitivity in relative response characteristics of PANI- DBSA thin film sensor is studied as a function of the concentration of NH3 gas over the range 1 ppm to 50 ppm and the observed response is shown in Fig. 2. It is readily noticeable from the Fig. 2 that the value of sensor film resistance in the presence of gas increases continuously with the increase in gas concentration. This is attributed to the increase in deprotonation and/or localization of polarons in the PANI-DBSA sensing layer with increasing adsorption of NH3 gas molecules on its surface. Further, the sensor was found to regain the initial value of sensor resistance (Ra), after removal of NH3 gas except for a small drifting in the baseline (Fig. 2). No particular trend in baseline shift is observed with respect to the concentration.

The variation of sensitivity versus concentration of NH3 gas for prepared PANI-DBSA thin film sensor is shown in Fig. 3. The sensitivity in relative response was found to increase linearly from 0.415 to 1.241 with increase in the concentration of NH3 gas from 1 to 50 ppm, showing linearity in the response of prepared PANI-DBSA thin film sensor towards ammonia. It is observed that the sensitivity increases linearly with increase in the concentration of NH3 gas from 1 to 500 ppm approximately. However, beyond 500 ppm the curve tends to saturate. In essence, the sensitivity versus concentration curve exhibits logarithmic behavior. As linearity is desirable in the device operation, the prepared PANI-DBSA sensing film shows considerable promise in the concentration regime of 1-500 ppm. Beyond 500 ppm it can be conveniently calibrated to find the sensitivity as a function of analyte concentration.

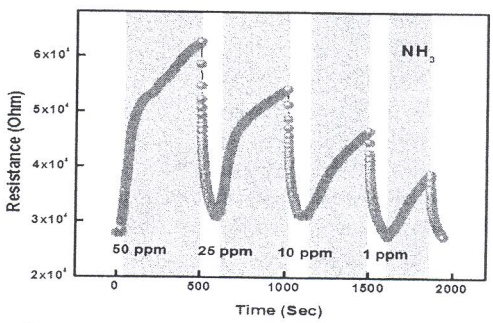

Fig. 2. Sensing response of PANI-DBSA thin film sensor towards different concentrations of ammonia gas

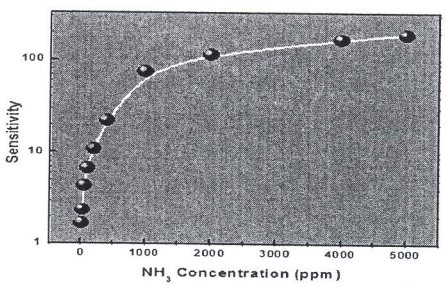

Fig. 3. Sensitivity vs. concentration curve of PANI-DBSA thin film sensor

IV. CONCLUSION

Ammonia gas sensor based on nanostructured thin film of PANI-DBSA has been successfully fabricated via a spin coating onto the glass substrate pattern. The fabricated sensor detects ammonia at a 1ppm level quantitatively and reversibly at room temperature operation. The PANI-DBSA thin film gas sensor exhibits good sensitivity at various ppm levels of ammonia. The characteristics like enhanced response or sensitivity (0.415) and the response speed (153 seconds) at lowest ppm level along with repeatability, linearity and reversibility claimed a cost-effective and environment-friendly gas sensor for ammonia.

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