Dodecyl benzene sulfonic acid (DBSA) doped polyaniline (PANI-DBSA) has been synthesized by chemical oxidative polymerization of aniline monomer in the presence of DBSA. The UV-visible spectroscopy and X-ray diffraction measurements confirm the formation of PANI and its doping by DBSA. SEM images show the formation of submicron size rod shaped PANI particles. A vibrating capacitor based ammonia gas sensor was prepared by spin coating PANI-DBSA film over copper (Cu) substrate. The sensor exploited Kelvin probe technique to monitor contact potential difference between PANI and Cu as a function of time and ammonia concentration. Upon exposure to 30 ppm ammonia, the sensor displays response time of 329 s, recovery time of 3600 s, and sensitivity value of 1.54 along with good repeatability.

1. Introduction

Ammonia has vast applicability like use in agricultural sector, chemical industries, medicinal fields, refrigeration systems, and so forth [1–4]. However, due to its toxic nature, application of ammonia also contributes to air pollution. The hazardous effect of ammonia can be felt around few hundred ppm gas concentration [5]. Its pungent odor and irritation effect start to affect the human beings below 50 ppm level [2, 6, 7]. Therefore, there is a need for the development of ammonia gas sensor for timely detection of ppm level concentrations of ammonia.

In the past, metal oxides based ammonia gas sensors have been developed with fast response and high sensitivity [8, 9]. However, they have disadvantages like complex fabrication steps, high power consumption, high temperature operation, and so forth [7, 10, 11]. In this context, conjugated polymers and their nanocomposites have shown great promise as gas sensing material due to advantages in terms of facile synthesis; tunable electrical and optoelectronic properties; processing via solution route; good sensitivity of their thin film based sensor towards a number of acidic/basic gases; improved response, recovery, and sensitivity and, most importantly, room temperature operation [7, 12–17]. Among various conducting polymers, polyaniline (PANI) is considered the most promising material for gas sensing purpose, due to its low monomer cost, lab scale synthesis via chemical route, and flexibility in tuning of electrical properties, particle morphology, environmental/thermal stability, and processability via selection of dopant and adjustment of oxidation level [7, 12, 18, 19]. In particular, its ability to undergo nonredox doping via protonic acid dopants and undoping by base in reversible manner makes PANI an ideal candidate for sensing of a number of toxic gases having acidic/basic character or electron donating/accepting nature [7].

In the past, a number of papers reported the formation of PANI film based gas sensor that exploited change in resistance, optical property, resonance frequency, or contact potential difference (CPD) in response to ammonia gas or vapor [7, 10, 11, 20, 21]. However, there is no detailed report on the PANI based ammonia sensor that measures gas exposure actuated changes in CPD between PANI layer and metallic substrate. The CPD technique is considered advantageous as there is no requirement of electrical contacts, wire bonding, or complicated fabrication steps [22].
This paper elaborates dodecyl benzene sulfonic acid (DBSA) doped PANI film based ammonia gas sensor, which measures change in work function of the PANI film upon exposure to ammonia. The elongated PANI-DBSA particles are prepared by oxidative polymerization and the formation of PANI and its existence in doped emeraldine salt (ES) form are ascertained by X-ray diffraction (XRD) and UV-visible spectroscopy. The morphology of PANI-DBSA is observed using scanning electron microscopy (SEM). A sensing system is formed by deposition of a layer of PANI-DBSA over copper (Cu) substrate and the time dependent change in CPD between PANI and Cu is measured by Kelvin Probe for exposure to a given ammonia concentration. The sensor is tested for detection of ppm level concentration of ammonia gas and its sensing parameters (e.g., response time, recovery time, and sensitivity) are measured.

Materials Used. Aniline (Loba Chemie) was freshly double distilled before use. Ammonium persulfate (APS, (NH₄)₂S₂O₈), dodecyl benzene sulfonic acid (DBSA) (Acros), chloroform (Merck), and propanol (Merck) were used on as-received basis. Deionized water (resistivity > 10⁶ Ω·cm) was used for synthesis and washing.

Synthesis of DBSA Doped Polyaniline. DBSA doped PANI (i.e., PANI-DBSA) has been synthesized by chemical oxidative polymerization of aniline monomer via direct doping route using DBSA as dopant [23, 24]. The 0.1-mole aniline monomer was mixed with 0.3 M aqueous DBSA solution and the mixture was cooled to 0°C. Polymerization was initiated by the dropwise addition of aqueous solution of ammonium persulfate (0.1 mol in 100 mL deionized water) to reaction mixture and maintaining reaction mixture at 0°C under continuous stirring. After completion of polymerization, the formed dark green emulsion of DBSA doped PANI was deemulsified using propanol. The resultant mixture was filtered through sintered glass crucible and the precipitate so obtained was washed repeatedly till the pH of the filtrate became neutral. Subsequently, the filtered cake was dried and crushed to obtain PANI-DBSA powder. In the next step, a calculated amount of PANI-DBSA was dispersed in chloroform by sonication followed by filtration through Whatman 41 filter paper. The filtered PANI-DBSA/chloroform dispersion layer (Figure 1) was formed over copper substrate (8 mm * 8 mm) by spin coating at 1000 rpm.

Characterization. The optical spectra of the chloroform dispersion of PANI-DBSA were 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 Advance D8 system in the diffraction (2θ) range of 10–80° using CuKα (λ = 1.540598 Å) as 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. The gas sensor characteristics were recorded using a Kelvin probe gas sensing setup. The ammonia gas at 30 ppm concentration (ammonia-air mixture) was introduced into the test chamber and changes in CPD between PANI film and Cu substrate were recorded after every second using a data acquisition system.

2. Results and Discussions

2.1. X-Ray Diffraction Measurement. Figure 2 shows the XRD pattern of DBSA-PANI powder that displays three distinguished peaks at 2θ values of 20.5° (d = 4.32 Å), 25.2° (d = 3.52 Å), and 26.9° (3.31 Å). In particular, the existence of ~20° and ~25° peaks (which represent periodicity parallel and perpendicular to chain axis, resp.) confirms the formation of PANI. Further, the relative prominence of 25° peak confirms the existence of PANI in its highly doped (electrically conducting) ES form, which is expected to show good sensitivity towards basic gases like ammonia.

2.2. UV-Visible Spectroscopy. Figure 3 shows the UV-visible absorption spectra of PANI-DBSA dispersion in chloroform. The spectrum consists of three distinguished transitions centred on 346 nm (band-1), 431 nm (band-2), and 732 nm (band-3) wavelengths [23, 25]. Band-1 corresponds to π → π* transition of the benzenoid rings whereas band-2 and band-3 are attributed to polaron → π* and π* → polaronic transitions, respectively. The prominence of band-3 compared to band-1 shows that PANI is formed in its doped ES form. Exposure to basic gases like ammonia causes
partial undoping (shift towards emeraldine base, i.e., EB form) leading to systematic variation of relative intensity and position of these bands, which forms the basis of optical sensors. Interestingly, the undoping also leads to change in work function (WF) of PANI, such that $WF_{ES} > WF_{EB}$. Therefore, we exploited Kelvin probe technique to trace gas induced variation of WF difference between PANI-DBSA layer and Cu substrate.

2.3. Morphological Investigations. The SEM image of synthesized PANI-DBSA particles is shown in Figure 4 and it can be seen that the formed PANI-DBSA particles display rod-like structure with $\sim 0.2 \mu m$ diameter and $\sim 1 \mu m$ length. The decrease in particle size leads to increase in surface-to-volume ratio, thereby exposing more sites for interactions with incident gas. Further, the elongated particles are known to display improved charge transport. These factors are expected to improve gas sensing response.

2.4. Ammonia Sensing via Kelvin Probe Gas Sensing Setup. The Kelvin probe technique measures the change in work function (WF) in terms of change in contact potential ($\Delta CP$) between the sample and reference electrode (gold tip) and not as the absolute work function values [26]. Figure 5 shows the contact potential difference that corresponds to change in WF of material with respect to reference electrode.

The CPD measurement is based on the vibrating capacitor of Kelvin-Zisman [27] which is shown schematically in Figure 6.

Here, a capacitor is constituted by two electrodes; the first one is the sample mounted on a piezoelectric ceramic that work as an active electrode (S), whereas the other one is a gold tip based reference electrode (R). This capacitor with inherent capacitance C tends to charge under the influence of natural contact potential difference ($V$) so that the developed charge ($Q$) can be expressed as

$$Q = CV. \quad (1)$$

When the piezoelectric ceramic is polarized, the sample (S) is subjected to lateral vibration, leading to the periodic change of the capacitance, which in turn induces a pseudosinusoidal modulated current ($i$) in the circuit. This current produces an alternating voltage drop ($e_r$) across an external resistor which is amplified via lock-in amplifier into a direct voltage $E$ which is the direct measure of the CPD change under the test gas. In the beginning, a counter potential $V'$

![Figure 3: UV-visible spectra of PANI-DBSA dispersion in chloroform.](image)

![Figure 4: SEM image of PANI-DBSA powder.](image)

![Figure 5: Schematic representation of Kelvin probe measurement principle.](image)

![Figure 6: Circuit diagram of Kelvin probe measurement setup.](image)
is manually adjusted to cancel the initial CPD to a zero value under the dilution gas.

Gas sensing via Kelvin probe involves the measurement of variation of CPD versus time for a given test gas concentration [28]. When layer of DBSA doped PANI (ES) deposited over Cu substrate is exposed to ammonia, partial undoping converts the ES toward emeraldine base (EB) form. As already discussed earlier, such deprotonation induced undoping is accompanied by change in work function of the PANI-DBSA layer (shown schematically in Figure 7).

Figure 8 shows sensing response of PANI-DBSA/Cu substrate sensing element at room temperature upon exposure to 30 ppm gas concentration. Before exposure to ammonia, the CPD was +0.05951 V. However, after exposure to ammonia gas (30 ppm), CPD showed an abrupt decrease followed by exponential change to attain a saturation value of −0.032227 V.

This can be ascribed to the sorption of ammonia gas molecules on the surface of sensing DBSA-PANI layer leading to deprotonation and change in oxidation level, which tends to increase the work function.

During the recovery stage, when ammonia supply was stopped and dry air was passed through the system, ammonia desorption takes place, leading to restoration of doped state and original oxidation level. These changes we observed in terms of initial fast rise of CPD value followed by long exponential rise part. The response and recovery time value were 329 sec and 3600 sec, respectively. The sensitivity of the sensor toward ammonia can be expressed in terms of CPD values in the presence and absence of gas as

$$\text{Sensitivity} = \frac{(\text{CPD}_{\text{Ammonia}} - \text{CPD}_{\text{Dry Air}})}{\text{CPD}_{\text{Dry Air}}}. \quad (2)$$

On the basis of CPD variation, the sensor’s sensitivity for 30 ppm ammonia is found to be 1.54. In order to observe...
the reversibility and repeatability, the sensor was subjected to two sensing cycles (involving ammonia exposure, saturation, and recovery steps), keeping ammonia concentration at 30 ppm for each cycle. It was observed that, in the second cycle, response and recovery times and sensitivity values were almost the same as in the case of the first cycle. This demonstrates the good repeatability of the sensor which is extremely important for accurate detection and quantification of ammonia. Nevertheless, we feel that the CPD based sensor is a relatively new concept and modifications are expected in terms of active material designing, film forming techniques, active layer’s morphology, and selection of substrate, so that sensor’s response/recovery time as well as sensitivity can be further improved.

3. Conclusion

Submicron rod shaped particles of DBSA doped PANI have been synthesized by oxidative polymerization and coated onto copper substrate from chloroform solution. The PANI/Cu system is exposed to known ammonia concentration and its CPD is monitored over the time via Kelvin probe technique. The prepared gas sensor rapidly and reversibly detects up to 30 ppm ammonia gas at room temperature conditions. The sensor displayed response time of 329 sec, recovery time of 3600 sec, and sensitivity value of 1.54 with good repeatability. Nanostructuring of PANI, modulation of film morphology and thickness, and formation of nanocomposites are expected to further improve the sensing characteristics of such sensors.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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