

Performance Analysis of Ammonia Sensors based on Nanostructured PANI-DBSA Synthesised by Template Free Direct Doping Route using Surfactant and Indirect Doping Route

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Abstract— Prolonged exposure of ammonia results in many potential health hazards for humans as it interacts immediately upon contact with available moisture in the eyes, skin, oral cavity, respiratory tract and particularly mucous surfaces, thereby, causes cellular destruction and tissue necrosis. In this paper, we report for the first time a detailed comparison between ammonia gas sensing, spectral, structural, and morphological properties of the dodecyl benzene sulphonic acid doped polyaniline (PANI-DBSA) nanostructures synthesized using a template free direct route using surfactant dopants as structure directing agents and using indirect route. Two different samples of PANI-DBSA nanostructures have been prepared via template free direct route (Nanostructured DBSA doped PANI has been prepared by emulsion polymerization of aniline in the presence of DBSA) and indirect doping route (Nanostructured DBSA doped PANI has been prepared via chemical oxidative polymerization of aniline monomer). Different characterizations revealed that the spectral, structural, morphological, and ammonia gas sensing properties of the synthesized PANI-DBSA nanostructures are highly dependent on the synthesis route. Thin film of nanostructured PANI-DBSA prepared using template free direct route exhibited better ammonia gas sensing response (7.97) as compared to thin film of nanostructured PANI-DBSA prepared using indirect doping (3.24) due to availability of large number of grain boundaries and higher doping levels.

Keywords—DBSA; PANI; Ammonia Sensor; Template Free Direct Route; Indirect Doping Route.

I. INTRODUCTION

In the recent past, conducting polymers have been widely used as sensing thin film for ammonia gas which causes many potential health hazards for humans like rapid skin or eye irritation, olfactory fatigue, burning of the throat and nose, burning of respiratory tract, bronchiolar and alveolar edema, respiratory distress or failure due to airway destruction, [1] etc. However, among other conducting polymers, dodecyl benzene sulphonic acid doped Polyaniline (PANI-DBSA) nanostructures have been extensively explored for ammonia gas sensing [2], not only because of its tunable electrical (gas sensing) properties which can be easily tuned by adjusting degree of doping, but also due to its environmental stability and economic feasibility [3]. However, the electrical (gas sensing) properties of dodecyl

benzene sulphonic acid doped Polyaniline (PANI-DBSA) nanostructures are extremely sensitive toward oxidation states, dopant concentrations, and nanostructures surface morphology [3] which are highly dependent on PANI-DBSA synthesis process. To the best of our knowledge, no detailed analysis is available on the effect of PANI-DBSA synthesis process (direct/indirect) on spectral, structural, morphological, and ammonia gas sensing properties of PANI-DBSA.

In this present work we report complete preparation, characterization, and detailed comparative performance analysis of ammonia gas sensors prepared using nanostructured thin film of PANI-DBSA conducting polymers synthesized using template free direct route (by emulsion polymerized of aniline in the presence of DBSA) and indirect doping route (via chemical oxidative polymerization of aniline monomer and HCl as dopant followed by DBSA redoping). The effect of two different synthesis routes on various characteristics of the synthesized PANI-DBSA samples is investigated by various techniques (FESEM, TEM, FTIR, XRD, Raman Spectra, and UV-visible Spectra). Gas sensing experiments revealed that thin film of nanostructured PANI-DBSA prepared using template free direct route provides better ammonia gas sensing response as compared to the thin film of nanostructured PANI-DBSA prepared using indirect doping. This is due to presence of large number of grain boundaries resulted by the formation of elongated nanorod like structures in case of template free direct route synthesis. These grain boundaries along with oxidation states, doping level, interfacial polymerization, inter-grain coupling, and other microscopic features ultimately effects the ammonia gas sensing response. Therefore, in this paper, a detailed correlation is established between spectral, structural, morphological and gas sensing properties of PANI-DBSA synthesised by two different routes (direct/indirect).

II. MATERIAL SYNTHESIS & CHARACTERIZATION

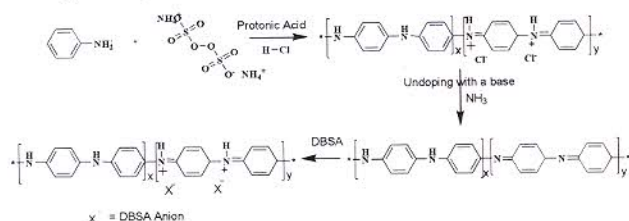
Different chemically pure chemicals used in this study were: Aniline (LobaChemie) as monomer, Ammonium persulfate as oxidant [APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$], dodecyl benzene sulfonic acid (DBSA), Hydrochloric acid (HCl), Isopropyl alcohol (IPA), Chloroform (CHCl_3), and De-ionized water with resistivity greater than $18 \text{ M}\Omega\text{-cm}$.

A. PANI-DBSA Synthesis via Template Free Direct Route (PD-Direct)

The main steps used for synthesis of PANI-DBSA via template free direct route (PD-Direct) were emulsion formation, polymerization, de-emulsification, and filtration. For details of the PANI-DBSA synthesis via template free direct route (PD-Direct), refer to our earlier research work [4].

B. PANI-DBSA Synthesis via Indirect Doping Route (PD-Indirect)

To synthesis PANI-DBSA via Indirect Doping Route (PD-Indirect), 0.1 mol of aniline and 1 mole of HCl were mixed in 1 liter water. Polymerization was initiated by the drop wise addition of aqueous solution of ammonium persulfate (0.1 mol in 100 mL de-ionized water) under same conditions and for same duration as in the case of direct route approach [4]. The base form of the polyaniline was obtained by treating the obtained polymer powder with 1 mol aqueous ammonia. It was followed by treatment with 0.3 mol aqueous DBSA solution, stirring for 2 h, de-emulsification, and filtration [4].



C. Characterization Results

The spectral, structural, and morphological characterizations of PD-Direct and PD-Indirect were done.

UV-Visible absorption spectra of PD-Direct (Red Color) and PD-Indirect (Black Color) are shown in Fig. 1(a). Spectrum of nanostructured PANI-DBSA formed by direct route (PD-Direct) shows three clearly distinguishable transition peaks. These peaks are at 351 nm ($\pi \rightarrow \pi^*$ transition of the benzenoid rings), 431 nm (polaron $\rightarrow \pi^*$ transitions), and 746 nm wavelengths ($\pi^* \rightarrow$ polaronic transitions). The spectrum of nanostructured PANI-DBSA formed by indirect route (PD-Indirect) shows that three distinguished transitions peaks located at 349 nm ($\pi \rightarrow \pi^*$ transition of the benzenoid rings), 431 nm (polaron $\rightarrow \pi^*$ transitions) and 735 nm ($\pi^* \rightarrow$ polaronic transitions). The prominence of peak for $\pi^* \rightarrow$ polaronic transitions (around 735-750 nm) compared to the peak for $\pi \rightarrow \pi^*$ transition (around 349-351 nm) shows the doping levels of the PANI polymer in both cases. Clearly presence of much developed band for $\pi^* \rightarrow$ polaronic transitions (around 735-750 nm) in case of PD-Direct as compared to that in case of PD-Indirect suggests the higher doping levels in case of PD-Direct. Same is confirmed by the higher relative intensity value of the band around 735 - 750 nm w.r.t. band around 349-351 nm for PD-Direct (1.5621) as compared to that of PD-Indirect (1.4284).

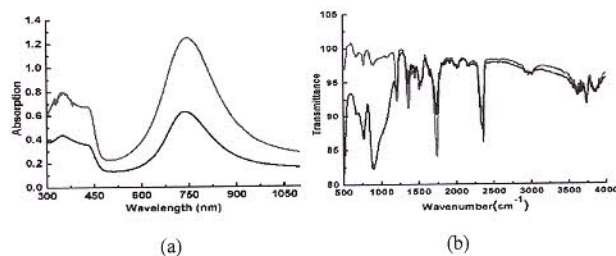


Fig. 1. (a) UV-Visible Characterization: PANI-DBSA Direct (Red Color) and PANI-DBSA Indirect (Black Color), (b) FTIR Characterization: PANI-DBSA Direct (Red Color) and PANI-DBSA Indirect (Black Color).

The FTIR spectra of PD-Direct (Red Color) and PD-Indirect (Black Color) are shown in Fig. 1(b). The characteristic bands corresponding to DBSA doping are located at 1221 cm^{-1} (corresponds to C-N⁺ stretching in the polaron form) and 1457 cm^{-1} (assigned to the presence of benzenoid rings). A comparison of the intensity of the band at $\sim 1220 \text{ cm}^{-1}$ (I_{1220}) relative to $\sim 1460 \text{ cm}^{-1}$ band (I_{1460}) gives a qualitative idea about the doping level. As revealed by FTIR spectra, the higher value of I_{1220} / I_{1460} in case of PD-Direct (4.84) as compared to the case of PD-Indirect (2.35) is the clear indication of the higher doping of DBSA in PD-Direct.

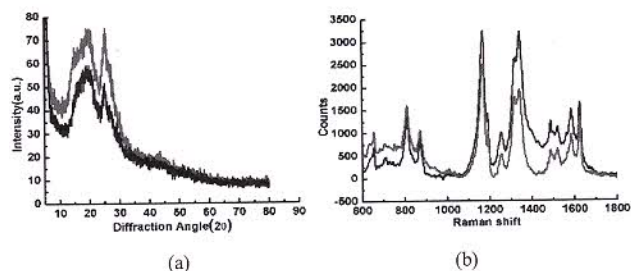


Fig. 2. (a) XRD Spectra: PANI-DBSA Direct (Red Color) and PANI-DBSA Indirect (Black Color) (b) Raman Characterization: PANI-DBSA Direct (Red Color) and PANI-DBSA Indirect (Black Color).

The XRD patterns for PD-Direct (Red Color) and PD-Indirect (Black Color) are shown in Fig. 2(a). The main characteristic peaks associated with DBSA dopant concentration in PANI are located at 2θ values of $\sim 20^\circ$ and $\sim 25^\circ$. Increasing doping level causes variation of the relative intensity of the $\sim 20^\circ$ (I_{20°) and $\sim 25^\circ$ (I_{25°) peaks [3]. It is observed that $I_{25^\circ} / I_{20^\circ}$ ratio is more in the case of PD-Direct (1.0132) as compared to the case of PD-Indirect (0.8902), which indicates that the achieved doping level is more in case of PANI-direct. This is consistent with the UV-visible and FTIR observations.

Raman spectra showing structural fingerprint of PD-Direct (Red Color) and PD-Indirect (Black Color) are shown in Fig. 2(b). The band at 1502 cm^{-1} is assigned to C=N stretching. Band at 1343 cm^{-1} corresponds to C-N⁺ stretching. The counts (C) of band at 1502 cm^{-1} significantly decreases with higher doping levels. It is observed that C_{1343} / C_{1502} ratio is more in the case of PD-Direct (3.053) as compared to the case of PD-Indirect (2.856), which confirms higher doping in PD-Indirect.

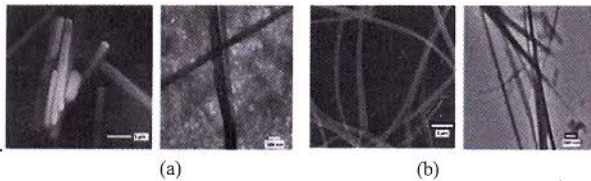


Fig. 3. Morphology Characterization: (a) PANI-DBSA Direct: SEM Image (Left Side) and TEM Image (Right Side), (b) PANI-DBSA Indirect: SEM Image (Left Side) and TEM Image (Right Side).

In case of PD-Direct, the FESEM and TEM results (Fig. 3(a)) show the clear formation of rod like structures with about 250 -300 nm diameter and about 1 μ m length. In comparison, the FESEM and TEM images of PD-Indirect (Fig. 3(b)) reveals the formation of nanofibers like structure (about 150-160 nm diameter). The large number of grain boundaries present in nanorods structure (PD-Direct) as compared to nanofiber structure (PD-Indirect) displays better electrical properties which causes better ammonia gas sensing response (Observed in Experimental Results). However, the overall ammonia gas sensing response is also effected by doping levels, oxidation states, interfacial polymerization, inter-grain coupling, and other microscopic features. Based on experimental results it is concluded that, under our experimental conditions, a micellar elongation procedure [3] dominated in case of PD-Direct due to presence of DBSA leading to the formation of nanorods structure, whereas unelongated growth was more probable for PD-indirect resulting in the formation of nanofibers.

III. SENSOR FABRICATION & GAS SENSING

A. Sensor Device Fabrication

Two different sensor devices were prepared – One using PD-Direct and another using PD-Indirect. To prepare the devices, a calculated amount (100 mg) of PANI-DBSA nanorods/nanofibers was suspended in chloroform (10 ml) under sonication for 3 hours. It was followed by filtration through Whatman 41 filter paper. The so obtained viscous solution of PANI-DBSA nanorods/nanofibers was spin coated onto glass substrate (with platinum patterned interdigitated electrodes) at 1200 RPM to realize thin film constituted of PANI-DBSA nanorods/nanofibers [4].

B. Gas Sensing Results

The gas sensing response of both the sensors (PD-Direct based and PD-Indirect based) is recorded at same ammonia concentration by putting both the devices in the gas sensing chamber. The comparison results of observed change in resistance for both sensors (PD-Direct and PD-Indirect) for ammonia gas are shown in Fig 4. It is clear from the gas sensing results that the response of ammonia sensor based on PD-Direct (Red Color) is much better than that of the PD-Indirect based ammonia sensor (Black Color) and can repeatedly detect ammonia. The sensitivity in relative response characteristics $[(R_a - R_g) / R_a]$ where R_a is initial resistance in pure air and R_g is resistance in presence of ammonia gas] of PD-Direct based sensor at 300 ppm NH_3 concentration (Temperature: 27 $^\circ\text{C}$ and Relative Humidity: 50% RH) is 7.97 while of PD-Indirect based sensor is 3.24. The better sensitivity of PD-Direct based sensor (in all cases of Fig. 4) is due to presence of large number of grain

boundaries resulted by the formation of elongated nanorod like structures in case of PD-Direct along with effect of other parameters like oxidation states, doping levels, interfacial polymerization, inter-grain coupling, etc. In the presence of the ammonia gas, the sensor's resistance increases quickly and attains saturation due to increase in deprotonation/localization of polarons in the PANI-DBSA sensing layer with increasing adsorptions of NH_3 gas molecules on its surface [11]. After removal of ammonia, the sensor regains the initial value of the resistance.

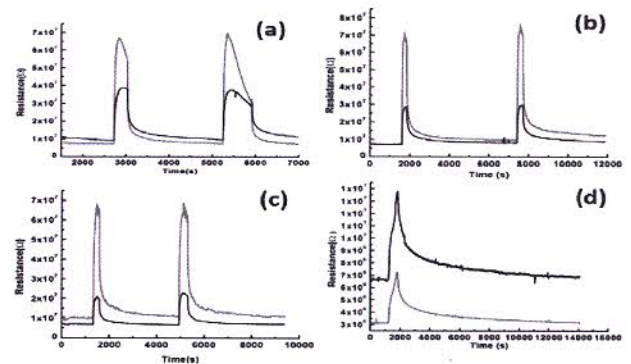


Fig. 4. Sensing responses of PD-Direct (Red Color) and PD-Indirect (Black Color) based Ammonia Gas Sensors: (a) Static Mode Sensing at 300 ppm of NH_3 (Temperature: 27 $^\circ\text{C}$ and Relative Humidity: 50% RH) (b) Static Mode Sensing at 300 ppm of NH_3 (Temperature: 45 $^\circ\text{C}$ and Relative Humidity: 50% RH) (c) Static Mode Sensing at 300 ppm of NH_3 (Temperature: 65 $^\circ\text{C}$ and Relative Humidity: 50% RH) (d) Dynamic Mode Sensing at 100 ppm of NH_3 (Temperature: 27 $^\circ\text{C}$ and Relative Humidity: 0% RH).

IV. CONCLUSION

We have presented the characterization of ammonia gas sensor, based on PANI-DBSA synthesized by two different synthesis routes, for healthcare applications. Nanostructured PANI-DBSA samples were synthesized using template free direct route (by emulsion polymerized of aniline in the presence of DBSA) and indirect doping route (via chemical oxidative polymerization of aniline monomer). SEM, TEM, FTIR, Raman Spectra, and UV-visible Spectra measurements revealed that the acquired PANI-DBSA morphology and doping levels are critically dependent on synthesis route. Experimentally it is observed that thin film of nanostructured PANI-DBSA prepared using template free direct route provides better ammonia gas sensing response (7.97) as compared to thin film of nanostructured PANI-DBSA prepared using indirect doping (3.24). This is due to presence of large number of grain boundaries resulted by the formation of elongated nanorod like structures in case of template free direct route synthesis. These grain boundaries along with oxidation states, doping levels, interfacial polymerization, inter-grain coupling, and other microscopic features ultimately effects the ammonia gas sensing response.

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