Synthesis and Characterization of PANI-DBSA/MWCNT nanocomposites for Ammonia Gas Sensing

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***Abstract*— Dodecyl benzene sulfonic acid (DBSA) doped polyaniline (PANI-DBSA) / multi-walled carbon nanotube (MWCNT) nanocomposites (PANI-DBSA/MWCNT) based gas sensor is prepared and characterized for ammonia gas, prolonged exposure of which results in many potential health hazards such as rapid skin irritation, olfactory fatigue, cellular destruction and tissue necrosis. Highly conducting dodecyl benzene sulfonic acid (DBSA) doped polyaniline (PANI-DBSA) / multi-walled carbon nanotube (MWCNT) nanocomposites were prepared by in-situ polymerization process. FESEM, TEM, XRD, and UV-visible measurements confirmed the formations of PANI-DBSA/MWCNT nanocomposites. Experimentally it is observed that thin film of PANI-DBSA/3wt.%MWCNT nanocomposites synthesized by indirect doping route provides better ammonia gas sensing response (2.65 at 100 PPM) as compared to thin film of nanostructured PANI-DBSA (1.25 at 100 PPM). The cross-selectivity results revealed that the developed sensor is highly selective to ammonia gas as compared to other gases.**

Keywords—DBSA; PANI; MWCNT; Ammonia Sensor; Indirect Doping Route.

I. INTRODUCTION

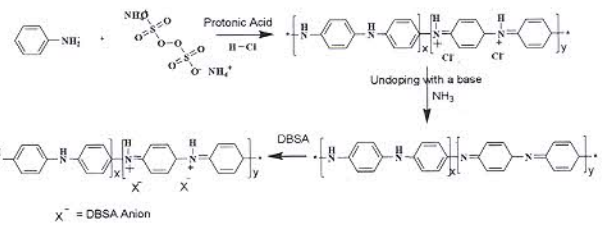
In the recent past, conducting polymers have been widely used as sensing thin film for ammonia gas [1] – [2] which causes many potential health hazards for humans like rapid skin or eye irritation, olfactory fatigue, burning of the throat and nose, burning of respiratory tract, bronchiolar and alveolar edema, respiratory distress or failure due to airway destruction, [3] etc. However, among other conducting polymers, dodecyl benzene sulphonic acid doped Polyaniline (PANI-DBSA) nanostructures have been extensively explored for ammonia gas sensing [4]. But in the recent past, PANI-DBSA multi-walled carbon nanotube (MWCNT) nanocomposites (PANI-DBSA/MWCNT) are also considered as potential candidates for ammonia gas sensing due to their improved electrical properties which can be easily tuned by adjusting degree of doping. In this present work we report the complete preparation, characterization, and detailed comparative performance analysis of ammonia gas sensors prepared using nanostructured thin film of PANI-DBSA and PANI-DBSA/3wt.%MWCNT composites synthesized using indirect doping route.

II. MATERIAL SYNTHESIS & CHARACTERIZATION

Different chemically pure chemicals used in this study were: Aniline (LobaChemie) as monomer, Ammonium persulfate as oxidant [APS, $(NH4)_2S_2O_8$], dodecyl benzene sulfonic acid (DBSA), Hydrochloric acid (HCl), Isopropyl alcohol (IPA), Chloroform ($CHCl_3$), and MWCNT.

A. PANI-DBSA/MWCNT Synthesis via Indirect Doping Route

To synthesis PANI-DBSA/MWCNT via Indirect Doping Route (PD-Indirect), first a calculated weight percentage of MWCNT was dispersed in 1 liter water followed by mixing of 0.1 mol of aniline and 1 mole of HCl into it. 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 [5]. 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 [5]. The synthesis reaction for PANI-DBSA is shown below.



B. Characterization Results

UV-Visible spectrophotometer (Perkin Elmer lambda 25) is used to record the optical spectrum of the chloroform dispersion of PANI-DBSA. UV-Visible absorption spectra of PANI-DBSA and PANI-DBSA/MWCNT with different weight percentages are shown in Fig. 1. UV-Visible absorption spectra of Band -1 and Band -3 in PANI-DBSA/MWCNT display the Blue Shift representing that MWCNT is added into the PANI can increase the intermolecular interaction and widened the energy band gap.

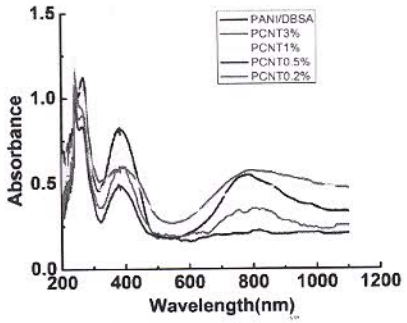
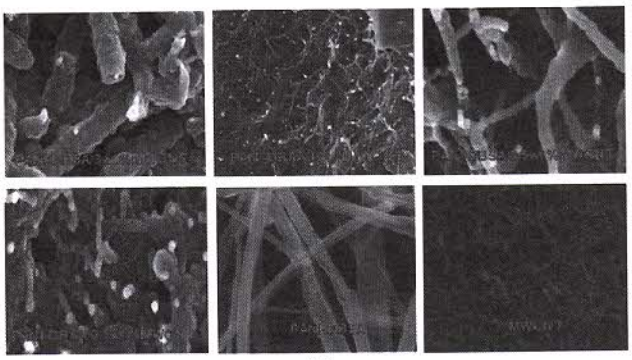
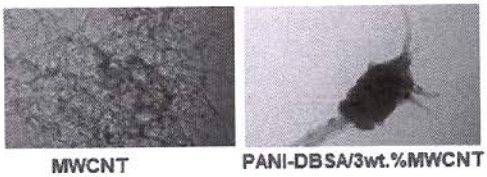


Fig. 1. UV-Visible Characterization of PANI-DBSA and PANI-DBSA/MWCNT with Different Weight Percentages.

The Field emission scanning electron microscope (FESEM, X-MaxN, OXFORD Instrument, accelerating potential 10.0 kV) is used to investigate the surface morphology and results are shown in Fig. 2 (a). PANI-DBSA and MWCNT show the fiber like structure and entangled tubules like structure. The small size of nanotubes shows the high surface to volume ratio which results in large number of sorption sites to aniline monomer which can polymerize to form coating over the nanotubes. At very low weight percentage values of MWCNT, PANI coated tubes show random agglomerated morphology. At high weight percentage (3 %), wrapping of PANI-DBSA on MWCNT is clearly visible and synergic effect of this wrapping is expected to result highly selective and sensitive ammonia sensing as compared to others. Therefore, for further characterization and gas sensor preparation, we have considered the PANI-DBSA/3wt.%MWCNT nanocomposites. Wrapping of PANI-DBSA on MWCNT is also confirmed by TEM results (Fig. 2(b)).



(a)



(b)

Fig. 2. (a): FESEM Characterization of PANI-DBSA, MWCNT and PANI-DBSA/MWCNT Composites with Different Weight Percentages (b) TEM Characterization of MWCNT and PANI-DBSA/3wt.%MWCNT.

X-ray diffraction (XRD) pattern was recorded using Bruker Advanced D8 system in the diffraction (2θ) range of 5-80° using CuKα (λ= 1.540598Å) as radiation source. The XRD patterns for PANI-DBSA, MWCNT, and PANI-DBSA/3wt.%MWCNT are shown in Fig. 3. The pure MWCNT shows a sharp peak centred 2θ value of 25.81° which corresponds to the (0 0 2) planes of MWCNT. The peaks around 42.68° are due to the (1 1 0) and (1 0 0) graphitic planes plus small amount of catalyst particle encapsulated inside the walls of the MWCNTs. XRD pattern of DBSA–PANI powder displays three distinguished peaks at 2θ values of 20.5° (d=4.32Å), 25.2° (d=3.52Å) and 26.9° (3.31Å). The composites show the characteristic peaks of both PANI and MWCNT without any additional bands indicating absence of covalent interactions between the phases.

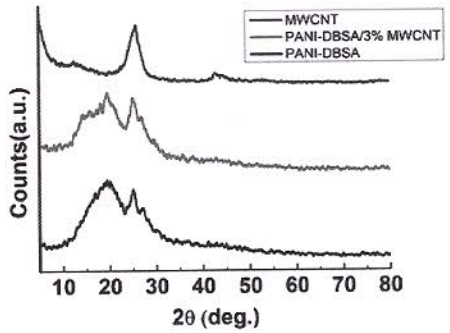


Fig. 3. XRD Specta of PANI-DBSA, MWCNT, and PANI-DBSA/3wt.%MWCNT.

III. Sensor Fabrication & Gas Sensing

A. Sensor Device Fabrication

To prepare the devices, a calculated amount (100 mg) of PANI-DBSA or PANI-DBSA/3%MWCNT nanostructures 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 1000 RPM to realize thin film constituted of PANI-DBSA nanorods/nanofibers [5].

B. Gas Sensing Results

The gas sensing response of both the sensors (PANI-DBSA based and PANI-DBSA/3%MWCNT based) is recorded at different ammonia concentration by putting both the devices in the gas sensing chamber. The comparison results of observed Sensing Response (in terms of Relative Response) for different concentrations of ammonia gas are shown in Fig 4. It is clear from the gas sensing results that the response of ammonia sensor based on PANI-DBSA/3%MWCNT (Black Color) is much better than that of the PANI-DBSA based ammonia sensor (Red Color). The sensing response is measured in terms of 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] at 27 ℃ Temperature and 0% RH Relative Humidity. Experimentally observed ammonia gas sensing

response for PANI-DBSA/3wt.%MWCNT nanocomposites based gas sensor is 2.65 at 100 PPM.

The cross-selectivity of the PANI-DBSA/3%MWCNT based sensor is also analyzed for different gases (Acetone, Benzene, Toluene, NO_2). The results are shown in Fig. 5. As clear from these results, the developed sensor is highly selective for ammonia gas as the sensing response (in terms of relative response) of the developed sensor is very poor for the other gases (Acetone, Benzene, Toluene, NO_2). The different concentrations of different gases are used for cross-selectivity experiment. This is due to non-availability of the gas cylinders of same concentration for all gases.

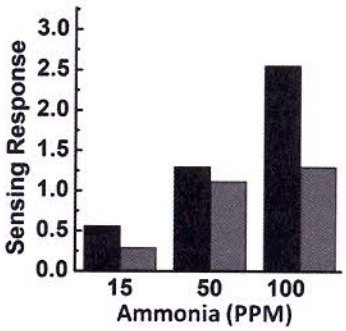


Fig. 4. Sensing responses of PANI-DBSA (Red Color) and PANI-DBSA/3wt.%MWCNT (Black Color) based Ammonia Gas Sensors (Temperature: 27 ℃ and Relative Humidity: 0% RH).

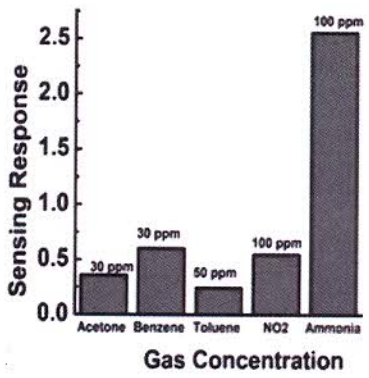


Fig. 5. Cross-selectivity of PANI-DBSA/3wt.%MWCNT based Ammonia Gas Sensors against Acetone, Benzene, Toluene, NO_2 (Temperature: 27 ℃ and Relative Humidity: 0% RH).

IV. Conclusion

We have presented the characterization of ammonia gas sensor, based on PANI-DBSA/3wt.%MWCNT nanocomposites synthesized by indirect doping route, for healthcare applications. Highly conducting polyaniline (PANI) / multi-walled carbon nanotube (MWCNT) nanocomposites were prepared by in-situ polymerization process. FESEM, TEM, XRD, and UV-visible Spectra measurements confirmed the formations of PANI-DBSA/MWCNT nanocomposites. Experimentally it is observed that thin film of PANI-DBSA/3wt.%MWCNT nanocomposites synthesized by indirect doping route provides better ammonia gas sensing response (2.65 at 100 PPM) as compared to thin film of nanostructured PANI-DBSA (1.25 at 100 PPM). The developed sensor is highly selective to ammonia gas as compared to other gases.

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