Chapter 7 Inorganic Doped Dl-Polylactide Polyaniline Based Composite for Methane (Ch4) Gas Sensing

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Abstract

Polyaniline (PANI) nonofibriles have been successfully synthesised by simple chemical-oxidation polymerization method using aniline as a predecessor at room temperature. It was synthesized using H3PO4 dopants. The structure, chemical groups, and electronic transition were investigated by SEM, FTIR, and UV Visible. We present the methane gas response of as-prepared H3PO4 doped DL–PLA/PANI-ES composite film at different concentration. The percentage (%) methane gas response was found to be 9 % at 500ppm.

Keywords: Polyaniline, Polylactide, Doping, Composite, Methane gas sensing

Introduction

Methane is the chief constituent of natural gas which is hazardous for both human and environment. Due to its highly flammable and explosive characteristics, even at low level (5–14%) concentration poses a serious threat. With the global population boom, more and more human lives are being endangered by the effect of CH₄ gas exposure [1]. That creates a demand for monitoring CH₄ gas for making the safety environments in homes, industries and mines. It is in great need of development of sensors for detecting methane gas quickly and accurately in the coal mine at ambient condition. Generally, metal oxide-based gas sensors such as ZnO [2], MoO₃ [3], SnO₂ [4], TiO₂ [5], ZrO₂ [6], spinel compounds [7] etc. have been used. All the above sensors require high temperature for sensor operation, which is expensive. Researchers have put their effort for making room temperature-based sensors. In spite of considerable efforts, room temperature-based sensors for CH₄ gas sensing has not been found hitherto, the problem being of vital to industry as well as general public.

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To meet this demand, a new class of sensor materials is underway, including efforts to prepare the sensor, such as conducting polymer based sensor, which can work at ambient condition. In the conducting polymer family, PANI is one of the members with good environmental and thermal stability coupled with ease of processability [8] and doping-dedoping features [9]. In spite of above advantages, PANI film is brittle and highly moisture sensitive. This is due to the ionic electroactive nature of PANI polymer and it makes the limits for commercial applications. The stability of PANI polymer can be improved by making in composite with thermoplastic polymer such as poly (methyl methacrylate) (PMMA), polyvinyl chloride (PVC), polystyrene (PS), and polyurethane (PU) as stabilizer [10–13]. The stability of PANI polymer could be enhanced by covalently grafting with polymers [14,15]. We selected DL-PLA polymer in the composite preparation because of its strong interaction with ionic electroactive polymer such as PANI polymer. This interaction can change potentially the surface properties such as surface charge, wettability, conformational and dimensional changes on bioactive materials. Despite of all above mentioned properties, one of the most important issues related to the applications of biodegradable polymer in electronic engineering is to reduce the degradation of conducting polymers. There are some reports on the use of PLA with multiwalled carbon nanotubes (MWCNT) [16], conducting polymers such as PANI [17], and form composites. That showed improved polypyrrole [18] to surface resistance/conductivity properties compared with neat one. Therefore, the use of biodegradable polymer with conductive polymers is a very important and challenging task. Our goal was to prepare an environmental stable PANI composite having better electrical properties for sensor and other electronic applications.

In this chapter, we have reported the methane gas sensing characteristics of H_3PO_4 doped DL-PLA/PANI-ES composite. Such characteristics of H_3PO_4 doped DL-PLA/PANI-ES composite we have demonstrated first time to achieve CH₄ gas response at room temperature.

Experimental Details

At first, DL-PLA films were prepared by solution casting technique. During the DL—PLA preparation, DL-PLA and CHCl₃ were used as polymer and solvent, respectively. 2 g DL-PLA was put to 20 mL of CHCl₃ in a 100 mL beaker. It is continuously stirred for 3 h at room temperature. The transparent soluble product was poured into a ptridish having diameter 10 cm. It is left in air for the solvent evaporation. After solvent evaporation, DL-PLA film formed. The films removed from ptridish and cut into small pieces, which are used for their characterizations and preparation of composites.

Room temperature H_3PO_4 doped DL-PLA/PANI-ES composites was prepared by *in situ* technique through chemical oxidation polymerization method. During the composite preparation, aniline and DL-PLA film (1 cm²) was taken as monomer and base material, respectively. In this composite preparation, 3 mL of aniline was added to 105 mL of aqueous 1 M H₃PO₄ solution. The solution was stirred continuously for 0.5 h and slightly yellowish solution (**Solution 1**) was obtained. Then a DL-PLA film (1 cm^2) was put into solution 1. It is also stirred continuously for 12 h. **Solution 2** was prepared by adding 7.47 g of ammonium perdisulphate (APS) in 60 mL of 1 M H₃PO₄. Then **solution 2** was added drop wise to the DL-PLA mixed solution 1 for 1 h for the polymerization to occur. The color of DL-PLA film was observed to change from white to light green and finally to dark green as polymerization continue to proceed. The reaction mixture was maintained under constant stirring for 10 h to complete the polymerization. The resulting H₃PO₄ doped DL-PLA/PANI-ES composite was finally washed with deionised water several times and dried in the ambient atmosphere [**19**]. The flow chart of preparation of HCl doped DL-PLA/PANI-ES composites is shown in **Scheme 1**.



Scheme 1. The flow chart of preparation of H3PO4 doped DL-PLA/PANI-ES composite

Characterization Techniques

Surface morphologies of DL-PLA film and H₃PO₄ doped DL-PLA/PANI composites were analyzed using scanning electron microscope (SEM, Carl Zeiss Supra 40). Samples were needed gold coating before start SEM measurements.

In ATR-FTIR analysis, DL-PLA film and $\mathrm{H_3PO_4}$ doped DL-PLA/PANI 193

composites were characterized by Thermo Nicolet Nexus 870 spectrophotometer in the range $400-4000 \text{ cm}^{-1}$.

The prepared material in the UV–Visible region was studied by UV–Visible (Micropack UV–VIS–NIR, DH 2000) spectroscope.

For gas sensing studies, the prepared doped composite film (~25 $^{\circ}$ C) was taken. For this measurement, the surface of the material is electroded with silver paste strip of 8 mm length, 1.5 mm width, and separated from each other by 4 mm. The methane gas sensing behaviour was estimated by measuring the resistance change before and after gas exposure. This measurement was done using The CH₄ gas sensing performances of these materials are characterized by DC resistance measurements. From this measurement, the response (S) is estimated through the resistance change between air (R_a) and in test gas environment (R_g), using the following relations [**19**]:

Re sponse (%) =
$$\frac{R_a - R_g}{R_a} \times 100$$

Results and Discussion

Figure 1 shows SEM images of DL–PLA film (A) and H_3PO_4 doped DL–PLA composite (B). In Figure 1 (a), it is observed that no nanowires were deposited on DL–PLA film at room temperature. Smooth surface was observed for neat DL–PLA film. H_3PO_4 doped composite film [Figure 1 (b)] indicates fibrous-like morphology. The diameter of the fibre was found in nano regimes. The nanofiber appears to be non–uniform as distributed over the DL-PLA film. The average diameter was estimated and was 131 nm. This might occur after establishing the polymerization reaction. Because of high surface area of polyaniline, it is favorable for the sensor application.



Figure 1. SEM image of DL-PLA film (A) and H3PO4 doped DL-PLA/PANI Composite (B) [19]

Inorganic Doped Dl-Polylactide Polyaniline Based Composite for Methane (Ch4) Gas Sensing

ATR-FTIR spectra of DL-PLA. H₃PO₄ doped PANI composite were shown in Figure 2. The absorption band position(s) and its assignments of as two materials such as DL-PLA, H₃PO₄ doped PANI composite were specified in Table 1. Absorption bands of DL-PLA was found at 2995, 1759, 1616 and 1216 cm⁻¹ and have been attributed to C-H stretching, C=O stretching, C-O stretching of ester and C-O-C stretching vibration, respectively. The other bands were observed at 1453. 1361 and 1363 $\rm cm^{-1}$ and has been represented the stretching vibration of C-H deformation [19]. This signifies that all the bands of DL-PLA polymer are retained. The important absorption band positions and it assignments of H₃PO₄ doped PANI were found at 1554, 1475 and 1108 cm⁻¹ corresponding to quinoid, benzoid and C=N stretching, respectively [19]. The presence of quinoid (1475 cm⁻¹) and benzoid ring (1554 cm⁻¹) vibrations, these groups are indicated the salt form of polyaniline (PANI-ES) [19]. From **Table 1**, it is observed that N-H bands of H₃PO₄ doped DL-PLA/PANI composite appeared at 3289 cm⁻¹. The N-H stretching bands appeared. This is due to the existence of amine group on DL-PLA polymer film. The C=N, C=O, C-O and C-O-C stretching bands do not change considerably.



Figure 2. FTIR spectrum of H3PO4 doped DL-PLA/PANI composite [19]

Figure 3 is shown UV Visible spectrum of H₃PO₄ doped DL-PLA/PANI Composite. PANI–ES shows mainly two type of electronic transitions *i.e.*, π – π ^{*} and polaron transitions, respectively within the range of 250–1000 nm of UV Visible spectrum [19].

There is no such transitions are found in DL–PLA film [19]. This indicates the absence of conducting sites in DL–PLA film. Both π – π ^{*}, and polaron band types transitions were found in H₃PO₄ doped PANI salt film. This indicates the oxidation form of aniline [19].

The H_3PO_4 doped DL-PLA/PANI-ES composite was prepared for testing the CH₄ gas in different concentrations and balanced with synthetic air. During this gas sensing testing, the different gas concentrations (50 ppm, 100 ppm, 200 ppm, and 500 ppm) are used.



Figure 3. UV-Visible spectrum of H3PO4 doped DL–PLA/PANI composite [19]

The sensing measurement is operated at room temperature. Some have reported that PANI polymeric nanofibers are a well-known sensing material for hydrocarbon gases such as CH₄, H₂ [19, 20]. H₃PO₄ doped DL-PLA/PANI-ES composite is employed for sensor performance against a well-known polymer system.

Fig. 4 shows the dynamic responses of methane gas using H_3PO4 doped DL-PLA/PANI sensor material as film. The sensor response is recorded typical resistance transients of the tested materials. From the **Fig. 4**, it is the clear that the test gas *i.e.*, CH₄ gas is on, the resistance of sensor materials is decreased. During the recovery (*i.e.*, when the synthetic air is on), the resistance is increased. This means that the base resistance is regained. The percentage of response is assessed at room temperature using the expression

Re sponse (%) =
$$\frac{R_a - R_g}{R_a} \times 100$$

Here, (R_a) and (R_g) are the sensor resistance, which is measured by the exposure of air and test gas respectively. Using the above expression, the percentage of response (%) was estimated to be 0.00288 %, 0.4255 %, 3.5 % and 9 % for 50 ppm, 100 ppm, 250 ppm and 500 ppm concentration of methane, respectively. Minimal base-line is drifted, which is indicated in the Figure 4. It is observed when the sensing element is switched back and forth between air and test gas environment. In addition, the base line is found to be shifted downward as indicated in Fig. 4 and 5. From the Figure 4 and 5, it clears that the % response increases with the increase in CH₄ gas concentration. Also, it is found to be non-linear in nature [20- 22]. The resistance change in sensor materials is due to the interaction between the used materials surface

and CH₄ gas molecules [23,24]. The highest resistance is found to be 1.174 K Ω at 500 ppm CH₄ gases. Also, the lowest resistance is measured to be 0.0384 K Ω at 50 ppm CH₄ gases. It is believed that the smaller number of methane gas (*i.e.*, at 50 ppm) molecules are expected to interact with prepared sensor materials surface *i.e.*, PANI surface. It results poor response, *i.e.*, small change in the resistance [25].

During the exposure to 50 ppm of CH₄ gas balanced in synthetic air, the prepared sensor responded negligibly (0.00288 %). Different concentration exposers, *i.e.*, 50 ppm to 100 ppm, 250 ppm, and 500 ppm of CH₄ gas, the sensor materials response differently. J. D. Fowler et al. [26] suggested that the chemically absorbed H₂ gas molecules can react with oxygen molecule, which is present in the environment to form H₂O. They also exposed that the occurrence of H₂O molecules ruins the ability of PANI to sense CH₄ gas analytes. Presence of H₂O molecules in the sensing environment, it might also deteriorate the polyaniline-based sensor materials at high CH₄ gas concentrations (**Fig. 4 and 5**). This is due to the existence of 21 % oxygen in used synthetic air. Also, it was noticed that the diameter of the polyaniline nanofibers has a direct effect on their sensing performance [23].

CH₄ is a reducing gas. The interactions with the sensing materials are largely governed by the chemical properties of each material. CH₄ gas sensing mechanism for polyaniline-based sensor materials is still not understood. Chemisorption may occur between CH₄ gas molecules and the charged amine nitrogen sites of the polyaniline chain. The dissociation of the CH₄ bond leads to the formation of new N-H bonds with the amine nitrogen in the polyaniline chain. Consequently, the charge transfer between neighbouring nitrogen atom of amine. This signifies the polaronic form of polyaniline, *i.e.*, called doped state of polyaniline. After removal of the methane gas from the gas source, synthetic air expose to the sensor materials (contained polyaniline chains).



Figure 4: The resistance transient of H₃PO₄ doped DL-PLA/PANI-ES composite film measured at various CH₄ gas concentrations (ppm) in ambient condition [19]



Figure 5: The % response with different concentration of H3PO4 doped DL-PLA/PANI-ES composite [19]

It is a completely reversible reaction [21]. The doped state of polyaniline is the highest conducting state and hence, conductivity is more. Therefore, during the exposure of test gas, the PANI film resistance is decreased (as observed from **Fig.4 and 5**). The methane gas molecules diffuse more because the polyaniline nanofibers provide more surface area for gas diffusion. PANI nanofibers have been observed in SEM image, which is presented in **Figure 1**. Therefore, the charged amine nitrogen sites on the PANI backbone are largely accessible to CH_4 gas molecules resulting in the dominant PANI CH₄ gas sensing mechanism.

Conclusions

 H_3PO_4 doped DL–PLA/PANI-ES composite have successfully prepared by chemical-oxidation polymerization process. We have investigated the CH₄ gas sensing performance at room temperature of H_3PO_4 doped DL–PLA/PANI-ES composite. We have found that the H_3PO_4 doped DL-PLA/PANI-ES composite based gas sensor response (%) is 9 % at 500 ppm of CH₄ gas. The response (%) was calculated to be 0.00288 %, 0.4255 %, 3.5 % and 9 % for 50 ppm, 100 ppm, 250 ppm and 500 ppm concentration of methane, respectively.

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References

- Borowski, W. S. 2004, A Review of Methane and Gas Hydrates in the Dynamic, Stratified System of the Blake Ridge Region, Offshore Southeastern North America, Chemical Geology, Vol. 205 pp. 311-346.
- [2] Jun, J. H., Yun, J., Cho, K., Hwang, I.-S., Lee, J.-H., and Kim, S. 2009, Necked ZnO Nanoparticles-based NO₂ Sensors with High and Fast Response, Sensors and Actuators B, Vol. 140, pp. 412-417.
- [3] Barazzouk, S., Tandon, R. P., and Hotchandani, S. 2006, MoO₃-based Sensor for NO, NO₂ and CH₄ Detection, Sensors and Actuators B, Vol. 119, pp. 691-694.
- [4] Xi, L., Qian, D., Tang, X., and Chen, C. 2008, High Surface Area SnO₂ Nanoparticles: Synthesis and Gas Sensing Properties, Materials Chemistry and Physics, Vol. 108, pp. 232-236.
- [5] Hu, P., Du, G., Zhou, W., Cui, J., Lin, J., Liu, H., Liu, D., Wang, J., and Chen, S. 2010, Enhancement of Ethanol Vapor Sensing of TiO₂ Nanobelts by Surface Engineering, Applied Materials & Interface, Vol. 2, pp. 3263-3269.
- [6] Fidelus, J.D., Lojkowski, W., Millers, D., Grigorjeva, L., Smits, K., and Piticescu, R. R. 2007, Zirconia Based Nanomaterials for Oxygen Sensors-Generation, Characterisation and Optical Properties, Solid State Phenomena, Vol. 128, pp. 141-150.
- [7] Satyanarayana, L., Reddy, C.V.G., Manorama, S. V., and Rao, V. J. 1998, Liquid– Petroleum-Gas Sensor Based on a Spinel Semiconductor, ZnGa₂O₄, Sensors and Actuators B Vol. 46, pp. 1-7.
- [8] Macdiarmid, A.G., Chiang, J.C., Richter, A.F., and Epstein, A.J. 1987, Polyaniline: a New Concept in Conducting Polymers, Synthetic Metals, Vol. 18, pp. 285-290.
- [9] Focke, W.W., Wnek, G.E., and Wei, Y. 1987, Influence of Oxidation State, pH, and Counter ion on the Conductivity of Polyaniline, Journal of Physical Chemistry, Vol. 91, pp. 5813-5818.
- [10] Omastova, M., Pavlinec, J., Pionteck, J., Simon, F., and Kosina, S. 1998, Chemical Preparation and Characterization of Conductive Poly (methyl methacrylate)/Polypyrrole Composites, Polymer, Vol. 39, pp. 6559-6566.
- [11] Singh, V., Mohan, S., Singh, G., Pandey, P. C., and Prakash, R. 2008, Synthesis and Characterization of Polyaniline-carboxylated PVC Composites: Application in Development of Ammonia Sensor, Sensors and Actuators B, Vol. 132, pp. 99-106.
- [12] Cairns, D. B., Armes, S. P., Chehimi, M. M., Perruchot, C., and Delamar, M.

1999, X-ray Photoelectron Spectroscopy Characterization of Submicrometer-Sized Polypyrrole-Polystyrene Composites, Langmuir, Vol. 15, pp. 8059-8066.

- [13] Njuguna, J., and Pielichowski, K. 2004, Review: Recent Developments in Polyurethane-based Conducting Composites, Journal of Materials Science, Vol. 39, pp. 4081-4094.
- [14] Peng Wang, P., Tan, K.L., Zhang, F., Kang, E.T., and Neoh, K.G. 2001, Synthesis and Characterization of Poly (ethylene glycol)-Grafted Polyaniline, Chemistry of Materials, Vol. 13, pp. 581-587.
- [15] Chen, Y., Kang, E.T., Neoh, K.G., and Tan, K.L. 2000, Chemical Modification of Polyaniline Powders by Surface Graft Co-polymerization, Polymer, Vol. 41, pp. 3279-3287.
- [16] Yoon, J.T., Lee, S.C., and Jeong, Y.G. 2010, Effects of Grafted Chain Length on Mechanical and Electrical Properties of Nanocomposites Containing Polylactide-grafted Carbon Nanotubes, Composites Science and Technology, Vol. 70, pp. 776-782.
- [17] Yang, J., Wang, X., Wang, X., Jia, R., and Huang, J. 2010, Preparation of Highly Conductive CNTs/Polyaniline Composites Through Plasma Pretreating and *in situ* Polymerization, Journal of Physics and Chemistry of Solids, Vol. 71, pp. 448-452.
- [18] Lee, Y.K., Lee, K.J., Kim, D. S., Lee, D.J., and Kim, J.Y. 2010, Polypyrrolecarbon Nanotube Composite Films Synthesized Through Gas-phase Polymerization, Synthetic Metals, Vol. 160, pp. 814-818.
- Panigrahi, M, Majumdar, S.B, and Adhikari, B. 2011, H₃PO₄-doped DL-PLA/PANI composite for Methane gas sensing, IEEE explorer, Vol. 97, pp. 1–7 (ISBN No.= 978-1-4577-2035-2, 8-10 Dec. 2011, Nanoscience, Technology and Societal Implications (NSTSI), 2011 International Conference)
- [20] Wu, Z., Chen, X., Zhu, S., Zhou, Z., Yao, Y., Quan, W., and Liu, B. 2013, Room Temperature Methane Sensor Based on Graphene Nanosheets/Polyaniline Nanocomposite Thin Film, IEEE Sensors Journal, Vol. 13, pp. 777-782.
- [21] Al-Mashat, L., Shin, K., Kalantar-zadeh, K., Plessis, J. D., Han, S. H., Kojima, R. W., Kaner, R. B., Li, D., Gou, X., Ippolito, S. J., and Wlodarski, W. 2010, Graphene/ Polyaniline Nanocomposite for Hydrogen Sensing, Journal of Physical Chemistry C, Vol. 114, pp. 16168-16173.
- [22] Lu, G., Ocola, L. E., Chen, J. 2009, Reduced Graphene Oxide for Roomtemperature Gas Sensors, Nanotechnology, Vol. 20 pp. 445502-445511.
- [23] Fowler, J. D., Allen, M. J., Tung, V. C., Yang, Y., Kaner, R. B., and Weiller,

B. H. 2009, Practical Chemical Sensors from Chemically Derived Graphene, ACS Nano, Vol. 3, pp. 301-306.

- [24] Virji, S., Kaner, R. B., and Weiller, B. H. 2006, Hydrogen Sensors Based on Conductivity Changes in Polyaniline Nanofibers, Journal of Physical Chemistry B, Vol. 110, pp. 22266-22270.
- [25] Fowler, J. D., Virji, S., Kaner, R. B., and Weiller, B. H. 2009, Hydrogen Detection by Polyaniline Nanofibers on Gold and Platinum Electrodes, Journal of Physical Chemistry C, Vol. 113, pp. 6444-6449.
- [26] Sadek, A. Z., Baker, C. O., Powell, D. A., Wlodarski, W., Kaner, R. B., Kalantar-zadeh, K. 2007, Polyaniline Nanofiber Based Conductometri Acoustic Wave Gas Sensors-effect of Nanofiber Diameter on H₂ Response, Journal of IEEE Sensor, Vol. 7, pp. 213-218.