Sensing of Picric acid through fluorescence studies of PANI-IPN film

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Abstract

An interpenetrating polymer network (IPN) film for sensing of Picric acid (PA) is prepared by chemical assembly of polyaniline-polyvinyl alcohol (PANI-PVA) film by casting on a glass substrate. The prepared IPN film is employed for the detection of a representative nitroaromatic compound (NAC), in the present case, (PA), for both in solution and in vapor phase of the analyte. This molecular design combines the advantages of IPN film based on single layer chemistry and the signal amplifications as effective way to create novel sensing film for the detection of NACs and other high energy materials (HEMs). Significant static fluorescence quenching was observed for the IPN films within a few seconds of treating with PA solutions. The vapour phase detection of PA was observed on IPN films with good response times. Almost linear increase in the sensitivity calculation obtained through the electrical resistivity measurements within 30.0 min is observed. The structural study of the IPN films before and after treatment with PA is studied employing FTIR spectrometer and stereozoom microscope. Fluorescence quenching experiments on the IPN films showed that these films can be efficiently reused for two successive cycles. The electrical resistivity studies showed the film to sustain the vapour phase detection for a single measurement. The fluorescence studies and the electrical resistivity studies showed that the films are potential candidates for detection of PA vapours.

Keywords: PANI-IPN film, Fluorescence, FTIR, Morphology, Sensing behavior.

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1. Introduction

The unique behaviors of conducting polymer are used for various electrical and electronic devices[1]. Conducting polymers (CPs) in the form of molecular wires have received more attention in the field of nanotechnology due to its similarity in metal like conductivity [2]. Multi functionality of nanostructured conducting polymer is very essential in nano technological applications (NEMS). The electromagnetical functionality of nanostructured conducting polymer has increased attention due to its optical, electromagnetic interference shielding, and making the of electro-chronic and sensing devices [3,4]. From the synthetic point of view the IPN can be in two varieties first a sequential IPN in which one network is swollen and another one is polymerized in the presence of it [5], whereas second is a simultaneous IPN in which both of the network precursors are synthesized at the same time through independent and non-interfering routes [6].

Trace detection of nitroaromatic compounds is of major importance for finding hidden explosive materials also known as HEMs. The need for detection becomes even more important as the HEMs are nonvolatile, and all the HEMs possess electron withdrawing nitro groups. Until now sniffers using advanced materials viz., carbon nanotubes and nanocomposites are being tested for their applicability [7-9]. Synthesis of these advanced materials and using them in devices is a hard task. While some aspects may be addressed through the use of advanced instrumentation viz., LCMS, 3D X-rays, the design of robust, sensitive and discriminating sensing materials remains an emerging frontier area of intense research [7].

While sniffer dogs are doing commendable service, they suffer from some inherent reasons, which include their ability to distinguish between different HEMs, periodic health problems and tiredness after sensing from sometime [7]. To overcome these difficulties, CPs, gated hybrid materials and organic molecules are being periodically tested [8-13]. CPs offers a countless opportunities to interact with the analyte receptor molecules to act as transducer. The IPN film has shown the fluorescence and the electron withdrawing groups like nitroaromatics can absorb the exciton from the fluorophore. The earlier reports on MEH-PPV, DP10-PPV, BuPA, fluoranthenene based dyes and some other conjugated polymers have also shown the same behavior [10, 12, 14]. The PANI-PVA IPN films are much easier to synthesize and the results themselves show its usability. It is a prototype which can detect PA a very basic nitroaromatic explosive. Some of the CPs and functionalized CPs that are successfully tested through fluorescence quenching include polyethersulfone, polysilanes, polyphenyl acetylenes, diketopropyrrrole based polymers, SnO2-PANI hetero structures etc. Catherine et al. [14], have reported that a structural disorder plays a critical role in controlling the charge carrier mobility and thereby confirmed the role of torsional angle in diketo polypropyle based CPs in the detection of NACs. Swager way back in 1995 [15] used the term energy migration in conjugated polymers (also other term for CPs) and ligand functionalised CPs, for the quick response of fluorescence signals. An excellent review by Swager et al. [8] clearly classified the types of polymers and the reasons for their sensibility towards HEMs. Swager et al. [8, 15, 21] clearly explains the principle of amplified response due to the energy efficient migration to occupied receptor sites. Gokcen et al. [16] have discussed a very fast detection of DNT and TNT employing polyethersulphone. The authors [16] have clearly explained the π stacking present in the thin films of CPs employed.

Some of the very interesting and exotic organic molecules viz., fluoranthenene and fluoranthenene based fluorescent based chemosensors for the detection of NACs are investigated by Satish patil et al. [10], Ankit et al. [17] have employed electron rich triphenylene based sensors for trace detection of PA in solid, liquid and contact modes. They also employed to ethyl mienies to increase the π stacking and obtained high sensitivity. A possible mechanism is proposed based on the combined effect of ground state charge transfer complex formation and resonance energy transfer between sensor and the analyte. They confirmed their studies on the basis of Critical X-ray diffraction studies.

Ramon et al in their pioneering work [9, 11, 18-20] of gated materials employing functional hybrid materials for the optical recognition of NACs explains critically on the supramolecular interactions. The authors in their critical review on Optical chemosensors and reagents to detect HEMs, explain the role of hybrid materials and the efficiency of detection of NACs to the trace level. It is understood from their work, that gated hybrid materials will form one of the highly promising materials in future for the detection of NACs and identifications of many of the HEMs at trace levels.

The sensitivity towards the detection of trace quantities of nitro groups comes from the phenomenon inherently possessed by conducting polymer called signal amplification effect [8] The backbone of these CPs act as a molecular wire, enabling the rapid propagation of an excitation thought the individual polymer chain [8].This highly distinct property of CP takes over head with any other materials available to date, that act as chemosensors [8]. However to the knowledge of the authors, a comprehensive report on another important CP viz., conducting form...
of PANI and its analogues is not available for the trace detection of NACs, though PANI shows excellent fluorescence behavior. Some reports on PANI and its composites in the detection of liquefied petroleum gas (LPG), NH₃ and many other hazardous gases [22, 25] are available. However PANI and its analogues suffer from solubility effect, which is an essential condition needed for the formation of PANI films. Considering the importance of CPs in the detection of NACs and the difficulty encountered by PANI and its analogs for casting as films, we undertook the present work. In this report we present a novel way to employ PANI in the form of IPN films for the sensing of PA. The present study involved casting PANI-PVA IPN films and presents them as potential candidates for sensing NACs in liquid and vapour state of the analyte. The IPN film is characterized by employing structural techniques. All the HEMs have nitro group which are electron withdrawing, fluorescence quenching may be allowed when compounds contains these groups interact with CPs which are known to possess excess of electron which can donate electron forming an exciplex complex. The possible interaction of PA with PANI-PVA IPN is pictorially represented below. Figure 2, shows the interaction of PA with the π-π stacking bond of PANI. The electron migration in the PANI chain gets absorbed by the electro deficient oxygen atom of the PA moiety. The resonance in the nitro groups in the PA structure thus stabilizes the electron, thus forming an exciplex complex and leading to drastic fluorescence quenching.

2. Experimental

2.1 Synthesis of polyaniline-PVA IPN film

Aniline, ammonium persulphate (APS), benzene, hydrochloric acid (HCl), polyvinyl alcohol (PVA) and methanol was commercially procured and employed in the study. In situ doping polymerization method is adopted for the synthesis in the presence of HCl as dopant, solvent were double distilled before use. The synthesis process is as follows: 2% of aniline monomer is dissolved in 5 ml of benzene and is polymerized in the 10% aqueous solution of PVA in the presence of aqueous acidic HCl solution as dopant and ammonium persulphate as an oxidizing agent at room temperature. This resulted in the absorption of aniline monomer within the crossed linked PVA matrix forming an interpenetrating polymer network (IPN) within a few minutes after the addition of APS the solution becomes dark green color indicating the beginning of polymerization. The solution is then kept for overnight for complete polymerization in a vacuum desicator. The film was prepared by casting method by spreading the final solution on the glass substrate and dried in air, then the film was washed with methanol and air dried.

2.2 Characterization

Further the film was characterized through spectroscopic techniques (FTIR and Fluorescence), Sensing, and electrical conductivity measurement and morphology (stereozoom microscope). The IPN films showed excellent stability towards moisture, aqueous and organic solvent, without any swelling or deformations or change in dimensions even after repeated soaking in these solvents for more than ten hours.

5.0 ppm PA was prepared from Analar grade PA using methanol and is studied for the fluorescence quenching study and sensitivity study. (Note: Below this concentration it is not detected with the said conditions).

3 Results and Discussions

3.1 Characterization techniques

FTIR Studies was undertaken employing Thermo Fisher ATR Nicolet model using diamond (iSS) in the range 4000-400 cm⁻¹. Fluorescence studies were carried out using Spectrofluorometer (ELICO SL 174). The 1 cm² film with thickness of 0.4 μ was used for the measurement. Sensing properties are studied using sensor setup connected to Keithely high precision multimeter. All the above said studies of PANI-IPN film were carried out before and after exposure to PA vapors.

3.2 FTIR studies

Figure 1a is the FTIR spectrum of the IPN film. This spectrum has major peaks associated with PANI. The band observed at 3210 cm⁻¹ is due to the νOH strong stretching of the PVA. The high intensity bands at 1596 cm⁻¹ and 1463 cm⁻¹ is due to the presence of benzenoid ring and quinoid ring respectively and a peak observed at 1052 cm⁻¹ is due to the B-NH = Q vibration. Figure 1b is FTIR spectrum of the IPN film on exposure to PA vapors. The broad intensity peak observed at 3210 cm⁻¹ indicates the stretching of νOH band, the peaks observed from 1304 cm⁻¹ to 1545 cm⁻¹ is strong and belongs to the stretching frequency of the nitro group of the PA sensed by the film, thus confirming the exciplex formation due to fluorescence quenching. The electron withdrawing group from PA may have absorbed the electron transfer within the chain of PANI, which resulted in the lowering the intensity of the 1052 cm⁻¹ peak in figure 1b.


3.4 Stereozoom microscopy

Optical image of the IPN film before and after exposure to PA vapours obtained from stereozoom microscope are shown in figure 3(a) and (b). These films are obtained from the sensitivity studies stated below. The images are taken at the zoom of 200 X. figure 3(a) shows film is smooth and possessing chemical homogeneity, whereas the figure 3(b) shows chemical heterogeneity on the surface of the film due to the presence of nitro group. The physical nature of the film also got disturbed with the presence of concentric rings on the surface. These rings which are chemically different from the film are understood to be caused by nitro moieties. The texture of the film is seen to possess cracks. Thus the optical images help in understanding the surface morphology of the films prior to and after sensing.

Figure 3: a. Optical images of PANI-PVA IPN film before exposed to PA. b. Optical images of PANI-PVA IPN film after exposed to PA

3.5 Recycling studies

Reusability or recycling studies for films are essential to know their suitability for device fabrication. For more cheaper and economic devices, the films have to be found suitable for reuse. The films have to retain their chemical and mechanical sturdily, while retaining their morphology, and response times, along with the temperature of measurement, on repeated uses. In addition to these characteristic features the films also should necessarily retain the same emission frequency. In the present investigation, we report the reusability studies of the IPN films. Once quenching occurs, the films have to regain their fluorescence before testing their efficiency for reuse. This is done through washing the films in alcohol.

Figure 5 shows the fluorescence recycling studies of IPN film on repeated exposure to the saturated PA vapors.

Figure 5: Time dependent quenching studies

IPN film (FL-1) is first exposed to PA vapors at room temperature for a few seconds and the fluorescence emission was measured; FL-2, as expected showed fluorescence quenching due to saturated PA vapors exposure. The FL-2 was then given alcohol washings to remove the electron withdrawing nitro groups bonded on to the film and later the film is air dried. The fluorescence is measured again for this film (FL-3). The film FL-3 was found to show almost a similar value of intensity, thus indicating its suitability for the second run. Film FL-3 is then subjected to PA vapours, and within a few seconds showed similar quenching (FL-4) as that of film FL-2. The film FL-4 was then washed with alcohol and air dried for its reusability for the third run. The film FL-5 show much decrease in fluorescence intensity and upon exposure to PA vapours show a very marginal quenching (FL-6). We looked into the morphology changes (not represented here), and noticed that, the film FL-6 had deformed in shape with visible cracks and tear on the surface. From this experiment we understand that our IPN films possess ability and suitability for second reuse in sensing of PA vapours. Figure 4 shows the reusability studies of IPN film exposure to saturated PA vapors.

Figure 4: Reusability studies of IPN film exposed to saturated PA vapors

(IPNPA= PANI-PVA IPN film exposed to PA)
(IPNPA after washing= PANI-PVA IPN film exposed to PA then washed with alcohol)

3.6 Resistivity sensing studies

Generally device manufacturing involves sensing through the changes observed in resistance of the analytes. Electrical resistivity measurements are performed on the films employing a high precision setup. The dimensions of the film(s)
employed were 1.0 cm², and having a thickness of 0.4 μ. The film is placed in a sensor setup chamber (not shown) which is connected to Keithley high precision multimeter. Saturated PA vapors were supplied in sensor chamber through vacuum condenser using an adaptor. The PA vapors were supplied for 30.0 min. The resistance of the sample is continuously measured. The observed incremental increase in resistance values are noted for every 5 min interval and are shown in figure 5 as sensitivity vs time. From the resistance to sensitivity values conversion to sensitivity is calculated as shown in equation 1 and 2, below:

\[ \rho = \frac{RA}{l} \]  
\[ %S = \frac{R_{pm} - R_{rs}}{R_{rs}} \times 100 \]  

Where \( \rho \) is the resistivity of the sample, \( R \) is the resistance, \( A \) is the cross sectional area, \( l \) is the length of the sample, \( S \) is the sensitivity, \( R_{pm} \) is the resistance of the PA vapours and \( R_{rs} \) is the resistance of the \( N_2 \) gas which is purged.

The increase in resistivity is very slow in the very beginning (up to 10.0 min), and thereafter increases fast (up to 20 min). After this the increase in resistivity is linear, and around 50.0 min saturation is reached. A significant increase in %S from 0.2 to 0.55 is reached in 30 min.indicating that the IPN films are also potential materials for device application when sensitivity is a quantity for measure.

4 Conclusion

In the present investigation, the PANI-PVA IPN film as potential material for sensing of hazardous vapours viz., PA vapours is established employing two different techniques viz., the fluorescence technique and the electrical resistivity measurement. The fluorescence study has conclusively found to be a good technique in terms of response time, stability of the film, and its reusable for a minimum of two successive runs. The electrical resistivity technique showed promising results, with a significant increase in sensitivity values, but required longer response times. PA did not decompose during vapourisation because the temperature applied is 80°C. Decomposition of PA will not start below 163°C at said conditions [26]. As the morphology of the film showed permanent damage, the film was not further studied for reusability. The detection/sensing of other explosives like TNT, HNS, DNOC, nitrobenzenes using fluorescence technique and the electrical resistivity technique showed sensitivity is a quantity for device application when sensitivity is a quantity for measure.

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