

Bile salt incorporated polypyrrole thin film for ethanol sensing

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Polypyrrole (PPy)-bile salt composite was used for sensing ethanol vapor. PPy was synthesized by interface polymerization for subsequent fabrication of thin film of its composite with bile salt, by in-situ co-dispersion method and then exposed to ethanol vapour. Sensing was visualized through changes in morphological, structural and optical characterizations. The ethanol exposed film showed larger agglomeration as revealed in its surface morphology on scanning electron microscope (SEM) and greater crystallinity as seen through X-Ray diffraction (XRD). Fourier transform infra red (FTIR) and nuclear magnetic resonance spectroscopy (NMR) of the ethanol incorporated film also gave signature of the presence of bile salt and alcohol. Alcohol incorporation pattern resulted in increase in electrical conductance from 7.08539×10^{-5} mA/V to 8.0356×10^{-5} mA/V, as determined from current voltage characterizations. Average molecular weight (M_n) obtained from gel permeation chromatography changed from 6160 to 10300 on ethanol intake. Photoluminescence (PL) intensity was quenched and the PL peak shifted from 430 to 409 nm on ethanol exposure. Changes in morphological, structural, optical and electrical properties of the composite on ethanol exposure showed its prospective application for sensing ethanol.

Keywords: Polypyrrole, Bile salt, Composite, Sensing, Ethanol

Conducting polymers (CPs) possess significant electrical conductivity, which makes them suitable for use in electronic devices, functional electrodes, electrochromic appliances, sensing technology and other novel applications¹. Because of their unique electrochemical properties, CPs have attracted considerable interest in the development of chemical sensors and biosensors². CP has a planar structure with delocalized π -electron density both above and below the molecular chain³. This configuration facilitates entrapment of biomolecules in its main chain by means of cross-linking⁵, thus often used to immobilize biomolecules for fabrication of biosensor⁴, which is an integrated electronic device used for sensing, and made up of some biological material coupled with a transducer⁵.

Immobilization of a biomaterial on a CP also increases its functional stability⁶, though usually decreases its activity. Polypyrrole (PPy) is an

important class of CP which has been extensively used for its environmental stability and ease of fabrication, in addition to other novel properties⁷. Depending on their fabrication techniques, CP composites are found to take part in exchange of charge carriers with a material in gaseous state in contact and the changing pattern of charge distribution results in changing of electrical resistance of the CP⁸. These changes can be effectively used for sensing the gas or vapour in contact.

Fixation of an enzyme on a CP matrix by membrane confinement increases the electrical and mechanical properties of the latter⁹. Being highly effective and specific under ambient conditions, the enzymes are generally used biological catalysts that enhance the rate of reaction by lowering the energy of activation. Though they are mostly stable at low temperatures and neutral pH, their stability can be easily disturbed by external pressure and temperature, extreme pH, organic solvents, freezing, drying and by oxidative chelating or denaturing agent¹⁰. However, these problems of enzyme immobilization in external environment can be reduced with their derivatives. Choline oxidase (ChOX), a derivative of cholic acid is such an enzyme which shows sensing properties when immobilized in a CP matrix¹¹. In this study, bile salt, another derivative of cholic acid has been used

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Abbreviations: ChOx, choline oxidase; CP, conducting polymer; FTIR, Fourier transform infra red; GPC, gel permeative chromatography; NMR, nuclear magnetic resonance; PL, photoluminescence; PPy, polypyrrole; SEM, scanning electron microscope; XRD, X-Ray diffraction.

as a substitute of ChOX. It is a naturally occurring derivative found in liver and gallbladder of animals. Several methods have been used for immobilization of biomolecule in a transducer⁹⁻¹².

In this study, we have used the method of entrapment for fabrication of thin films of PPy and its bile salt composite, which have been subsequently characterized for any change in their morphological, optical and electrical properties after exposure to ethanol.

Materials and Methods

Pyrrole was obtained from Renkhem Ranbaxy (New Delhi, India) and FeCl₃ and HCl from E. Merck (India), while bile salt purchased from Fisher Scientific (India) were used. Pyrrole was repeatedly distilled under vacuum, while other materials were used without further purification prior to use, because of their high purity. De-ionized water was used as solvent.

Fabrication techniques

Polypyrrole (PPy) was prepared by interface polymerization method using toluene-water interface, by taking 1 M pyrrole in toluene and 1 M FeCl₃ in aqueous solution of 1 M HCl^{13,14}. PPy membrane formed at the interface was immediately taken out, dried and repeatedly washed with deionized water and methanol to remove any unreacted oxidant and oligomers and then dried again. PPy-bile salt composite was prepared by dispersing the dried PPy in an aqueous solution of bile salt. The ratio of bile salt to PPy was kept at weight proportion of 1:10. The resultant solution was then subjected to magnetic stirring at room temperature. Thin film of the composite was casted on glass substrate by spin casting the resultant dispersion which was dried under dynamic vacuum afterwards.

Characterization

The surface morphology of the films was studied by scanning electron microscope (SEM) in FESEM (JEOL LA 6380, Japan). XRD was carried out in X-Part pro-diffraction 1830 X-Ray Diffractometer and fourier transform infra red (FTIR) in SHIMADZU FTIR Affinity1. Gel permeation chromatography (GPC) was performed in Waters 2414 RI detector (Model1515) with tetrahydrofuran (THF) standard column. Room temperature photoluminescence (PL) spectra were taken in an F-2500 FL spectrometer with excitation wavelength

of 350 nm. Nuclear magnetic resonance (NMR) was obtained in an NMR spectrometer Bruker 400.

The conductivity was determined by current-voltage (I-V) measurements in the voltage range of -20 to +20 V using Keithley Sourcemeter (Model 2400). Configuration of electrode attachment was that of a two probe method. This was facilitated by attaching two fine copper wire contacts on the surface of the films by means of silver paste. These were fed to source meter for voltage supply and current measurement.

Results

Figure 1 shows the SEM image of the unexposed Ppy-bile salt composite (a) and that of ethanol exposed one (b). These showed microstructured particles, indicating characteristic bulk phase of the materials. Both the films showed agglomeration of particles, which was more significant in the ethanol exposed one. The results suggested binding of bile salt to the PPy chain, leading to a 'microstructure' and the effect was more prominent in the ethanol exposed one¹⁵.

The molecular structure of PPy-bile salt composites were studied using FTIR spectroscopy. These spectra are shown in Fig. 2. It was found that in addition to the characteristic PPy bands in the region of 2500-3400 cm⁻¹, there were additional bands at 1400, 726 and 474 cm⁻¹, indicating the presence of C-N, =C-H

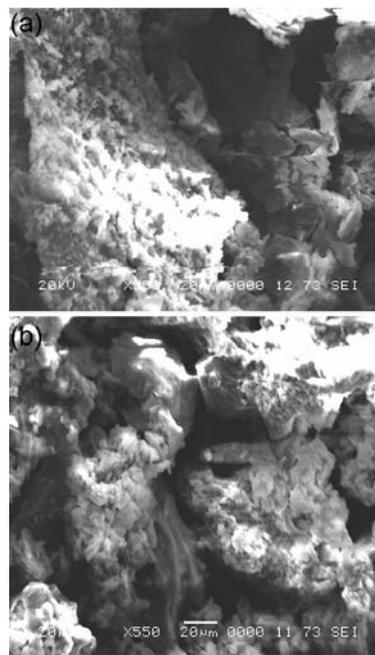


Fig. 1—SEM images of the pure (a) and ethanol treated (b) films

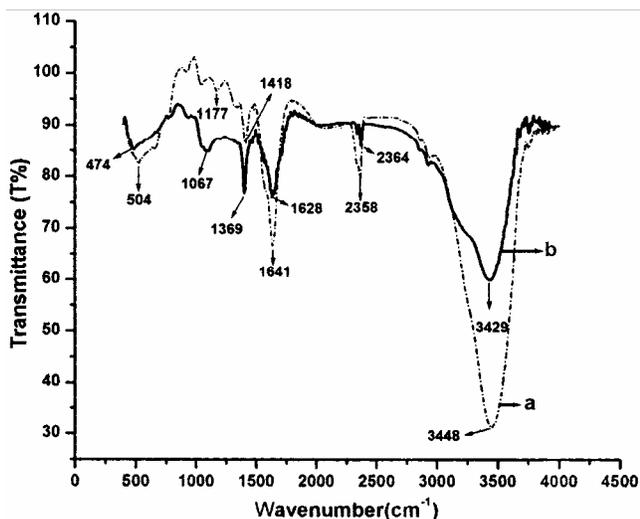


Fig. 2—FTIR spectra of pure (a) and ethanol treated (b) composite films

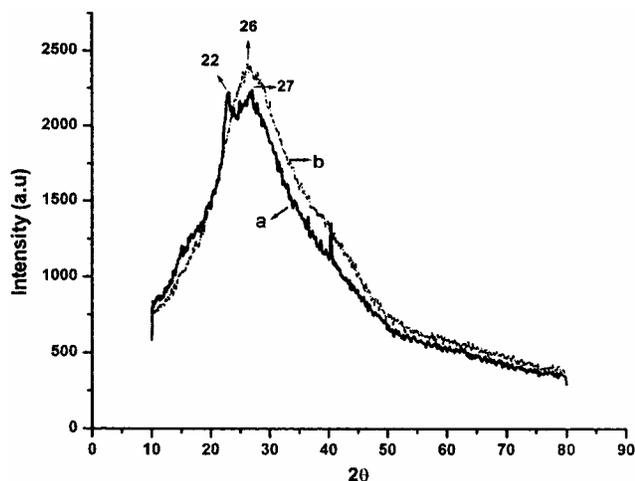


Fig. 3—XRD spectra of pure (a) and ethanol treated (b) composite films

and carboxylic/amino groups, respectively¹⁶⁻¹⁸. On ethanol exposure, overall decrease in intensity was observed, compared to the bands of untreated one with nominal shifts in the peak positions.

To observe the possible structural changes on ethanol exposure, XRD studies of the films were carried out and the results are shown in Fig. 3. The XRD pattern for untreated composite film gave peaks at 22° and 27° , indicating the partial amorphous nature of the composite^{19,20}. The twin peaks merged, when the film was exposed to ethanol and a single sharper peak appeared at $2\theta = 26^\circ$. At this point it may be inferred that a structural rearrangement leading to increased crystallinity had occurred in the molecular level of the composite on its exposure to ethanol²¹.

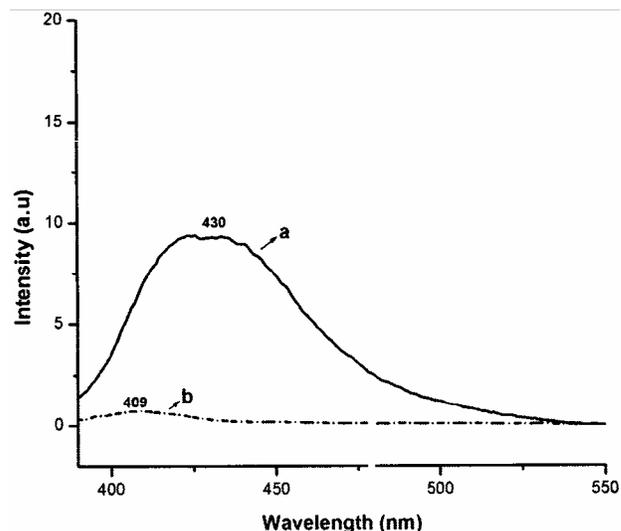


Fig. 4—PL spectra of the pure (a) and ethanol treated (b) PPy-bile salt composite films

Photoluminescence (PL) peaks of the films were studied in order to visualize any possible influence in its optical properties due to treatment with ethanol. The room temperature PL spectra for excitation wavelength of 350 nm clearly showed PL quenching in the ethanol exposed film (Fig. 4). This might be due to the fact that molecular binding of ethyl alcohol with the composite created some intermittent levels to hinder the pathway for luminescence.

To visualize the effect of sensing through electrical properties, we measured current-voltage (I-V) characteristics of both the types of films. The results depicted in Fig. 5 showed double non-linear behavior for both exposed and unexposed films. However, non-linearity was not very prominent and can be approximated to ohmic behavior. The measured values of slopes of the straight line portion of the two curves were respectively found to be 7.08539×10^{-5} mA/V for unexposed film and 8.0356×10^{-5} mA/V for the exposed one. Further, PPy composite with polyvinyl alcohol (PVA) has shown power law behavior for I-V (i.e. $I \propto V^n$)²². However, such behavior was not observed in our study. Bile salt acted as a secondary dopant, resulting in optimized band gap of PPy composite and changed its conductivity pattern. This might be due to the reason that pure PPy with randomly oriented microscopic particles and with weak linkage among the molecules resulted in relatively lower conductivity and non-ohmic behavior²³. But, the presence of bile salt in the composite functioning as secondary dopant helped it to acquire a granular structure, leading to improved

compactness of the latter²⁴. This compactness might further increase with its exposure to ethanol vapour, resulting in stronger coupling through the grain boundaries, ultimately increasing its conductivity and exhibiting near-ohmic nature in I-V.

Figure 6 shows the ¹H NMR spectra of both the films. The peak at 3.434 for the unexposed was found to be shifted to 3.676 for the ethanol exposed one, which might be due to additional spin-spin interaction of the latter²⁵. Thus, pyrrole ring

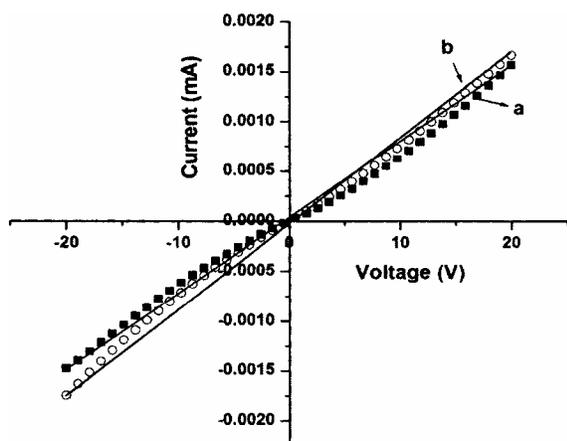


Fig. 5—I-V characteristics of the unexposed (a) and exposed (b) PPy-bile salt composite films

experienced a moderately high field shift on incorporation of bile salt, giving rise to chemical shift of the main pyrrole ring, which might undergo a significant structural change, when exposed to alcohol vapour²⁶.

Molecular weight, as determined by gel permeation chromatography increased on exposure to alcohol for both PPy and its composite; though this increase was marginal in PPy, it was significant in case of the composite, when exposed to ethanol. The number average molecular weight (M_n) of PPy-bile salt composite changed from 6160 to 10300 when exposed to ethanol, while its weight average molecular weight (M_w) was found to be increased from 6220 to 10940 on exposure to ethanol. FTIR and NMR analysis also showed changes in molecular structure of the composite which was further modified on ethanol exposure. Thus, the molecular weights obtained in the two states were in conformity with the FTIR and NMR analysis. Further, the observed poly dispersity index ($\frac{M_w}{M_n}$) of the composite was approximately found as unity, indicating that polymerization was completed in one phase which was confirmed by SEM micrographs also, showing similar granular sized particles in their surface morphology.

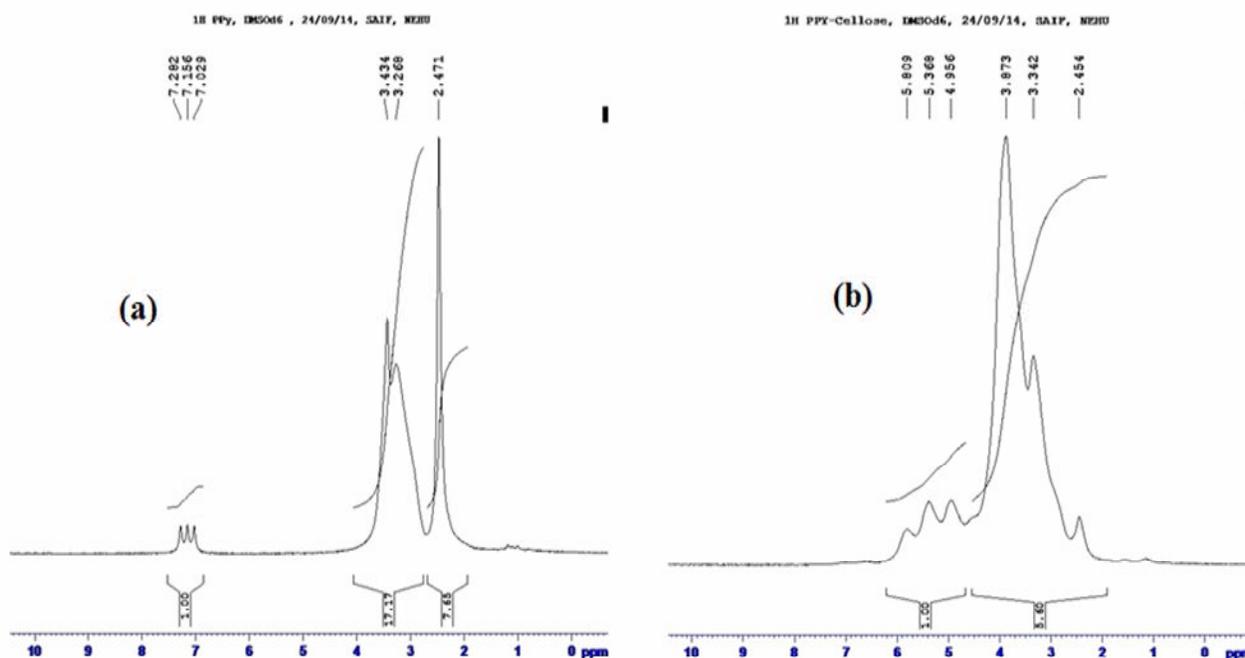


Fig. 6—NMR spectra untreated (a) and ethanol treated (b) composite films

Discussion

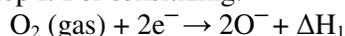
Electrical conductance of PPy on ethanol exposure was observed to be enhanced. Doping and dedoping in PPy is mainly facilitated through redox reaction in this type of CPs. Ethyl alcohol in contact with PPy acts as a dopant²⁷ and is responsible for modification of the electronic structure of PPy and additional intermittent energy levels are formed between its valence and conduction band, i.e., within the band gap, making the energy gap effectively narrower and subsequently rendering PPy behave like a semiconductor²⁸.

The change in electrical conduction of the composite was attributed to the modification of its surface charge configuration due to formation of polarons and bipolarons in the doped state, subsequent to ethanol exposure²⁹. In our experiment, bile salt PPy composite film was exposed to ethyl alcohol vapor for different exposure times of 30, 45, 60 and 90 s. Significant change in conductivity of the composite was observed for 45 s exposure in the operating voltage above -20 V due to increase in inter-chain conductivity³⁰. However, no change was observed in conductivity below 30 s, so the response time of the sensor was considered as 30 s.

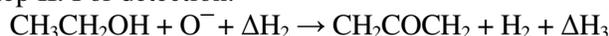
Mechanism of sensing

Mechanism of sensing from chemical point of view might be explained in two steps in the light of adsorption of ethyl alcohol (CH₃CH₂OH) over the surface of metal oxide based chemical sensor. The reaction sequence may be written as³¹,

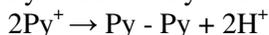
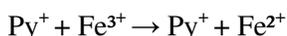
Step I: For sensitizing:



Step II: For detection:



In chemical polymerization of polypyrrole, Py is monomer and Py⁺ is the radical cation, which can dimerise with expulsion of H⁺ in presence of FeCl₃ which might take the form, such as



When the composite was exposed to ethyl alcohol vapour, the gas molecules reacted with O⁻ ions previously absorbed in the surface as shown in step II, releasing electrons, thereby increasing its conductivity, thus making it a prospective sensing material. The current-voltage (I-V) characteristic was ohmic in nature at a high voltage, when the catalytic

effect of bile salt was stimulated to break the bipolarons in the PPy composite, forming a layer of free electrons as surface charge layer and enhanced the conductivity of the material³².

Conclusion

Ethanol sensing of PPy-bile salt composite was tested using the morphological, structural, optical and electrical properties. SEM and FTIR results indicated incorporation of bile salt and alcohol in the composites. Incorporation of ethanol resulted in shifting of peaks for H-bonding in FTIR spectra due to exchange of active protons in OH and NH. Sensing was visualized by remarkable change in the XRD pattern, leading to merging of peaks and increase of crystallinity in the ethanol exposed film. The increase in relative molecular weight due to exposure of ethanol vapor on the composite supported the observations made in other characterizations on morphology and structural properties. PL spectra also showed the signature of sensing by significant inhibition of PL intensity in the treated film. Increase in conductivity at the operating voltage range of -20 to +20 V might cause enhancement of H⁺ ions formation in PPy-bile salt composite, where bile salt might be acting as a catalyst at that range of operating voltage. Bile salt being basic in nature with optimum pH 7-9, becomes electro active at that voltage and ethanol vapor acted as a promoter in its catalytic action of charge exchange. The results indicated potential application of the composite as a material for sensing of ethanol in vapor state.

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