Sensing element for detection of polar organic vapours on the base of polyaniline-composite – Effect of substrate surface area

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Abstract. Conductive polymer polyaniline (PANI) was synthesized by oxidative polymerization of aniline hydrochloride as a source of aniline and ammonium persulfate as an oxidation agent. The polymerization process is relatively easy and cheap. The reaction was carried out in presence of polymer substrate, in our case polyethylene terephthalate (PET) as a representative of smooth surface substrate and polyvinylidenfluoride (PVDF) nanofibers membrane as a representative of porous substrate. Both these substrates were covered by polyaniline (PANI) and used as a sensing element for organic vapors detection. The detection was made by measuring and the record of the change of resistivity during adsorption and desorption of saturated vapors. The result shows that sensitivity decreases with increasing polarity of chosen solvent in order N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc) and Dimethyl sulfoxide (DMSO). The PANI base sensing element on PVDF substrate improves sensitivity, selectivity and it also has good reversibility and repeatability.

1. Introduction

Conducting polymers were first discovered in 1976 by MacDiarmid, Shirakawa and Heeger [1]. Conducting polymers can be sorted into many categories according to their functional groups e.g. poly-acetylene, poly-pyrrole, poly-aniline. Polyaniline (PANI) is a member of conductive polymer family which is widely used. Polyaniline can be synthetized in three different types of oxidation states: leucoemeraldine, pernigraniline and emeraldine. Leucoemeraldine and pernigraniline show the insulating properties and emeraldine base, too. Emeraldine salt is a conductive polyaniline polymer. The basic site (imine and amine group) in the polymer backbone of the emeraldine base can be protonated with strong acid to produce emeraldine salt leading to the increase of conductivity due to the effect of charge transfer in the polymer backbone. Polyaniline in Emeraldine salt form has a unique behavior, including a wide range of electrical [2], electrochemical and optical properties [3], as well as good stability [4].

The changes of physicochemical properties of PANI occur in response to various external stimuli are used in various application e.g. Organic electrodes [5], actuators and sensors [6, 7]. Different membranes has been used to coat PANI and used sensors. We are using PET foil and PVDF membrane as substrate for PANI. Nickel-deposited PET membrane entwined with microbial pili-like poly(vinyl alcohol-co-ethylene) (PVA-co-PE) nanofibers are used for sensing alcohol [8]. Functionalization of track-etched PET membrane, selectively used for hydrogen purification [9]. PVDF membrane also used for sensing

purpose. Gold coated PVDF sandwich array are used for detection of ultratrace 2,4-dinitrotoluene (DNT) [10]. Assembly of multi-walled carbon nanotube/gold nanoparticle (CNT/AuNP) nanocomposites on PVDF membrane was used for Surface-enhanced Raman spectroscopy (SERS) [11]. Qiangxian Huang and co-workers used PVDF for Dynamic Micro Force Sensing Probe [12]. Functionalized track-etched PVDF membrane by poly-4-vinyl pyridine (P4VP) used for monitoring trace mercury in water [13]. With poly(aminophenylboronic acid), PVDF membrane used for sensing glucose [14].

The aim of this contribution is synthesis polyaniline emeraldine salt using aniline hydrochloride and ammonium persulfate. Two different kind of substrates are used. One is smooth PET foil and another is porous PVDF nanofiber membrane. Using two different substrates (PET foil and PVDF nanofibers membrane) for in situ polymerization. From the experimental data it is clearly indicates the PVDF membrane is more sensitive as compared to PET foil.

2. Experimental

The aniline hydrochloride (1.29 g, 10 mmol) was dissolved in 50 ml of distillated water. Another 50ml of distillated water was added to ammonium persulfate (APS) (1.56 g, 6.7 mmol). The solutions mentioned above were prepared separately. The solutions were transferred to the 150 ml beaker and mixed together to reach the polymerization mixture. The substrate was inserted in the reaction mixture. Then the solution was stirred at 500 rpm. The reaction was carried out at room temperature. The reaction mixture was left for 24 hours without disturbing. After that the membrane was removed, washed with distilled water for three times and dried in air room temperature. FTIR spectra of the PANI coated and uncoated PET and PVDF membrane were collected on the NICOLET 6700 FTIR Spectrophotometer using attenuated total reflectance ATR-FTIR. Scanning electron microscope Nova NanoSEM 450 (FEI) with Schottky field emission electron source operated at acceleration voltage ranging from 200 V to 30 kV was used for surface morphology. Further, the membrane was cut in small pieces and response was measured by the two point's method technique using multimeter Sefram 7338.

3. Results and discussion

Conductive polymer polyaniline (PANI) was synthetized by oxidative polymerization of aniline hydrochloride with ammonium persulfate (APS) to reach emeraldine salt. The synthesis was made on two different substrates PET foil and PVDF membrane which is made by electrospinning technology. Figure 1 shows the IR spectroscopy of coated and uncoated PET and PVDF membrane. In IR spectra of PANI coated PET foil (Figure 1a), peak at 1585 cm^{-1} is due to the quinoid ring and at 1498 cm^{-1} due to the stretching of the benzoic rings. The peak at 1304 cm^{-1} is due to the C-N stretching. Peak at 810 cm^{-1} is due to the N-H out of plane bending vibrations [15-16]. From these peaks it is clearly indicates the presence PANI on PET foil. The same peaks are also observed with almost the same values (1591 cm^{-1}, 1498 cm^{-1}, 1304 cm^{-1}, 811 cm^{-1}) in the PANI coated PVDF membrane (Figure 1b).

Figure 2 shows the morphology of the pure and PANI coated PET and PVDF membrane. PET foil clearly shows the planer surface which is representer of non-porous substrate (Figure 2a). When coated with PANI, PET foil shows the presence of nano particles having average diameter 165.5nm. In contrast Pure PVDF membrane shows the randomly oriented and porous nanowoven structure which is typical for electrospinning process. The average diameter of nano fibers is 138.24 nm ± 30.41. The average diameter of fibers present in the PANI coated PVDF membrane get increased, and goes upto 266.84 nm ± 67.77 which clearly indicates the increment by 128.60 nm after coating by PANI. It also shows the some spherical particles of PANI.

These two membranes were used as a sensing element for polar solvent, namely: N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc) and Dimethyl sulfoxide (DMSO). These three solvents were chosen with respect to their polarity. The polarity index increases in this order and sensitivity decreases (Table1). The measurement was made on the base of the recording of the change of the resistivity of sensing elements during adsorption and desorption cycles. Figure 3 showing four adsorption and desorption recycles for each solvent.
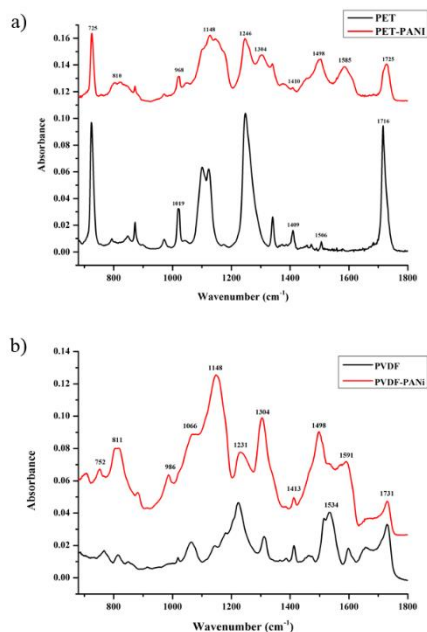
Figure 1. IR spectra of a) pure and PANI coated PET foil; b) pure and PANI coated PVDF membrane.

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The percentage of sensing for PVDF membrane is more than that of PET foil in every analyte (Table 1). The nanofiber structure in PVDF membrane is more jugged and porous. The porous structure improves the sensitivity during adsorption cycles when the molecules of analyte are adsorbed. Desorption cycles indicate good reversibility of this process. Both adsorption and desorption are on physical base, so no chemisorption occurs (Figure 3). As compared to PET foil as a substrate there is no porosity and so adsorption and desorption process is lower compared to a PVDF membrane.
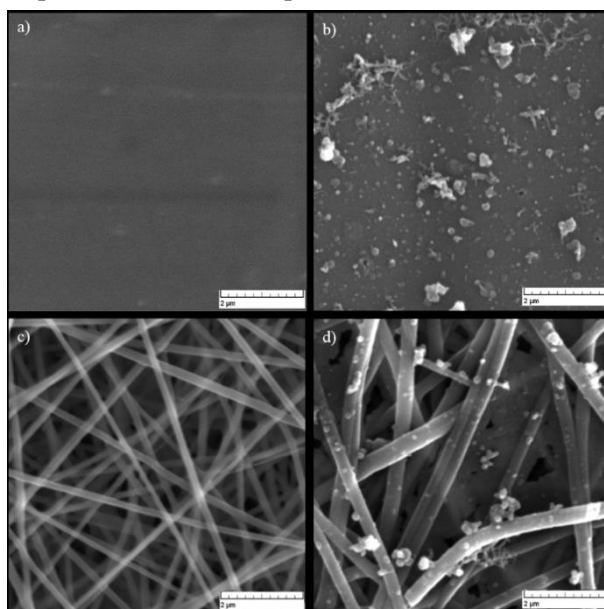

Figure 2. a) SEM analysis of polymer (PVDF) base substrate made by electrospinning method. b) SEM analysis of polyaniline spherical particles attached on nanofibers surface during in situ polymerization. c) SEM analysis of polyaniline spherical particles on a PET foil.
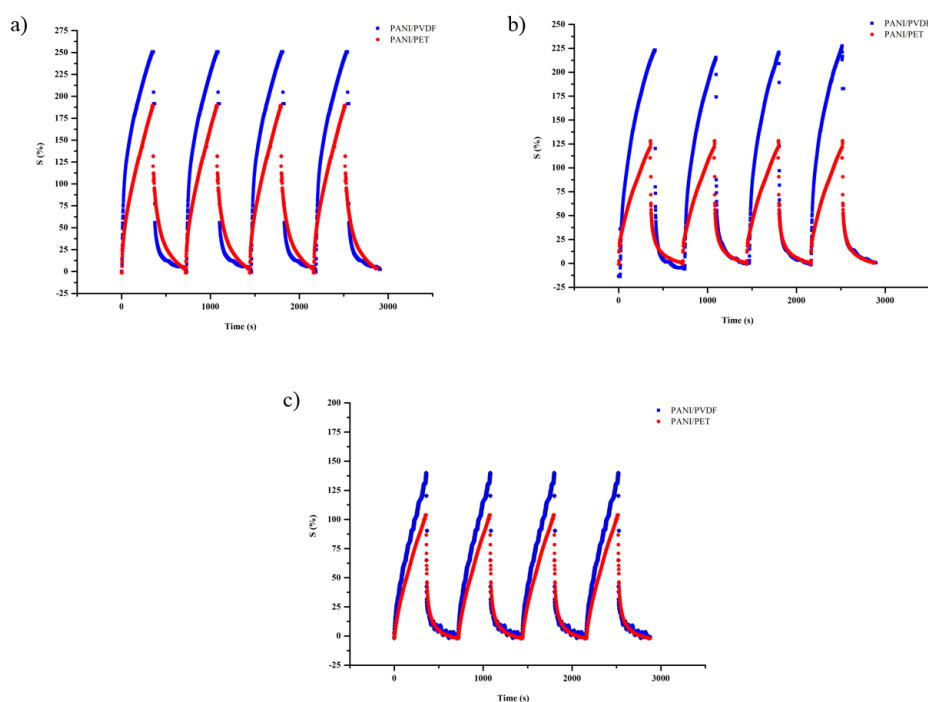
Figure 3. Change of sensitivity S in % during four adsorption/desorption cycles for tree different polar solvents a) N,N-Dimethylformamide (DMF),b) N,N-Dimethylacetamide (DMAc) and c) Dimethyl sulfoxide (DMSO).

Solvent	Vapore pressure at 20 °C [kPa]	Volume in air [%]	Polarity index	PANI on PET foil S [%]	PANI on PVDF membrane S [%]
DMF	0.36	0.36	6.4	185	250
DMAC	0.20	0.20	6.5	124	214
DMSO	0.05	0.05	7.2	104	140

Table.1 Physical properties of chosen solvents and sensitivity response for PANI coated PET and PVDF membrane.

4. Conclusion

Electrically well conductive polymer polyaniline was synthetized by oxidative polymerization. The polymerization process was carried out in the presence of two different substrates, planer PET foil and porous and nano fibrous PVDF membrane. Sensing property of these two membranes were measured against three different solvents and it shows that PANI coated PVDF membrane show good response as compared to the PANI coated PET foil. The surface area plays an important role in improving sensitivity and selectivity of the prepared sensor.

Acknowledgements

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