SENSING ELEMENT BASED ON POLYANILINE COMPOSITES FOR POLAR ORGANIC VAPOURS DETECTION

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Abstract

Electrically conductive polymer, polyaniline (PANI), was synthesized by oxidative polymerization of aniline hydrochloride as a source of aniline and ammonium persulfate as an oxidation agent in form of PANI layer formed from PANI nano-particles. The reaction was conducted in presence of polymer substrate, in our case polyethylene terephthalate foil (PET) as a representative of smooth surface substrate and polyvinylidenfluoride (PVDF) nano-fiber membrane as a representative of porous substrate. Both substrates were covered by PANI layer in situ and used as a sensing element for organic vapors detection. The detection is based on change of PANI resistivity during adsorption and desorption of vapors. The result shows sensitivity, selectivity, reversibility and repeatability of sensor responses for both principal PANI sensors onto vapors like N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc) and Dimethyl sulfoxide (DMSO). The sensor based on PVDF nano-fiber membrane poses improved sensing properties like sensitivity and reaction time compated with sensor basen on smooth surface PET substrate.

Keywords: Nano-particle, gas sensor, PANI, composite, VOC

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.

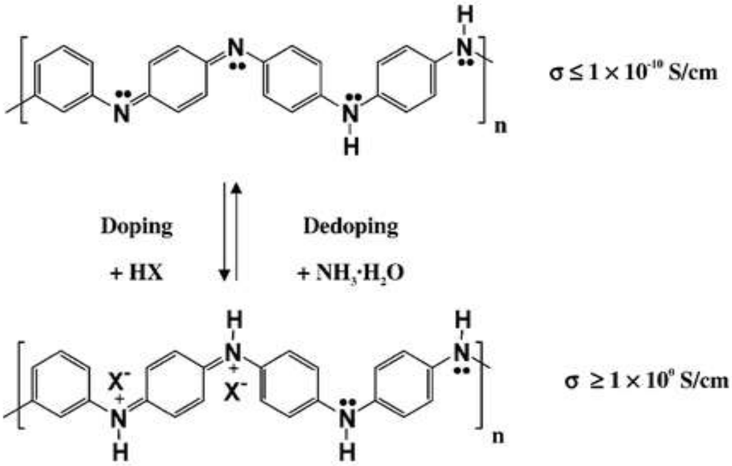

Fig. 1 The scheme of repeat unit of the emeraldine oxidation state of polyaniline in the undoped, base form (top), and the fully doped, acid form (bottom). HX represents any protonic acid [5].

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 Fig. 1. 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 and they are used in various application e.g. organic electrodes [6], actuators and sensors[7,8]. The aim of this contribution is in synthesis of polyaniline emeraldine salt in form of nano-particles adhered in form of electrically conductive layer on surface of two different substrates like PET foil and PVDF nano-membrane. Prepared composites were tested as gas sensors for vapors of three different volatile organic compounds, VOC, like N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc) and Dimethyl sulfoxide (DMSO).

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 Fig.2. The substrate was inserted in the reaction mixture. Then the solution was stirred at 500 rpm. The reaction was carried out at 19 °C by using thermostatic chamber. 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 at 19 °C overnight. Further, the membrane was cut in small pieces and measured by the two point method.

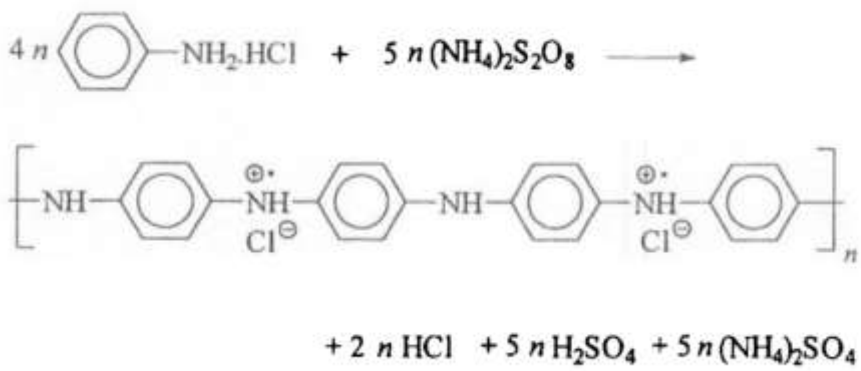

Fig. 2 The schematic illustration of oxidation polymerization of aniline hydrochloride with ammonium persulfate (APS) to receive emeraldine salt.

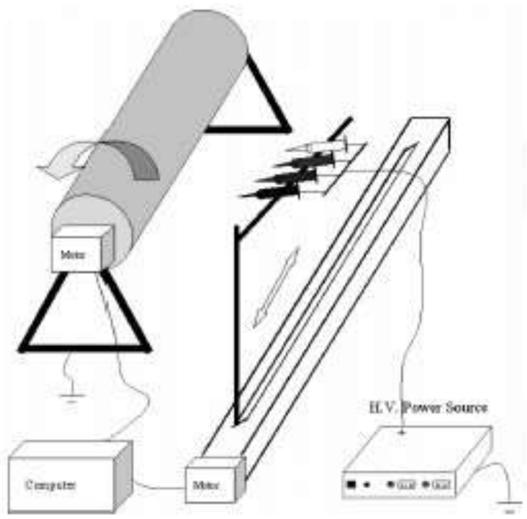

Fig.3 The schematic illustration of multi-jet electrospinning setup. [9]

Polyvinylidenfloride PVDF membrane was made by electrospinning process Fig. 3. In this case was used multi-jet electrospinning machine Spinline 120 (SPUR Zlín, s.r.o.). The voltage between electrodes was 120 kV and distance between electrodes was 27 cm. We used PVDF in solution form. PVDF was dissolve in N,N-Dimethylformamide (DMF) to reached 5% solution. The fabrication process was made at 25 °C and 55 % of relative humidity.

3. RESULTS

Conductive polymer polyaniline (PANI) was syntetized by oxidative polymerization of aniline hydrochloride with ammonium persulfate (APS) to reach emeraldine salt. The scheme of chemical reaction is shown in Fig. 2. The synthesis was made on two different substrates PET foil and a membrane made by electrospinning technology which produces nanofibers. SEM analysis shows a randomly oriented and porous nanowoven structure Fig.4 a) which is typical for electrospinning process. Fig. 4 b) displays PVDF nanofibers with deposited PANI layer made of PANI nanoparticles together with some larger spherical shape particles also embedded on nanofibers. Fig. 4 c) presents PANI layer adhered onto PET foil together with some larger spherical particles.

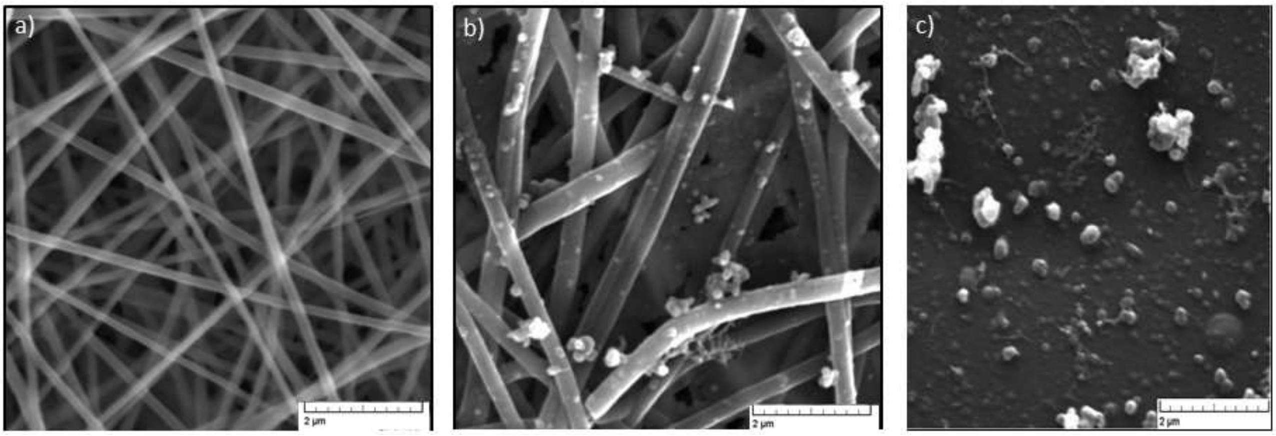

Fig 3 a) SEM analysis of polymer (PVDF) base substrate made by electrospinning method. b) SEM analysis of PVDF PANI coated composite, c) SEM analysis of PANI/PET composite.

In the first case polyvinylidenfloride PVDF was used. The PVDF membrane was made by electrospinning process from PVDF solution in DMF. The nanofibers structure indicates that the substrate surface is more jugged and porous. The porous structure improves the sensitivity during adsorption cycles when the molecules of analyte are adsorbed. The molecules of analyte are attached on surface of polyaniline particle by physical sorption. Desorption cycles indicate good reversibility of this process.

The measurement was made on the base of the recording of the change of the resistivity of sensing elements during adsorption and desorption cycles. Adsorption and desorption last 6 minutes cycles. The effect of resistivity change is caused by deprotonation of polyaniline sensitive layer in present of organic vapors.

A polyethylene terephthalate (PET) foil was used as a substrate for PANI spherical particles. There is no porosity in the substrate. The adsorption and desorption process in respect of sensor responses is lower compared to a PVDF substrate.

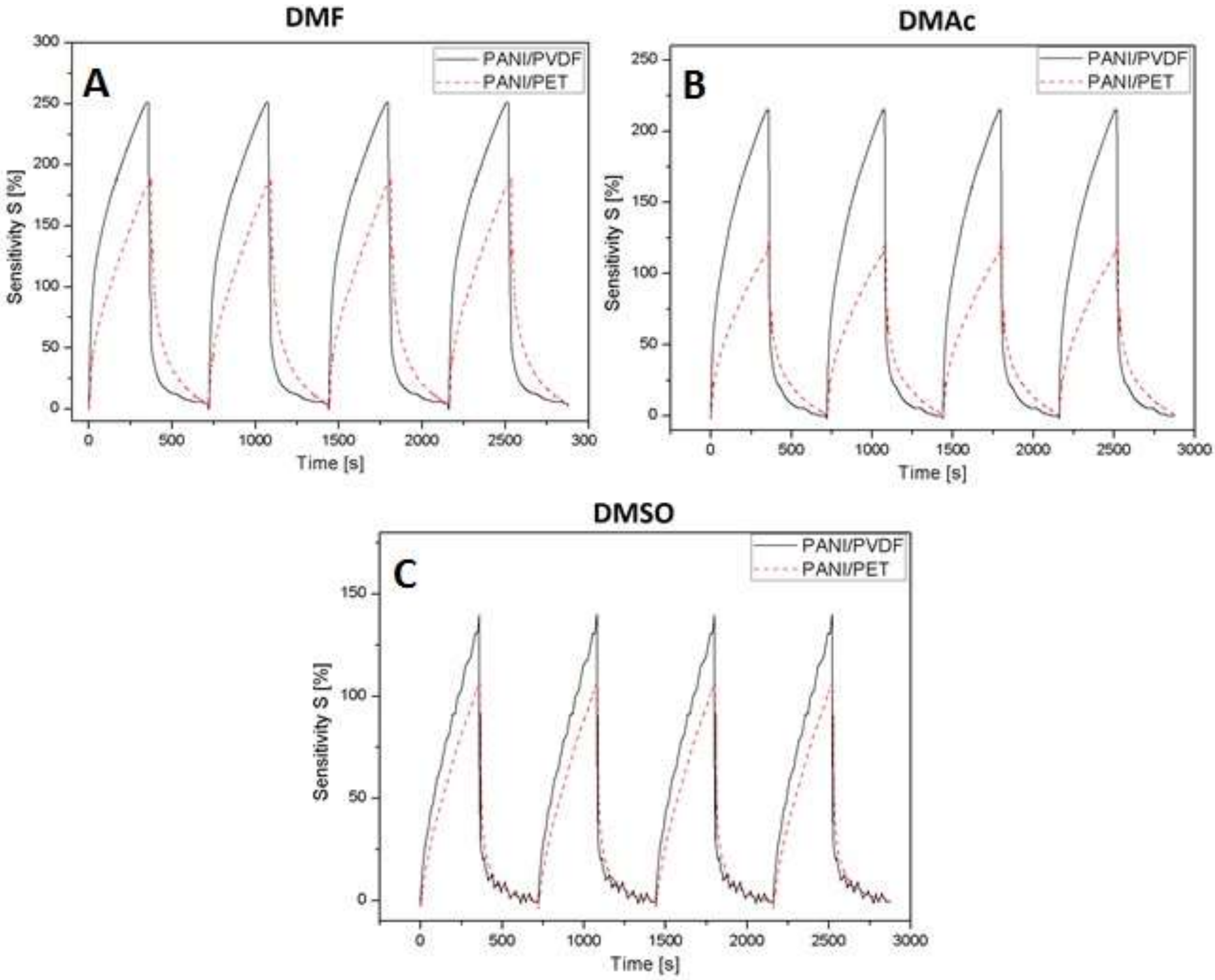

Fig. 4 Sensor response, S in %, during four 6 min adsorption/desorption cycles for vapors of tree different polar solvents: a) N,N-Dimethylformamide (DMF),b) N,N-Dimethylacetamide (DMAc) and c) Dimethyl sulfoxide (DMSO)

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 and vapor pressure of their saturated vapours, Tab. 1.

4. CONCLUSIONS

Electrically well-conductive PANI layer made of PANI nanoparticles was synthetized in situ by oxidative polymerization on two different polymeric substrates like PET foil and PVDF nano-membrane. The polymerization process was modified by using aniline hydrochloride instead of aniline which is used in common polymerization techniques. From practical point of view, these both sensors are able to detect polar solvents and they also show good selectivity. The surface area plays an important role in improving sensitivity and selectivity of the prepared gas sensor. The sensitivity increase with increasing volume faction of analyte in air. Sensor layer is more sensitive for lower polar organic vapors in order DMF,DMAC and DMSO.

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

Solvent	Vapor pressure at 20 °C [kPa]	Volume fraction in air [%]	polarity index	Sensitivity S[%] PANI on PET foil [%]	Sensitivity S [%] PANI on PVDF membrane [%]
DMF	0.36	0.35	6.4	185	250
DMAC	0.20	0.19	6.5	124	214
DMSO	0.05	0.04	7.2	104	140

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