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High sensitivity sensor development for Hexamethylphosphoramide by polyaniline coated polyurethane membrane using resistivity assessment technique



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ABSTRACT

Hexamethylphosphoramide is considered as one of the harmful of all carcinogens. In the present work, detection of Hexamethylphosphoramide by using a polyaniline coated polyurethane membrane was carried out and device is constructed to show its practical application using resistivity assessment technique. Polyurethane nanofiber membrane was prepared by electrospinning process. A modified synthetic method used to coat polyaniline onto a polyurethane membrane found to be effective to prepare a uniform and electrically conductive coating and promising for sensing a carcinogen like Hexamethylphosphoramide. Sensing performance may be attributed to the large resistance change in polyaniline because of the deprotonation when exposed to the Hexamethylphosphoramide environment. However, it is interesting to know that the high sensitivity of polyaniline modified polyurethane membrane toward Hexamethylphosphoramide is used as a promising gas sensor for the detection of said carcinogen using resistivity assessment technique at room temperature.

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1. Introduction

Hexamethylphosphoramide (HMPA) is very essential solvent widely used for organic, organometallic compounds and selectively for gases as it is highly soluble in both phases, aqueous and organic. It is also used as a UV inhibitor in plastics, polymerization catalyst and also for many other purposes [1,2]. Apart from that, HMPA had shown some adverse effects on human health by skin adsorption, inhalation and from contamination of ground water [3,4]. It shows carcinogenicity in rats in form of inhalation. The toxicity of HMPA is from low to moderate, but IARC (International Agency for Research on Cancer) had classified it as human carcinogen [5]. The oxidative products of HMPA itself revealed as mutagenic to *Drosophila*. It possesses strong carcinogenic properties [6]. Moreover, the oxidized products of HMPA are destructive to human health. Until now there isn't any report of a way of sensing HMPA. Till now only few methods are reported for the detection of HMPA [7]. In the present paper, for the first time, the sensing of HMPA at very low concentration in air is discussed by using polyaniline (PANI) coated polyurethane (PU) membrane.

From among various different conducting polymers PANI is selected because some of its properties like high sensitivity, high

stability, fast response, low cost and well-behaved electrochemistry are well suited for developing any novel composite material. Until now there are many reports which have described the sensing property of PANI toward different gases by making composite of it with other nano-materials [8–10]. PANI/Au nanocomposites are used for sensing triethylamine acetic acid, ethanol, methanol, acetonitrile, water, ammonia and toluene [11,12]. Different PANI composites were used for sensing urea in water [13,14] and in addition to the enhancement of its sensitivity was done by PANI-graphene nanocomposites [15]. Doping with camphorsulfonic acid, the thin films of PANI are used for detection of ammonia at room temperature [16]. By preparing salts of PANI using several acids like HCl, HBr, HClO₄, different organic and inorganic solvents were sensed [17]. Some of the well-known advantages of using PANI are graphene-PANI composites used for the Hydrogen sensing [18], PANI on PU detected chloroform as reported [19] and through PANI multiwall carbon nanotube composites, and CO₂ was captured [20].

A few reports are there which shows the preparation and morphology of conductive PANI [21] and water based PU blends [22,23]. A semiconductive PANI/PU-epoxy nanocomposite was prepared and characterized by different analytical techniques [24]. Modification of PU latex was done by synthesizing PANI by oxidative polymerization of aniline in presence of PU latex. Modified PU latex shows good conductivity and typical mechanical properties

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[25]. By coating PU with PANI and PANI silver nanoparticles Prabhakar and co-workers had shown some excellent antibacterial property by bacterial adhesion and the cell culture studies [26].

Recently we reported use of the oxidized carbon nanotubes/PU composite for detection of tensile stress [27]. By enmeshing of PU membrane with carbon nanotubes and melting it in one piece, the prepared composite can show corresponding resistance changes after being compressed, bent, extended and exposed to chemical vapors (ethanol and heptane). This paper presents the study of sensing HMPA by using the PANI coated PU nanofiber membrane. It also reveals modified synthesis of PANI by using aniline hydrochloride and Ammonium persulfate (APS) and its coating on PU nanofiber membrane. Further the resistivity assessment technique shows its direct application in real life.

2. Material and methods

2.1. Materials

Granulated polyurethane elastomer DP 2590A was obtained from Bayer Material Science. Aniline hydrochloride and ammonium persulfate (APS) were purchased from Sigma Aldrich. Water used from a Millipore Milli-Q system (conductivity $\leq 0.1 \mu\text{S cm}^{-1}$).

2.2. Instruments for the measurement

FTIR spectra of the PU membrane and its coated sample with PANI were collected on the NICOLET 6700 FTIR Spectrophotometer using attenuated total reflectance ATR-FTIR.

The Scanning Electron Microscope (SEM) Vega LMU, produced by Tescan Ltd., was used to observe the morphology of PANI coated PU membrane. Carbon targets were used to deposit the samples and to suppress charging and increase electron emission. The samples were coated with a thin Au/Pd layer. The regime of secondary electrons was chosen for observation.

SETARAM SETSYS Evolution 1200 thermogravimeter was used to study the thermogravimetric behavior of the samples. Under an inert atmosphere of helium (5.5 purity, SIAD TP) samples were examined with a flow of gas of about $30 \text{ cm}^3/\text{min}$ and at the pressure of 101.325 kPa (i.e., 30 sccm) for all experiments. A platinum crucible was used for the sample, the weight of which was about 4 mg. The rate of temperature increment was kept at $10 \text{ }^\circ\text{C}/\text{min}$ and this exists in the range from the ambient temperature to $600 \text{ }^\circ\text{C}$ for sample analysis.

UNI-T UT71C Multimeter connected with a holder was used to measure time dependent resistance of PANI coated PU membrane.

2.3. Synthesis of the PU membrane

PU membranes were prepared by using an electrospinning process as described in the previous papers, wherein granules of the elastomer Desmopan DP 2590A were used [28,29]. The obtained PU membrane was of thickness $18 \mu\text{m}$, and utilized in further experiments.

2.4. Coating of PANI on PU membrane

We have modified previously reported method [21] by directly using aniline hydrochloride and APS. The solution of aniline hydrochloride (50 ml, 1.29 g, 10 mmol) was prepared and 50 ml solution of APS (1.56 g, 6.7 mmol) was added into it. The entire reaction was carried out at room temperature. To this reaction mixture, PU membrane was kept in a hanging in position. Reaction mixture was stirred for 24 h. After that membrane was removed,

washed with distilled water three times and air-dried overnight. Furthermore, the membrane was cut into small pieces having dimensions $5 \times 15 \text{ mm}$ and used for sensing purposes.

2.5. Detection of HMPA

PU membrane with deposited PANI film was placed on a planar holder with Cu electrodes fixed on both sides of it. The holder with the stripe was quickly transferred into an airtight conical flask full of HMPA vapors layer of which HMPA solution was at the bottom. After a 1 min adsorption cycle, the holder was promptly removed from the flask and for the next minute the sample was measured in the desorption mode. The resistance measurement was performed for 6 adsorption–desorption cycles.

2.6. Fabrication of a resistivity assessment

An instrument is designated for a resistivity assessment of PANI coated PU membrane in a range from 1 to 68 k Ω . A reached value is indicated optically by light emitting diode and optionally acoustically by piezo siren. An adjustment of required value, which is indicated, is executed by a 10-turn precision potentiometer with a lock (it is against to undesired setting change). The range of the instrument is divided into five segments with maximal values: 500 Ω , 970 Ω , 1500 Ω , 2000 Ω and 68,000 Ω .

The adjustment of required value must be checked by an accurate laboratory ohmmeter, because the instrument doesn't include this ohmmeter. The setting accuracy depends on the accuracy of the used laboratory device. So a separate connector is involved on a printed circuit board (PCB).

A measurement is built on a comparative method, when an operational amplifier compares two values of a voltage on voltage dividers:

- (1) Divider built on the measured resistor.
- (2) Divider for the setting of required value.

The voltages of both dividers are measured on high precision resistors with 0.01% tolerance and high temperature stability (10 ppm/ $^\circ\text{C}$). A measuring current is limited to a maximal value 300 μA (if the device has a 3 V power supply) – the short circuit current (measured resistivity is approximately equal to 0 Ω), which it shouldn't lead to a self-heating of the measured resistor or material (a maximal power loss on the measured component is 9 μW).

MCP6001T operational amplifier was selected due to a reason of 3 V battery power supply (two AAA batteries). The operational amplifier is rail-to-rail type, maximal supply current is 100 μA and voltage range from 1.8 V to 6.0 V. Unfortunately, it has higher input offset (maximal 4.5 mV) than other precious types. A hysteresis was implemented against to voltage output oscillations of operational amplifier. It is built on positive feedback. In addition, a free position on PCB is left to place a capacitor for a stability improvement.

A Process of using the instrument:

- (1) Disconnect the settable divider of power supply.
- (2) Set the required value of divider by using laboratory ohmmeter.
- (3) Optionally lock a knob of the potentiometer.
- (4) Connect divider back to power supply, connect measured resistor or material.
- (5) If the required value of the resistance is achieved on measured component, it is optically or acoustic indicated.

3. Results and discussion

3.1. FTIR-ATR analysis of PANI/PU composite

Fig. 1 shows the FTIR-ATR spectra of the pure PANI, PU membrane and coated PU membrane with PANI. In IR spectra of PANI, peak at 1566 cm^{-1} is due to the quinoid ring and at 1483 cm^{-1} due to the stretching of the benzoic rings. The peak at 1292 cm^{-1} is due to the C–N stretching. Peak at 794 cm^{-1} is due to the N–H out of plane bending vibrations. Further, the peaks obtained at 1112 cm^{-1} and 1236 cm^{-1} are because of the stretching and twisting of C–C of alkyl chain [30,31].

The peak at 1700 cm^{-1} in IR spectra of PU is due to the C=O, at 1073 cm^{-1} is because of the C–O, and at 1415 cm^{-1} is due to the aromatic ring. The secondary amide groups are obtained at peaks 1527 cm^{-1} and 1594 cm^{-1} [32,33]. The peaks correspond to the PANI and PU membrane is observed in the PANI modified PU membrane, which clearly indicates the presence of PANI on PU membrane.

3.2. Thermogravimetric analysis

The thermal stability of PANI, pure PU and PANI coated PU membrane was done by TGA analysis (Fig. 2). In PANI, the decrease in weight below $100\text{ }^{\circ}\text{C}$ is due to the presence of water and at $200\text{ }^{\circ}\text{C}$ is for the dopant. The reduction seen in the amount after $300\text{ }^{\circ}\text{C}$ is caused by breaking of the backbone inside the polymer. In PU, the thermal decomposition starts at $280\text{ }^{\circ}\text{C}$ and ends at $345\text{ }^{\circ}\text{C}$ due to the degradation of urethane groups and second continuous degradation from $345\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$ is because of the decomposition of polyol groups [34–36].

The PANI modified PU membrane also shows degradation peaks related to the PU to some extent. It shows the reduction at $320\text{ }^{\circ}\text{C}$ because of the polymer and from $400\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$ due to the polyol groups in the PU.

3.3. Morphology study

The surface visualization of PU membrane was done by using SEM analysis. Fig. 3 shows the images of the PU and PANI coated PU membrane. The average diameter for the pure PU fibers is $120.20\text{ nm} \pm 28.46$, and for the PANI coated fibers of PU is $203.78\text{ nm} \pm 46.06$. From the pure and coated fibers of PU mem-

branes, it clearly indicates that there is a surface coating of the PANI on the PU fibers. Along with that, there are some nanoparticles which may be PANI nanoparticles having average diameter $139.62\text{ nm} \pm 27.22$.

3.4. PANI/PU composite as a HMPA sensor

A PANI-coated PU membrane was used for the purpose of HMPA sensing and resistive measurements have been carried out at room temperature. There is no need for doping and it can be directly used for sensing purposes. Fig. 4a shows adsorption/desorption cycle for HMPA using PANI modified PU membrane in terms of sensor response, S ($S = (R - R_0)/R_0$, where R_0 is the electrical resistance of the measured sample before exposing to HMPA vapors and R is resistance change after exposing to HMPA vapors), in percentage. The resistance of the sensor increases dramatically when exposed to the HMPA environment and when environment is replaced by pure air, the resistance almost comes back to its initial value as desorption is not exact 100%. Temperature was kept constant during the experiment at $25\text{ }^{\circ}\text{C}$ when sensor was exposed to saturated vapors of HMPA in air and back to pure air at this temperature. The measured sensor response for HMPA in air is relatively high, reaching values over 150% although the saturation of HMPA vapor in air was low. At the conditions described of experiment, the vapor pressure of HMPA is 0.07 mmHg , which represents a vapor concentration of 0.0092% (92 ppm). We have continued to measure the sensor response further and after five recycles, sensor shows the same response (Fig. 4b).

The adsorption of HMPA on PANI modified PU membrane may occur due to the interaction between oxygen of the HMPA and a proton on the –NH group, to form the $\text{P} = \text{O} + \text{H}$, while PANI itself turns into the base. When the HMPA environment is removed the HMPA returns to its original state. But desorption is not 100%, a few molecules of HMPA will still be present, so in the next cycle some residual resistance is observed. This deprotonating reaction causes electrical resistance in PANI which indicates that it can act as good sensor (Fig. 5).

3.5. Application as a sensor in real life

Evaluation of information about the resistance change in the comparator performed using the default values in ohms. Values on the comparator are fixed with the values of sensor. It is done

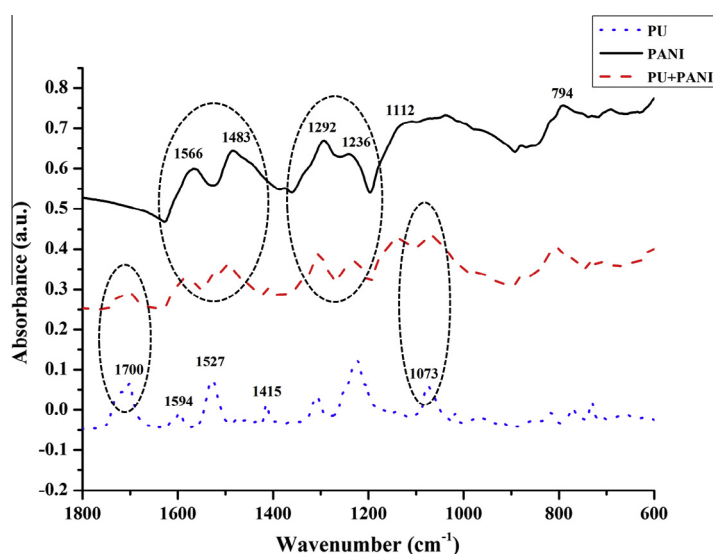


Fig. 1. FTIR-ATR spectra of PANI, PU and PANI modified PU.

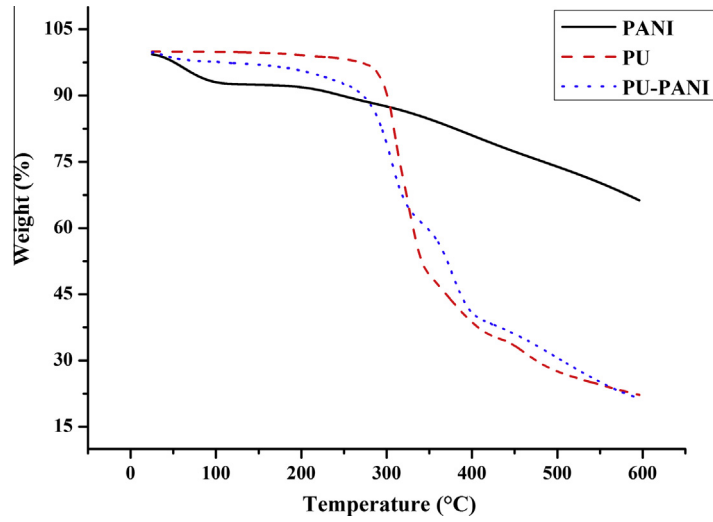


Fig. 2. TGA spectra of the PANI, PU and modified PU.

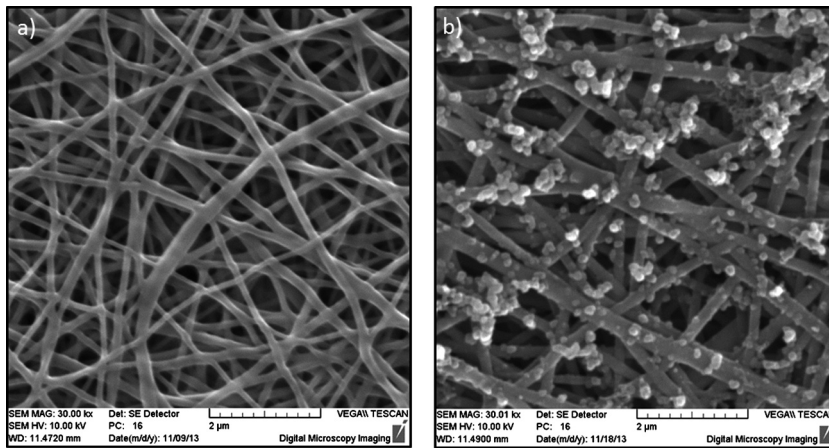


Fig. 3. SEM images of PU fibers (a) and PANI-coated PU fibers (b).

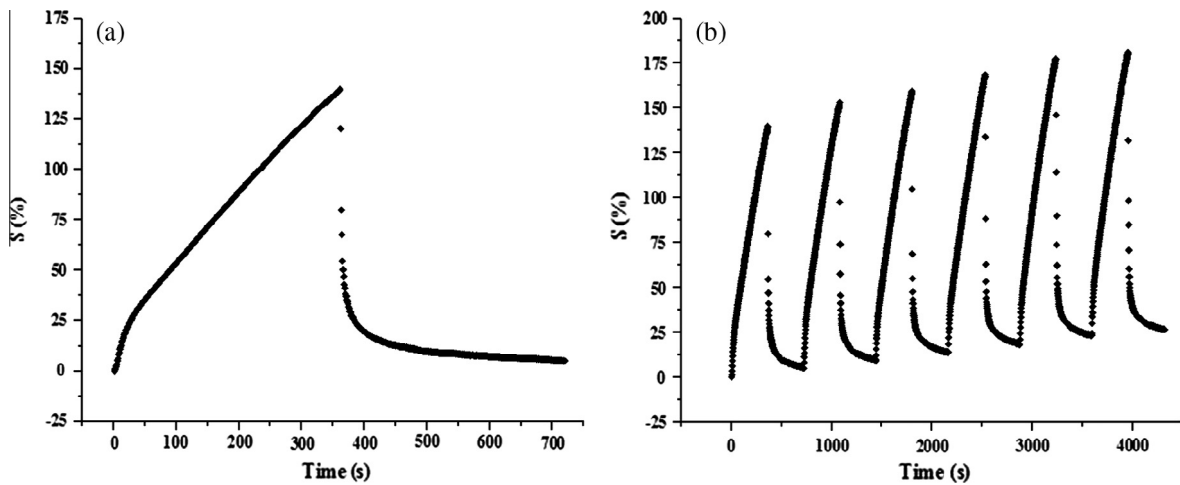


Fig. 4. (a) Single adsorption/desorption cycle and (b) six adsorption/desorption cycles for PANI coated PU membrane exposed to HMPA.

by integrated circuit designed MCP6001T (Fig. 6). When sensor exposed to the HMPA vapors, change in the status of comparator occurs due to change in resistance which automatically leads to start light and alarm, supported by video data (Supplementary

data). The sensitivity of the sensor can be influenced by adjusting the margin comparator value from which the signal has to run. This principle can be used for testing the sensors and also for simple application for the detection of hazardous chemical vapors.

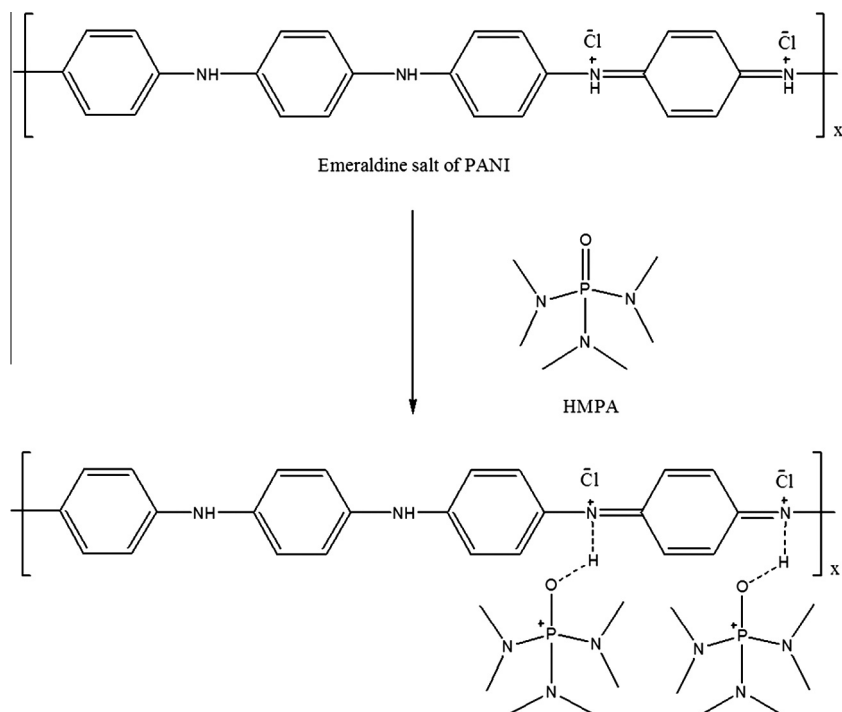


Fig. 5. Proposed mechanism for the detection of the HMPA by PANI.

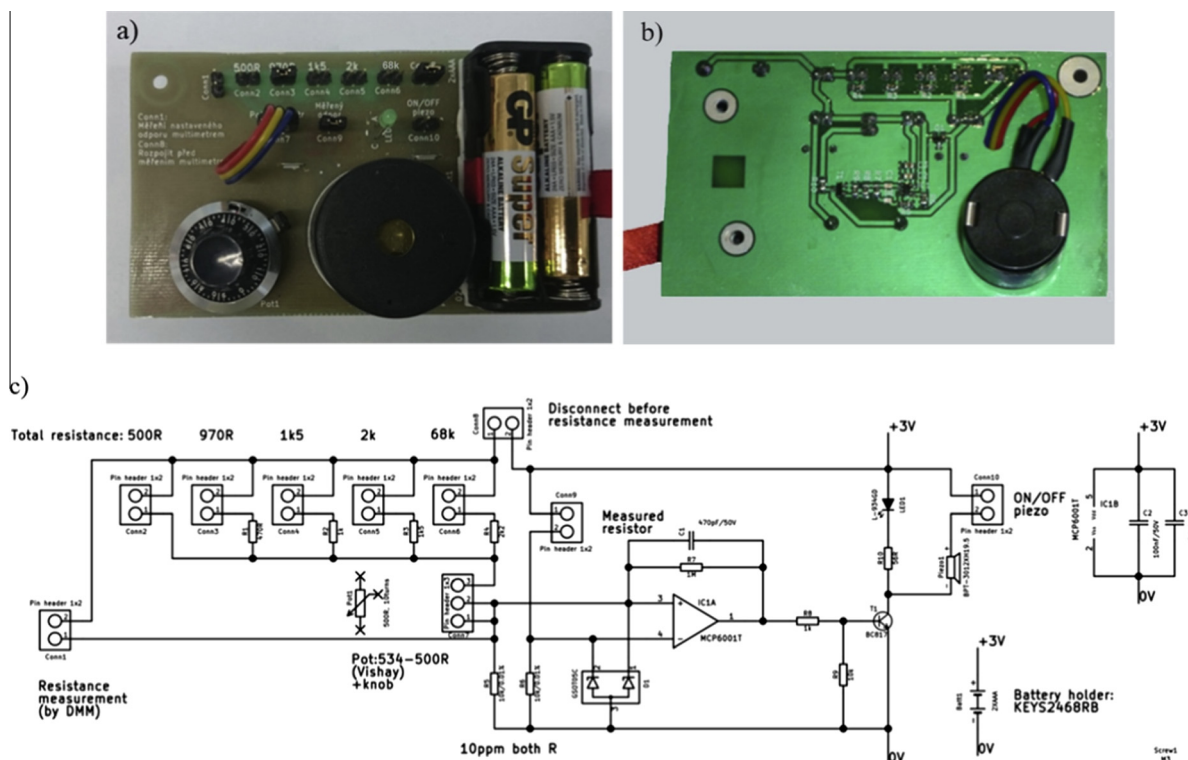


Fig. 6. (a) Front, (b) back side snapshots of proposed comparator. (c) Schematic representation of the proposed comparator.

4. Conclusions

In summary, for a detection of carcinogen like HMPA a modified method for synthesis of PANI and its coating on PU membranes has been described. PU membrane surface modification was confirmed by different analytical techniques such as ATR-IR, TGA and SEM

analysis. The experimental results reveal that a PANI-modified PU membrane shows very good sensing property toward HMPA. The prepared PU/PANI sensor is sensitive and its response is reversible over many courses of adsorption/desorption cycles, reaching a percentage change in value of sensor response of more than 150% for a HMPA concentration in air of 92 ppm. In addition

resistivity assessment technique offer great steps toward the practical realization of a HMPA sensor with high sensitivity.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.measurement.2016.03.078>.

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