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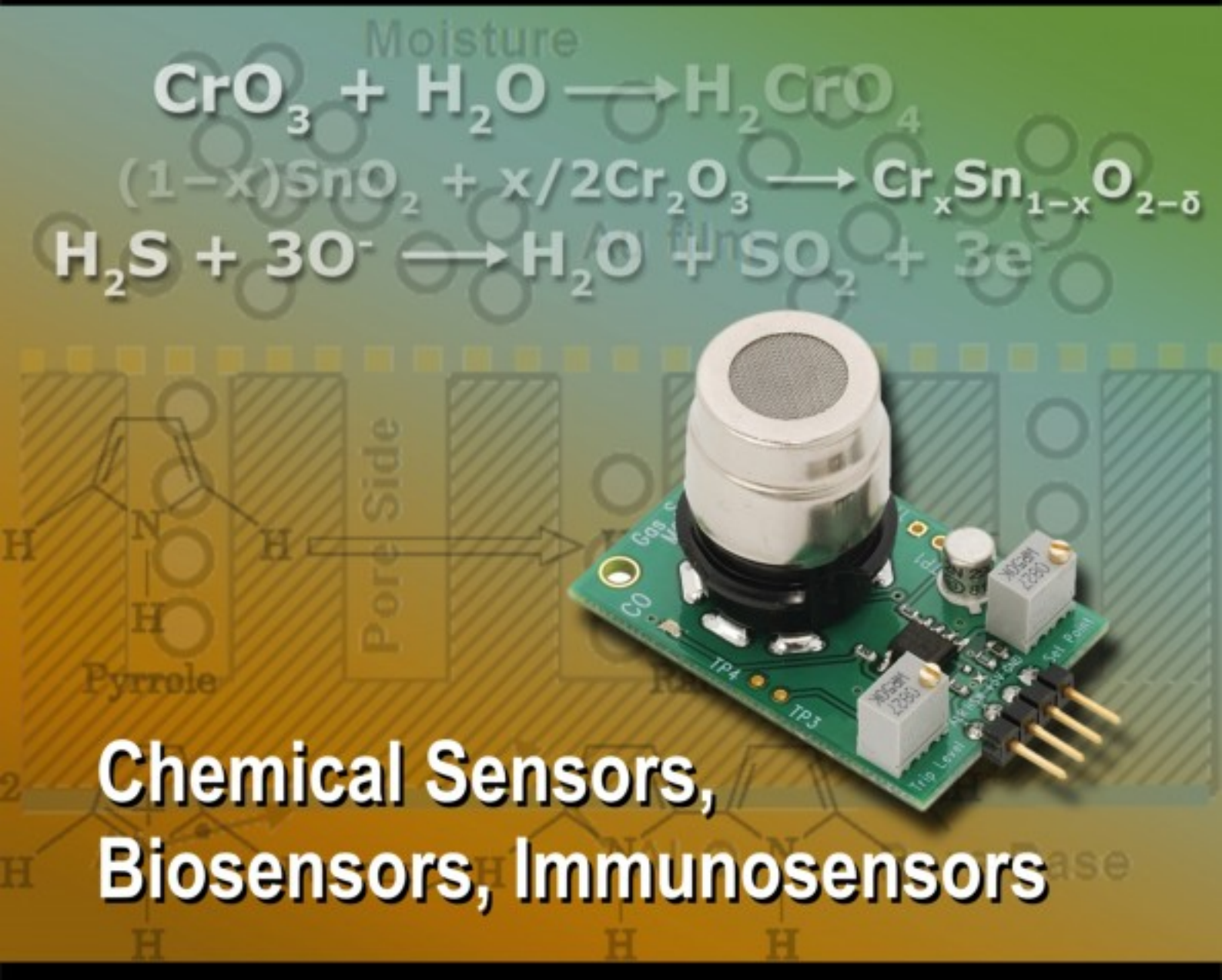
2/12

$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$

$$(1-x)SnO_2 + x/2Cr_2O_3 \longrightarrow Cr_xSn_{1-x}O_{2-\delta}$$

$$H_2S + 3O^- \longrightarrow H_2O + SO_2 + 3e^-$$



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Glass Surface Functionalized with Polyaniline as a Fast Responding Humidity Sensor

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Abstract: Polyaniline functionalized glass surfaces display excellent sensitivity and fast response to humidity. Functionalized glass surfaces were generated by first exposing hot glass surfaces to $SOCl_2$ and aniline monomers and then by chemical polymerization of aniline on the surface. After making electrical contacts using platinum wires, another layer of polyaniline covering the contacts was generated by electrochemical polymerization. The sensor thus made displayed fast and reproducible response to humidity. *Copyright © 2012 IFSA.*

Keywords: Polyaniline functionalized glass surface, Humidity, Sensor, FTIR of poly aniline exposed to humidity, Electron micrographs of functionalized glass surface.

1. Introduction

Semiconducting organic polymers have received attention of the researchers due to their versatility easy synthesis and low cost. They have found applications as sensors, molecular wires, light emitting materials and solar energy converters. Polyaniline is one such organic polymer that has been extensively studied. It has been reported that the direct current electrical conductivity of dry polyaniline is dependent on the gaseous environment to which polyaniline is exposed [1]. Nanofibers of polyaniline deposited between two gold electrodes responded to nitrogen dioxide gas by increasing

the resistance of the film [2]. The response time of the nanofiber film sensor was found to be independent of the film thickness. This has been attributed to the fast diffusion of gas in to the nanofiber film.

Application of polyaniline in detecting acetone, ethanol and ammonia has been reported [3]. An increase in resistance to a dc current has been observed when the sensor is exposed to acetone, ethanol or ammonia. Polyaniline based sensors have also been used in the detection of ions in aqueous media. They have been used in the detection of chloride ions [4] as well as hydrogen ions [5]. There are many reports concerning the humidity sensitivity of polyaniline films generated using different techniques. It has been reported that ultra thin polyaniline films generated using a layer by layer nano-assembly technique has fast response and improved sensitivity to humidity [6]. The long term stability, electrolytic degradation and polarization of polyaniline films during gas sensing have also been investigated [7]. It has been reported that the doping of polyaniline with polystyrene improved the stability of the films. Electrochemically deposited thin polyaniline films on stainless steel substrates have been studied for acetone vapor detection. It has been observed that the resistivity of the films increased when exposed to acetone vapor [8]. The response of polyaniline films to changes in humidity has been studied by Pandey et. al [1]. They have reported that the electrical resistance of emeraldine salt form of polyaniline decreased when polyaniline pellets were exposed to humidity. The electrical resistance progressively decreased as the relative humidity of the environment to which the films were exposed was increased. Chemically polymerized polyaniline in pellet form has been used in the study and scanning electron microscopy characterization revealed that the polymer matrix is amorphous in nature. These polymer pellets have responded to humidity changes in the range of 15 % to 90 % and had response times and recovery times of approximately four minutes duration. Activity of polyaniline in the detection of hydrogen gas has also been investigated [9,10]. It has been reported that hydrogen gas causes a reversible change in resistance of a thin film of polyaniline doped with camporsulfuric acid and the response to hydrogen gas is completely suppressed by humidity. However, no effect from oxygen gas has been observed [9]. Thin films composed of polyaniline nanofibers have also been tested for hydrogen gas sensitivity [10]. It has been reported that the use of nanofibers improved the response to hydrogen gas by decreasing the response time. Approximate response times reported are around 30s. However, the application of polyaniline films in the detection of hydrogen is limited due to the interference from moisture that may be present in the environment.

The use of thick layers or pellets in gas sensing creates a slow and tailed response due to slow diffusion of gases in to and out of the polymer matrix. Especially this effect is severe in the case of moisture sensing. Once moisture is absorbed, pellets or thick films require substantially long times to recover, making the sensor unsuitable for recording rapid changes in moisture levels. In the present article we report the construction of polyaniline functionalized glass surfaces which are fast responding to changes in moisture levels.

2. Experimental

2.1. Film Preparation

Ordinary laboratory glass rods (5mm in diameter) were chlorinated using thionylchloride (BDH) as follows. Glass rods were thoroughly cleaned using distilled water and refluxed in concentrated hydrochloric acid (BDH reagent grade) at 100 ^{0}C for 24 hours. The glass rods were then rinsed with distilled water and were heated to 400 ^{0}C in a furnace. These glass rods were then dipped in $SOCl_2$ (BDH reagent grade) for 2 min and again dipped in a freshly distilled aniline (BDH, reagent grade) for 2 min. Glass rods were then immersed in a chemical polymerization bath containing aniline (0.1M) hydrochloric acid (0.1M) and potassium persulfate (0.2M) for 24 hours at room temperature (27 ^{0}C). The above treatment developed a thin layer of polyaniline on the surface of glass. Then the glass rods

were rinsed with distilled water and dried in a desiccator. Electrical contacts were made by pressed platinum on the polyaniline layer, around the glass rods, at 1.0 mm separation. Electrochemical deposition of polyaniline covering the two platinum contacts and the first chemically deposited polyaniline layer was then carried out. This was done by immersing the sensor in a bath containing aniline (0.1M) and hydrochloric acid (0.1M) and by applying a potential of 1.2V for ~30 min against a platinum counter electrode. The glass rods were then rinsed with distilled water and dried. The resistance across the film measured between the two Pt wires was around 500 ohm. The procedure for functionalization of glass surface with aniline was adopted from the literature [11].

Sensors developed using the above procedure were tested by measuring the conductance across the two terminals after placing them in a controlled humidity environment. A portable conductivity meter, WPA model CM35 was used for conductance measurements.

Controlled humidity conditions were obtained by preparing saturated salt solutions in glass reagent bottles with airtight caps so that the head space above the solution to have the constant humidity environment. Following salts all were of reagent grade from BDH were used for this purpose. The salts and the relative humidity over a saturated aqueous solution are dry-$CaCl_2$ (0 %), LiCl (11 %), $MgCl_2$ (32 %), K_2CO_3 (43 %), $Mg(NO_3)_2$ (51 %), NaCl (75 %), KCl (83 %), KNO_3 (92 %), K_2SO_4 (97 %).

2.2. IR Characterization

Polyaniline was synthesized in a bath containing aniline (0.1M) hydrochloric acid (0.1M) and potassium persulfate (0.2M) for 24 hours at room temperature (27 ^{0}C). The bath was similar to the one used for depositing polyaniline on glass rods but did not contain the glass rods. The resultant polymer powder was rinsed with distilled water until the filtrate obtained was pH neutral. The cleaned powder was then dried in a desecrator for 24 hours containing dry $CaCl_2$ as the desiccant. The powder was then mixed with analytical grade KBr (BDH) and a thin pellet was prepared. The pellet was again dried in the desiccater and quickly transferred to the IR spectrometer (Varian 660-IR equipped with a DLaTGS detector) and the IR spectrum was recorded. The pellet was then exposed to moist air for 5 minutes and the IR spectrum was recorded again.

2.3. SEM Characterization

The glass surfaces coated with chemically polymerized polyaniline and electrochemically polymerized polyaniline on chemically polymerized polyaniline were analyzed using scanning electron microscopy facility at Uppsala University, Sweden. The samples were prepared under atmospheric conditions and they were not subjected to any other treatments thereafter. SEM pictures were obtained using LEO 440 scanning electron microscope at 6.0 kV.

3. Results and Discussion

The procedure described above produced an adherent polyaniline film on the glass rod. The sensor was fixed to an airtight stopper and inserted to the glass bottle containing the saturated salt solution and allowed to come to equilibrium prior to take measurements. It can be seen that the sensor responds almost to the full range of humidity. The log (conductance) Vs humidity produced a linear plot, (log(conductance) = 0.0146 * % humidity + 0.2534) with a R^2 value of 0.9947 (Fig. 1).

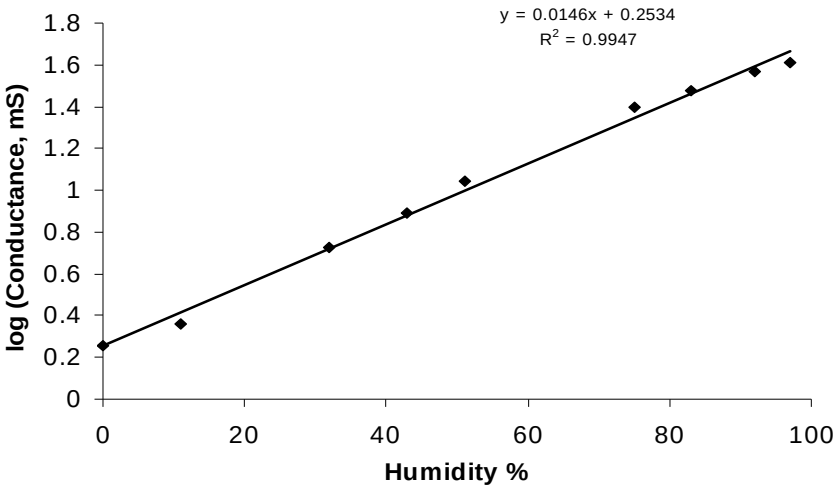

Fig. 1. Log (conductance) vs. relative humidity.

The conductance of the polymer film was measured using a conductivity meter and the output signal proportional to the conductance was recorded using a chart recorder. It can be seen from Fig. 2 that the sensor has a fast response to changing humidity conditions. The alternating humidity conditions were obtained by placing the sensor in a bottle containing dry $CaCl_2$ (0 % humidity) and then by taking the sensor out and exposing it to the atmosphere. The full cycle could be completed within 2 minute intervals and the response of the sensor remained reversible. It can be seen that the sensor responded instantly to changes in humidity. The response of the sensor to short pulses of exhaled air (~30 seconds) is shown in Fig. 3. After allowing the sensor to attain equilibrium under atmospheric conditions, air was exhaled on to the sensor from a distance of about 20 cm. The response of the sensor was recorded using the conductivity meter coupled to a chart recorder.

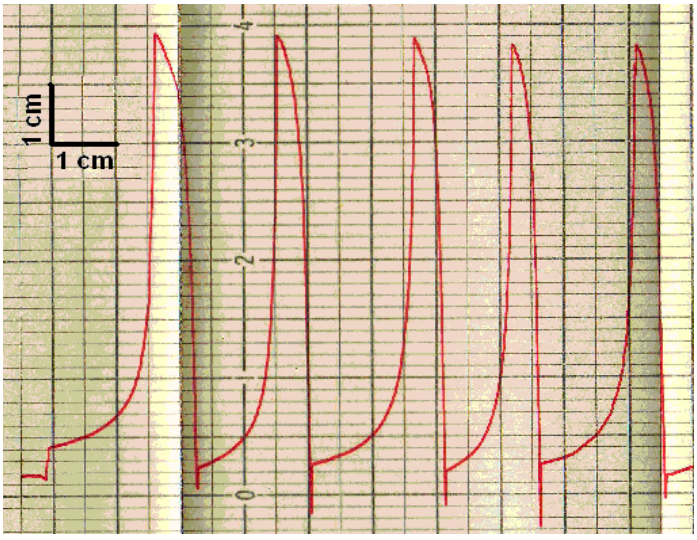

Fig. 2. Humidity sensor reproducibility; Cycled between two humidity levels.
(Scale X-axis 1 min cm^{-1} and Y-axis 2.0 mS cm^{-1}).

It can be seen from Fig. 3 that the response is quick and reproducible. After few pulses of exhaled air sending on to the sensor, the sensor was inserted to the bottle having 0 % humidity. The response of the sensor can be observed as a sharp drop of conductance labeled as a negative peak (peak labeled as A in Fig. 3).

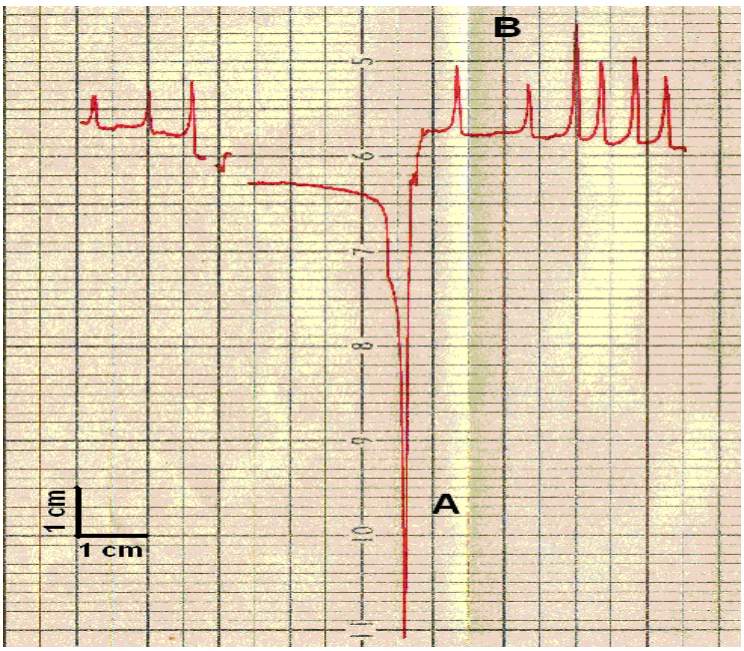

Fig. 3. Humidity sensor response; A – at 0% humidity, B-response to pulses of exhaled air (Scale X-axis 1 min cm^{-1} and Y-axis 2.0 mS cm^{-1}).

When the sensor was taken out of the bottle and exposed to the atmosphere, its conductance was quickly restored to the initial value. The conductivity of polyaniline film increased when the sensor was exposed to humid exhaled air. The conductivity increased when exhaled air reached the sensor. Conductivity changes due to pulses of exhaled air reaching the sensor are labeled as B. As calculated from data, the exhaled air reaching the sensor had ~87 % humidity. It must be mentioned that the exhaled air gets diluted as the air pulse travels through the atmosphere. Although no scientific conclusions can be drawn from the experiment with exhaled air, it shows the reproducible nature of the sensors response under different conditions.

Polyaniline powder synthesized by chemical polymerization under identical conditions of film development was analyzed by FTIR in order to observe changes that may occur during humidity sensing. The dry polyaniline pellet shows the characteristic peaks of the polymer in the region of 500 cm^{-1} -1800 cm^{-1} (Fig. 4 A) [1].

Exposure of the polyaniline pellet to moisture resulted the development of three new peaks in the FTIR spectrum (Fig. 4 B). The peaks at 3444 cm^{-1}, 1642 cm^{-1} and around 700 cm^{-1} are the characteristic peaks of water [12]. Quick generation and removal of the water peaks as observed in FTIR spectra clearly demonstrate that the adsorption and desorption of water on polyaniline is fast and reversible.

Films of polyaniline deposited on glass substrates were analyzed by scanning electron microscopy. The SEM pictures of chemically deposited polyaniline films on glass and electrochemically grown polyaniline on the initial layer of chemically deposited polyaniline are shown in Figs. 5 and 6 respectively.

The chemically deposited polyaniline layer is characteristic of a rather smooth surface with less prominent features. In contrast, the subsequent electropolymerization (on platinum conductors as well as on the initial polyaniline layer) caused the formation of more prominent ridge like structure. This secondary growth of the polymer may be responsible for the improved conductivity and good connectivity of the sensing polyaniline layer to the Pt electrodes.

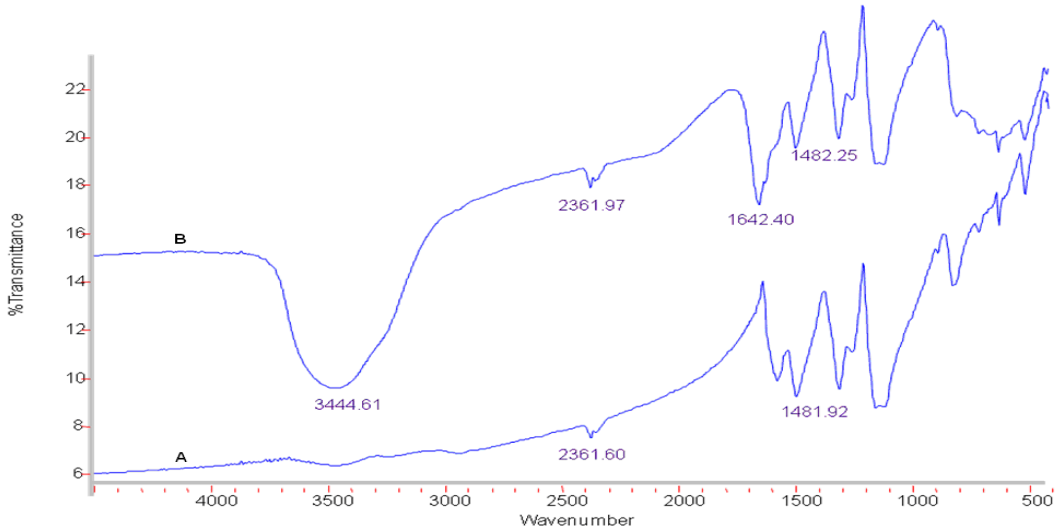

Fig. 4. IR spectra of polyaniline (A) Dried in $CaCl_2$ containing desscicater, (B) Exposed to moist air.

Further, the complete and uniform coverage of the glass surface by polyaniline as observed in SEM pictures (Figs. 5 and 6) suggest that the glass surface is not exposed to humidity. Therefore, the sensor response could be completely attributed to the response of the thin polyaniline layer. Further, a sensor without a layer of polyaniline did not give any response to humidity changes.

The fast response and quick recovery of humidity sensing can be attributed to the presence of a thin film where bulk diffusion does not significantly contribute to conductance. A mechanism to account for the enhancement of conductivity of polyaniline due to adsorbed water has been proposed in previous investigations [1, 9]. It has been proposed that the surface adsorbed water molecules assist in the conduction of electrons across the polymer molecules enhancing conductivity. The FTIR spectroscopic analysis shows that water is indeed adsorbed on polyaniline and therefore, it can be suggested that the same mechanism to be in operation. The stability of the sensor was evaluated by keeping the sensor open to atmosphere in the laboratory. It was observed that there was no significant change in response after one month of storage.

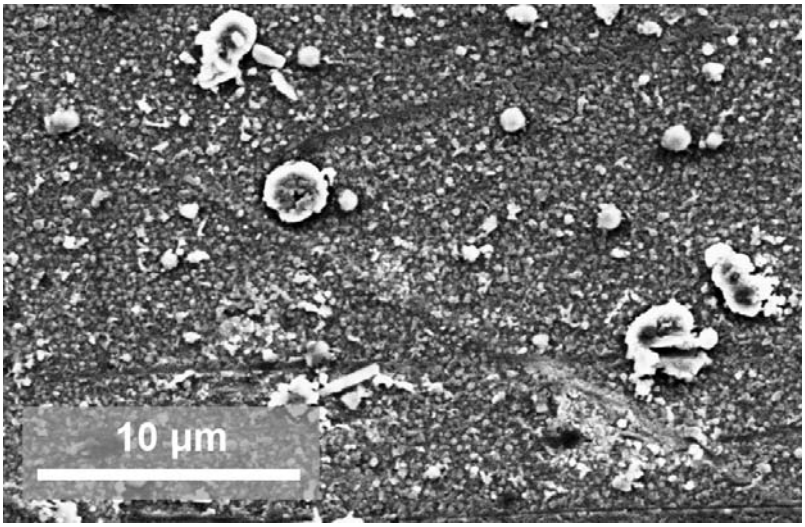

Fig. 5. Chemically polymerized aniline on glass substrate.

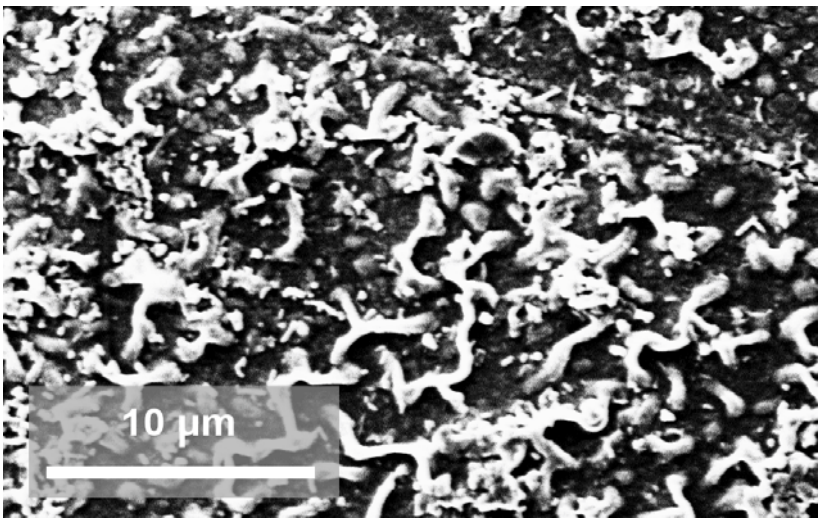

Fig. 6. Electrochemically polymerized aniline on glass substrate.

4. Conclusion

Glass surfaces can be used as substrates for the development of uniform films of polyaniline. The films display excellent sensing property towards humidity. The fast response to humidity changes and quick recovery can be attributed to the thin and uniform nature of the films. Electrochemical polymerization of aniline on chemically attached polyaniline improved the connectivity between the platinum wires and the polyaniline film resulting a very stable sensor.

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