Novel ammonia sensor based on polyaniline/polylactic acid composite films

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Abstract. We propose a new type of ammonia sensor based on composite film between polyaniline (emeraldine base) dissolved in dimethylformamide, and poly(DL-lactic) acid dissolved in chloroform. The two solutions were mixed in weight ratio of the components 1:1 and cast on Al₂O₃ substrate, on which silver electrodes were deposited previously. The active layer structure and morphology were examined by atomic force microscopy. The sensor resistance at constant humidity and different ammonia concentrations was measured. It was found that an increase in the ammonia concentration leads to resistance increase. This result is explained in the terms of ionic interactions between the polyaniline and the ammonia, which change the permittivity of the sensor active media. A response between 2% and 590% was shown depending on the ammonia concentration. The sensor is reversible and possesses response time of typically 100 s. Based on the changes of the sensor resistance, ammonia concentration from 10 ppm to 1000 ppm could be detected.

1. Introduction
Ammonia (NH₃) is one of the most widely produced inorganic chemicals, which is extensively used in many areas such as fertilizer production, clinical diagnosis and food processing [1]. However, ammonia is also a poisonous gas, which can cause both long term and immediate human health problems. For instance, even short-term exposure to 1000 ppm or above would lead to fatal respiratory system and lung disorder [2]. That is why there is an increasing interest in recent years in the development of ammonia detecting sensors.

There are several analytical techniques for gas detection - gas/liquid chromatography coupled with different detectors [3], ion mobility spectrometry [4], photoacoustic spectroscopy [5], surface-enhanced Raman scattering [6], and capillary electrophoresis [7], which usually use expensive, bulky and quite sophisticated equipment. Rapid real-time detection of the electronic sensors is a promising alternative to time-consuming laboratory techniques. The principle of operation involves conversion of chemical changes in sensing layer into electrically measurable response signal [8]. In this regard the application of conducting polymers, which reversibly change their characteristics depending on atmosphere composition, is a promising direction in development of sensing materials [9]. Among the family of conducting polymers, polyaniline (PANI) has attracted much attention due to its easy synthesis methods, good environmental stability, and because its surface charge characteristics can be easily tailored by changing the dopant during synthesis [10].

The PANI polymers exist in two forms – PANI salt and PANI base. Most of the ammonia sensors are produced using the salt form. In this case the contact of acid doped PANI with basic substances leads...
to its dedoping by deprotonation and can be used for ammonia/amines concentration determination [11].

Only a few attempts were done in the development of ammonia sensor working with PANI based form. The mechanism of the ammonia – PANI base interaction is proposed in figure 1 [12].

![Figure 1. Proposed mechanism of ammonia PANI base interaction.](image)

Polyaniline is a p-type material and when it interacts with NH$_3$, there is reduction in charge carrier density. Since the majority carriers (holes) density gets decreased due to electron donating nature of NH$_3$ gas. This results in decreasing the conductivity of material and film resistance increases [13].

A useful approach for the improvement of processability of conducting polymers involves blending them with soluble matrix polymers [14]. The blend films could potentially provide the following advantages: good mechanical stability; potential low cost; ease of measurement; operation at or near room temperature.

To the best of our knowledge and experience in this field, sensors based on polyaniline and polylactic acid have not been yet formulated and studied for detection of NH$_3$ gas. Following this idea the aim of the present work is developing of PANI base– polylactic acid blend films and investigating their sensing properties to ammonia.

2. Experimental

2.1. Materials

Polyaniline (emeraldine base) (PANI) with average molecular weight 65000 g/mol was purchased from Sigma-Aldrich and used without further purification and characterization. Poly(DL-lactic acid) (PDLA) with inherent viscosity 0.55-0.75 dL/g, delivered from Lactel Absorbable Polymers (USA), was used for the preparation of polymer matrix. All other chemicals were analytical grade purity.

2.2. Sensor fabrication

PANI/PDLA sensor was designed on Al$_2$O$_3$ substrate, on which silver electrodes were firstly deposited – figure 2. The dimensions of the substrate are 11 mm X 35mm, thickness 1mm. The electrodes are incorporated into two groups of 27 pieces in each; the distance between the electrodes is 0.2 mm. 2 \%w/v of PANI was dispersed in dimethylformamide using a Compact Ultrasonic Laboratory Device UP100H (Hielscher Ultrasonics GmbH, Germany) for 30 min at room temperature. Then the dispersion was filtered through MF-Millipore™ Membrane Filters, pore size 0.45 µm. 2 \%w/v of PDLA was dissolved in chloroform. The PANI dispersion and the PDLA solution were mixed by magnetic stirrer in weight ratio of the components 1:1 and cast on the Al$_2$O$_3$ substrate. In this way a sensing film with 1 µm thickness was constructed. Schematic structure of the ammonia sensor is shown in figure 3.
2.3. Characterization of PANI sensor
The sensor structure and morphology were investigated by AFM Nanosurf EasyScan 2. The gas sensing capabilities were carried out by High Precision LCR Meter GW INSTEK LCR-821. The changes in the resistance of the PANI/PDLA sensor was measured in the presence of air atmosphere and different ammonia concentrations. The humidity was maintained constant (RH 54 %) by use of desiccator. A known concentration of gas was injected in the desiccator by using a syringe. All measurements were done at room temperature. The response of the sensor was calculating using the following relation:

\[ \text{response} (\%) = \left( \frac{R_g - R_a}{R_a} \right) \times 100, \]  

where \( R_g \) is the sensor resistance when it is exposed to ammonia and \( R_a \) is the sensor’s own resistance in air atmosphere at room temperature and RH 54 %.

3. Results and discussion
3.1. AFM analysis
Surface morphology of the PANI/PDLA sensor was obtained using AFM – figure 4. A homogeneous distribution of PANI beads with average diameter of 500 nm in the PDLA matrix was observed. The roughness of the surface was calculated as 12.8 nm. This type of morphology insured large surface of the active PANI compound and facilitated the adsorption of bigger amount of gas molecules. In this way the response of the sensor increased.

3.2. Ammonia sensing study
The PANI/PDLA sensor was subjected to successive injection of ammonia gas in the range 10 ppm – 1000 ppm. Typical changes of the sensor resistance at different ammonia concentrations are presented in figure 5. The resistance increased rapidly by exposing the sensor to ammonia and recovered towards
the original value typically 15 min after reverting to the air (this part of the process is not presented on the graphs), indicating good reversibility of the active PANI/PDLA blend film. The change was faster and bigger at higher ammonia concentrations. At ammonia concentration of 1000 ppm the resistance values reached a plateau and then slightly decreased even though the sensor was still exposed to ammonia. This observation could be explained by the specific interactions between the reactive sites of PANI and the ammonia [12].

PANI emeraldine base (EB) in half oxidized and half reduced state had been used for sensor construction. When PANI/PDLA sensor is exposed to NH₃ gas, which possessed electron donating property, the ammonia accepts H⁺ ions from PANI (EB) by forming ammonium ion and converts it into pernigraniline base (fully oxidized) form. As a result the resistance of PANI/PDLA sensor increased. The pernigraniline base is unstable form of PANI. It is able to capture hydrogen and to convert to EB. The small reduction in the sensor resistance was due to reaching an equilibrium between the emeraldine base and the pernigraniline base at constant ammonia concentration. When the sensor was reverting to air, the pernigraniline base was converted back to emeraldine base and the sensor resistance recovered its initial value.

The response time of the sensor – the time for reaching plateau in the resistance/time dependence, depended on the ammonia concentration and decreased when the concentration increased. On the other hand the sensitivity of the signal, which could be expressed as the slope of the resistance/time dependence, was higher at the beginning of the measurement. Therefore it is convenient to calibrate the sensor using the response during the first 120 s of the measurement. Figure 6 presents the dependence of the response on the ammonia concentration 30 s, 60 s, 90 s and 120 s after the ammonia injection in the desiccator.
Figure 6. PANI/PDLA sensor response as a function of ammonia concentrations 30 s (R₃₀), 60 s (R₆₀), 90 s (R₉₀) and 120 s (R₁₂₀) after the ammonia injection.

All these dependences could be correlated to two-parameter power law:

$$response = a \cdot c^b,$$

where $c$ is the ammonia concentration.

The values for the parameters $a$ and $b$, as well as the coefficient of determination $R^2$, calculated for the correlation dependences at different times, are presented in table 1. Knowing the values of these parameters for the PANI/PDLA sensor, one can calculate an unknown ammonia concentration several times during the measurement and estimate the standard error of the measurement.

Table 1. Parameters $a$ and $b$ of the calibration power law dependences, constructed for the sensor response at different times after the ammonia injection.

| Time after the ammonia injection (s) | $a$     | $b$         | $R^2$ |
|-------------------------------------|---------|-------------|-------|
| 30                                  | 1.5±0.17| 0.82±0.018  | 0.998 |
| 60                                  | 5.7±0.50| 0.67±0.014  | 0.998 |
| 90                                  | 8.8±0.63| 0.62±0.011  | 0.998 |
| 120                                 | 12.5±1.34| 0.58±0.017  | 0.996 |

The sensor reliability was strongly dependent on the reproducibility and stability exhibited by the sensor material. The reproducibility of the PANI/PLA blend film sensor was measured by repeating the response measurement a number of times. Results showed that the response of the material was almost constant confirming the reproducibility of the sensor material. Furthermore, the response of the sensor remained about 90 % of the initial response after 60 days, which indicated an acceptable long-term stability.
4. Conclusion
A novel ammonia sensor was successfully developed by casting of PANI base – poly(DL-lactic) acid bled film on Al₂O₃ substrate. The AFM images revealed the morphology of the composites and confirmed homogenous distribution of PANI particles with average diameter 500 nm in the PDLA matrix. The gas sensing property measurement showed that the PANI/PDLA nanocomposite film sensors exhibited fast response/recovery rate, high sensitivity, good reproducibility and acceptable long-term stability over a concentration range from 10 ppm to 1000 ppm. This outstanding sensing performance may be attributed to the large surface of the PANI nanoparticles immersed in the PDLA polymer matrix. Therefore, the proposed PANI/PDLA nanocomposite film sensors are strongly potential candidates for NH₃ detection.

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References
[1] Zhihua L, Xucheng Z, Jiyong S, Xiaobo Z, Xiaowei H, Tahir HE, and Holmes M 2016 Sensor Actuat. B-Chem. 226 553-62
[2] Xu DM, Guan MY, Xu QH, and Guo Y 2013 J. Hazard. Mater. 262 64-70
[3] Chen G, Liu J, Liu M, Li G, Sun Z, Zhang S, Song C, Wang H, Suo Y and You J 2014 J. Chromatogr. A 1352 8–19
[4] Jazan E and Mirzai H 2014 J. Pharm. Biomed. Anal. 88 315–20
[5] Wang J, Zhang W, Li L and Yu Q, 2011 Appl. Phys. B: Lasers Opt. 103 263–69
[6] Jiang C, Liu R, Han G and Zhang Z 2013 Chem. Commun. 49 6647–49
[7] Fakhari AR, Breadmore MC, Macka M and Haddad PR, 2006 Anal. Chim. Acta 580 188–93
[8] Mikhaylov S, Ogurtsov N, Noskov Y, Redon N, Coddeville P, Wojkiewicz JL, and Pud A 2015 RSC Advances 5 20218-26
[9] Pawar SG, Chougule MA, Patil SL, Raut BT, Godse PR, Sen S., and Patil VB 2011 IEEE Sens. J. 11 3417–23
[10] Khuspe GD, Bandgar DK, Sen S and Patil VB 2012 Synth. Met. 162 1822–27
[11] Chabukswar VV, Pethkar S, and Athawale AA 2001 Sensor Actuat. B-Chem. 77 657-63
[12] Bandgar DK, Navale ST, Nalage SR, Mane RS, Stadler FJ, Aswal DK, and Patil VB 2015 J. Mater. Chem. 3 9461-68
[13] Molapo KM, Ndangili PM, Ajayi RF, Mbambisa G, Mailu SM, Njomo N, and Iwuoha EI 2012 Int. J. Electrochem. Sc. 7 11859-75
[14] Matsuguchi M, Io J, Sugiyama G, and Sakai Y 2002 Synthetic Met. 128 15-19