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1 Introduction

Development of miniaturized, low-cost electronic sensor techniques is important to make gas sensors generally available for a broad range of applications. There is a high demand for small and low-cost gas sensors for indoor and outdoor air quality monitoring, medical diagnostics and control of food quality or safety of industrial processes. Hydrogen sensors can, for example, be used in early leakage detection during its storage or transport (especially in vehicles powered by hydrogen fuel cells). Sensitive ammonia sensors can be used to ensure the safe operation of refrigeration systems. Oxygen sensors can be used to optimize the combustion in engines and power plants, and methane sensors can be used to detect gas leaks. Furthermore, several diseases can be detected by analysing trace gases in exhaled breath. The use of electronic sensors in these applications has the advantage that the signal can be easily read and recorded via low-end supporting electronics. The most of the commercially available sensors are based on metal oxides and operated at high temperatures (200 – 400 °C). Thus more and more attentions have been paid to the sensors fabricated from conducting polymers, which showed high sensitivities at room temperature. Low power consumption is necessary requirement for portable devices including cell phones.

2 Background

Polyaniline (PAni) is a conducting polymer, which is of great interest in gas sensing applications due to the ease of its synthesis and its capability to detect various gases [1]. Most of the scientific interest in PAni stems from its unique structure (Figure 1), which may exist in different oxidation states. If it is not fully reduced ($y = 1$), it may be protonated (typically by a Bronsted acid), which is a common mechanism of p-type doping of PAni. Resulting electrical conductivity may be as high as several S/cm.

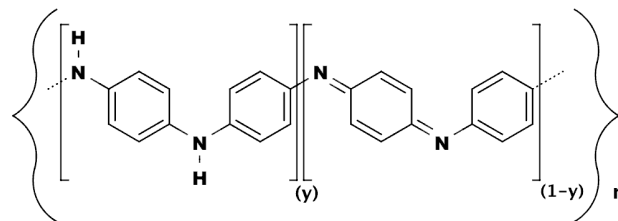


Figure 1 Chemical structure of PAni. Oxidation state vary with value of y .

If gas molecules adsorbed on PAni affect its protonation or oxidation state, their appearance can be detected as a change in electrical conductivity of PAni. Ammonia – as a strong deprotonating agent – became a kind of reference gas to compare different PAni-based sensors. However, very good sensitivity also to other gases (e.g. O₂, NO_x, H₂, CO, H₂S, etc.) was achieved at room temperature, which makes the PAni-based gas sensors advantageous

over the conventional metal-oxide sensors operating at high temperature (typically 200 – 400 °C). This opens a possibility to prepare very cheap sensors with low power consumption.

It should be noted that application of PANi in gas sensors is so far limited by its poor gas selectivity, rather slow response (typically several tens of minutes) and unstable level of baseline resistance. Different structures of PANi (including nanowires or nanoparticles) were proposed to enhance the response time of the sensor by increasing the surface-to-volume ratio. However they typically suffer from relatively poor reproducibility. Common solution of selectivity issue is to use several sensors with different sensitivities to various gases. Analysing multiple signals enables discrimination between gases by matching to the response pattern of particular gas. Tuning of the selectivity of a PANi-based sensor using nanoparticles is shown below.

Different studies have reported enhanced gas sensitivity of PANi nanocomposites containing inorganic nanoparticles [2–7]. Generally, properties of PANi are affected by nanoparticles in two ways. First, n-type semiconducting nanoparticles (e.g. TiO₂, SnO₂, etc. ...) may cause the formation of p-n heterojunctions at PANi/nanoparticle interfaces [8]. As a result, depletion regions may appear at PANi/titania interfaces. Due to the low local density of charge carriers, conductivity in depletion regions is relatively poor. When PANi is affected by deprotonating gas (e.g. NH₃), width of depletion regions increase, which amplifies the sensor response. Second effect of nanoparticles relays on their catalytic properties. Interaction between PANi and particular gas is facilitated by gas molecules adsorbed on a nanoparticle surface. Different nanocomposite structures were proposed comprising catalytic inorganic nanoparticles of Au [2], Cu [9], Pd[10] or Ag [11]. Nanoparticles placed on top of sensorial material contributes the most to the properties of the sensor as they are exposed to the ambient gases. Thus, instead of synthesis of nanocomposite, we just functionalized the thin PANi film by nanoparticles prepared in ionic liquids and immobilized on the PANi film.

Room temperature ionic liquids (ILs) – as media composed entirely of ions – have many unique physical properties that are expected to fit into numerous novel applications [12–18]. Negligibly low vapour pressure of many ILs makes them suitable for use in vacuum. Surface of an IL can be used as a substrate for sputtering deposition of metals or alloys to synthesize extremely clean nanoparticles [19,20]. Due to the absence of surfactants, nanoparticles synthesized in ILs show unique catalytic properties [21].

3 Research objectives

The main research objectives of this thesis are as follows:

- To examine the effect of oxygen plasma treatment to structure and sensory characteristics of a thin polyaniline (PAni) film.
- To synthesize and characterise the nanocomposites based on PAni and inorganic nanoparticles with n-type conductivity in terms of their structure, and electrical and sensorial properties.
- To investigate possibilities to prepare nanocomposites of conducting polymer with nanoparticles synthesized in ionic liquids.
- To investigate possible realizations of a technology that would enable several operations in an ionic liquid: e.g. electrochemical polymerization, electrophoretic deposition, etc.; with an aim to prepare a sensitive gas sensor operated at room temperature.

4 Summary of Achieved Results

In the first part of our study we focused on gas sensor based solely on PANi and tried to find a technological way to prepare this polymer reproducibly and integrate it into the gas sensing structure.

4.1 Gas Sensor Based on a Thin PANi Film

One of the important advantages of PANi is that it can be easily prepared in the form of thin film by *in-situ* chemical polymerization. Objects of complicated forms dipped into the polymerization solution are coated conformingly by a PANi film. We have shown that lift-off process, widely used in microelectronics, can be conveniently applied in patterning of a PANi film [22], though such an approach was not reported so far.

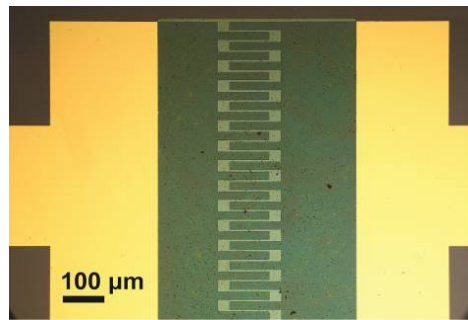


Figure 2 Thin PANi film deposited on gold interdigitated electrodes

Figure 2 shows the rectangle-shaped thin PANi film (green colour) deposited onto gold interdigitated electrodes (thickness of the film was around 110 nm). Since PANi is not soluble in common organic solvents (e.g. acetone), after removing the photoresist PANi remains only in the regions defined by the openings in the photolithographic mask. This way, PANi film can be easily integrated in microelectronic structures.

We have found a new way how to reduce the roughness of a thin PANi film. When a polymerization bath was agitated by a sonication (precise tuning of sonication time is critical to maintain the adhesion of the film) average roughness reduced from ~ 175 nm to ~ 19 nm.

To and enhance the sensitivity of the gas sensor to hydrogen, we proposed the new original technique employing the oxygen plasma treatment of thin PANi film.

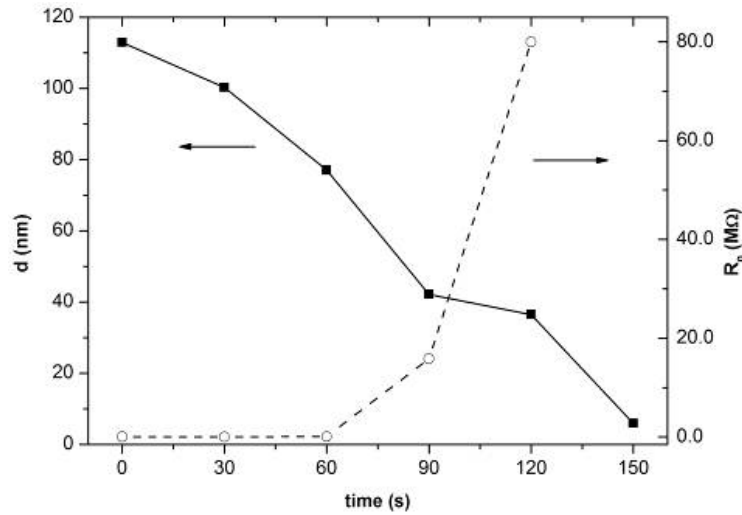


Figure 3 Thickness estimated from the AFM data and electrical resistance of a thin PANi film after variable durations of oxygen plasma treatment.

As shown in Figure 3, with duration of oxygen plasma treatment the thickness of PANi film reduces almost linearly. Thickness reduction contributes to the faster response of the sensor. With the treatment resistance of the sensor increases and after 90 s reached values as high as several MΩ.

Comparing the XPS and FTIR data after different times of plasma treatment we found that plasma modifies the PANi film into the finite depth (of around 40 nm). By proper adjustment of the treatment time the sensorial properties of PANi film can be modified while preserving the sufficiently low sensor resistance (due to the untreated PANi in bottom part of the film).

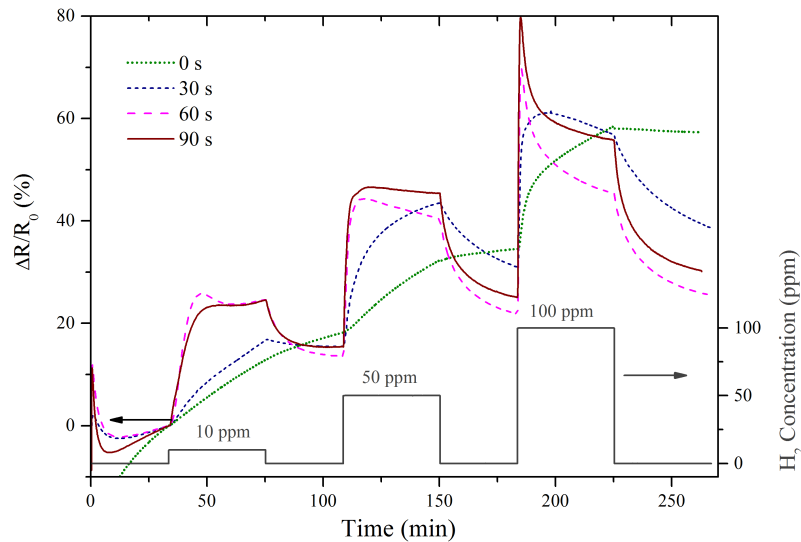


Figure 4 Resistance versus time response of PANi films exposed to 10, 50 and 100 ppm of hydrogen. The films were treated by oxygen plasma for 0 – 90 s.

Figure 4 shows the significant enhancement in response and recovery times of the gas sensor after 60 s of plasma treatment. Moreover, the sensitivity to hydrogen increased significantly to more than 20 % at concentration as low as 10 ppm.

PAni film represents the gas sensor that can be easily prepared at very low cost and operate at room temperature. To modify the properties such as sensitivity and selectivity, PAni can be combined with different inorganic nanoparticles. Firstly, we focused on titania nanoparticles (with n-type conductivity) and synthesized different PAni-TiO₂ nanocomposites by electrochemical polymerization *in-situ* on the surface of interdigitated electrodes. We also investigated the possibility to use IL as an electrolyte solution containing colloidal nanoparticles. Secondly, we focused on the metallic nanoparticles synthesized in ILs and immobilize them onto the surface of thin PAni film by the electrophoretic deposition.

4.2 PAni-TiO₂ Nanocomposites

To exemplify the effect of titania nanoparticles onto the depletion zone, we modelled the interface between the PAni and TiO₂ applying the formalism used in semiconductor physics. Figure 5a shows the band gap positions of both materials. To obtain the potential distribution at the heterojunction, we solved the Poisson equation for electrostatic potential,

$$\frac{d^2V(x)}{dx^2} = \frac{-q}{\epsilon_0\epsilon_r(x)} [p(x) - n(x) + N_D^+(x) - N_A^-(x)], \quad (1)$$

where $\mathbf{p}(\mathbf{x})$ and $\mathbf{n}(\mathbf{x})$ are densities of charge carriers (holes and electrons) in semiconductor structure. $N_D^+(\mathbf{x})$ and $N_A^-(\mathbf{x})$ are concentrations of immobile donors and acceptors, respectively. $V(\mathbf{x})$ is the electrostatic potential at position \mathbf{x} , \mathbf{q} is elementary charge and $\epsilon_0\epsilon_r(\mathbf{x})$ is permittivity. Adopting the formalism of effective densities of states also to PAni we estimated the energy band structure at TiO₂ – PAni interface (Figure 5b).

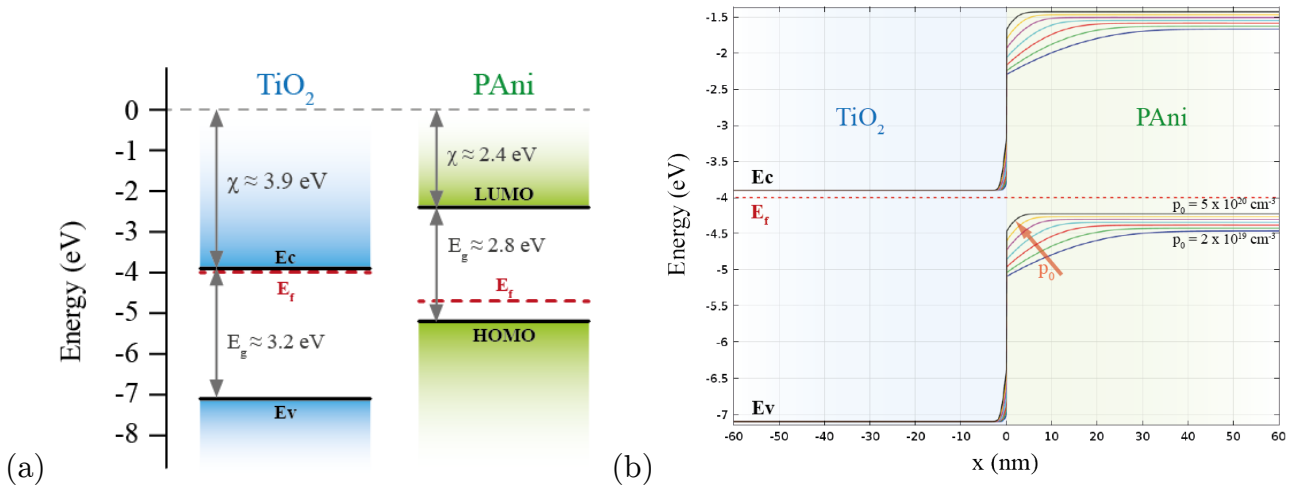


Figure 5 (a): Schematic energy diagram of TiO₂ - PAni heterostructure and (b): calculated energy band structure at the TiO₂ - PAni interface.

We were also able to derive the concentration of holes in PAni close to the heterojunction (Figure 6a). Hence, one can state that conductivity in this region is very low compared to the bulk PAni. Importantly, the thickness of such a depletion layer is in the range of tens of nm,

which is comparable to characteristic dimension of typical PANi nanostructures. Thus, we expected that even low content of titania would have significant influence to sensor's properties.

Our simulation of p-n heterojunction at PANi/titania interface showed that at low density of holes (p_0) the width of depletion region in PANi (x_p) is more sensitive to variations in p_0 (Figure 6b).

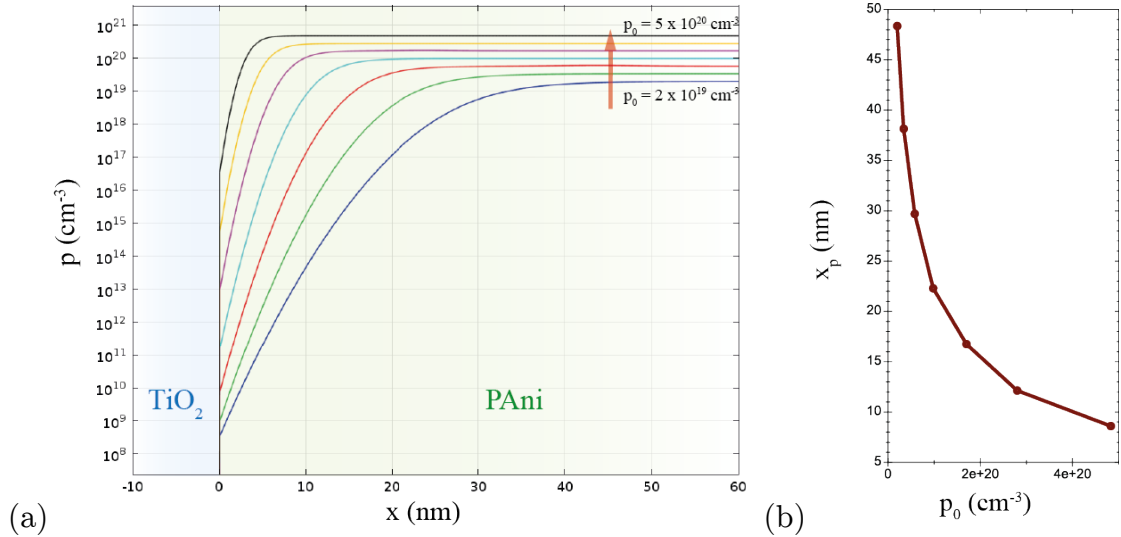


Figure 6 (a): Charge carrier (hole) density in PANi close to the TiO₂ – Pani heterojunction for various hole densities p_0 . (b): Width of depletion region in PANi versus the hole density p_0 .

4.3 PANi-TiO₂ Nanocomposites

We studied properties of PANi-TiO₂ nanocomposites synthesized by electrochemical polymerization in colloidal solution of nanoparticles. Electrochemical polymerization allows for an easy control of the final thickness of a nanocomposite and saving in the cost of sometimes very expensive nanoparticle material.

Depending on parameters of electrochemical polymerization, a nanocomposite was deposited in the form of a thin film (at low aniline concentration and fixed potential of working-electrode) or nanofibers (using cyclic voltammetry at higher aniline concentration). Although the former method resulted into a smooth film, we had to use an initial PANi film prepared by chemical polymerization to bridge the gap between the microelectrodes (10 μm wide). As a result we got a stacked PANi/PANi-TiO₂ sensor. The Content of aniline in the electrolyte was only 0.01 mol/L and we used fixed working-electrode potential of 1 V.

TEM micrograph in Figure 7 shows the plane view of a wedge-etched specimen prepared from the stacked sensor. Number of the titania nanoparticles (dark dots) is higher close to the top of the image (where the specimen is thicker) indicating that nanoparticles do not occur just on the surface but they are also embedded within the PANi film. The presence of titania was

confirmed also by small angle XRD diffraction. Detailed inspection of TEM micrograph revealed that the size of nanoparticles ranges from 12 to 4 or even less nanometres. Interestingly, there is almost no aggregation of the nanoparticles within PANi matrix suggesting that large aggregates are simply too big to be captured from the stirred solution onto the surface of PANi. This is another advantage of the electrochemical synthesis over the PANi-TiO₂ composites synthesized by chemical polymerization [23].

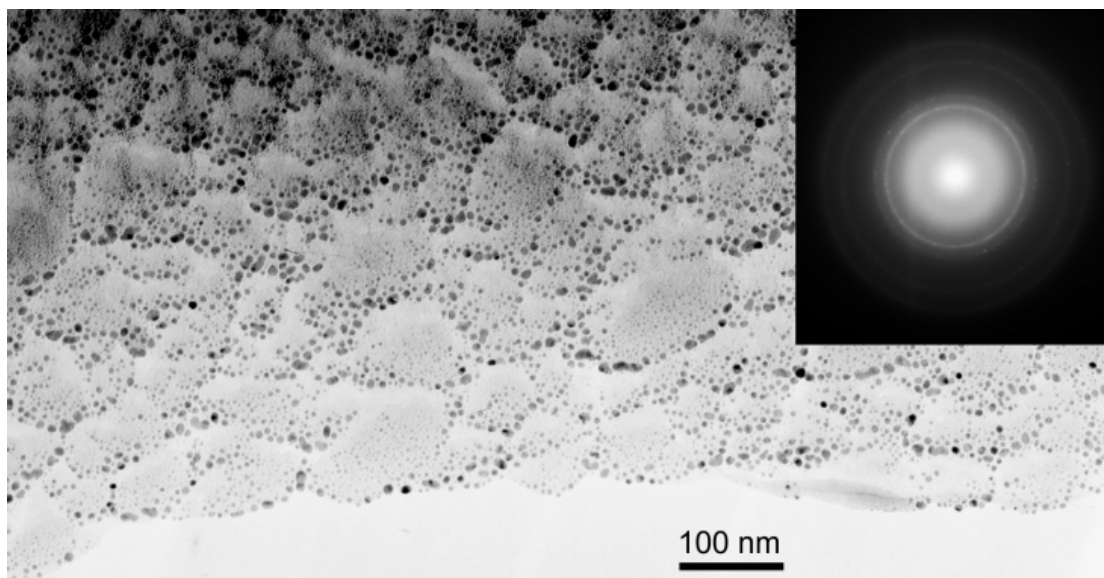


Figure 7 TEM micrograph of PANi-TiO₂ nanocomposite film (plane view). Electron diffraction pattern is inserted.

The stacked sensor PANi/PANi-TiO₂ sensor exhibited excellent ammonia sensitivity which exceeds 600 % at 100 ppm of NH₃. In spite that there was an initial titania-free PANi film, the baseline resistance of the sensor was relatively high; about 600 MΩ. We assume that high resistance is due to both the high polymerization potential – which decreases the doping level of PANi (oxidation state was turned to pernigraniline) [24] – and the depletion regions around titania nanoparticles. This is in good agreement with our expectations based on simple model of PANi/TiO₂ interface. As **Error! Reference source not found.b** suggests, the lower the conductivity of PANi (low value of p_0) the wider the depletion zones around nanoparticles. Moreover, at low density of holes (p_0) the width of depletion regions in PANi (x_p) is more sensitive to variations in p_0 (e.g. due to the gas adsorption). This explains the higher sensitivity of the sensor at low doping level of PANi.

We wanted to decrease the resistance of the sensor to the value more practical for applications. Therefore, we lowered the potential of the working electrode, increased the content of aniline in the polymerization solution (to 0.5 mol/L) and used cyclic voltammetry instead of fixed potential of working electrode to gain better control over the polymerization process. As a result PANi-TiO₂ nanofibers were deposited instead of a thin film. This implies

the different growth mode of PANi. In case of thin film the growth was presumably limited by monomer diffusion towards the electrode, since the monomer concentration was relatively low and polymerization happened almost instantly after the monomer molecule reached the surface of working electrode (due to high electrode potential). Cathodic and anodic limits of cyclic voltammetry were -150 mV and 850 mV. Since the content of aniline was higher and polymerization occurred only close to the anodic limit of the potential, we assume that PANi growth was limited by the rate of the polymerization.

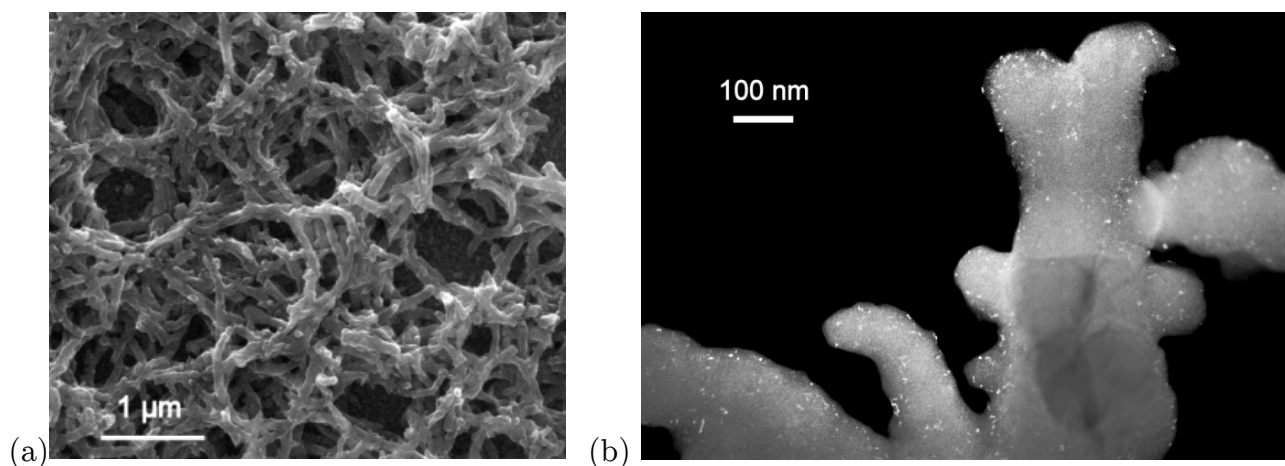


Figure 8 (a): SEM image of a PANi-TiO₂ nanocomposite after ten cycles of electropolymerization. (b): TEM micrograph of PANi-TiO₂ nanocomposite as observed in dark-field. Titania nanoparticles are visible as white spots.

SEM micrograph in Figure 8a shows the dense mesh of PANI-TiO₂ nanofibers deposited after ten polymerization cycles. Such a mesh can easily bridge the gap between the digits of the planar interdigitated electrodes. Presence of titania nanoparticles was confirmed by TEM inspection (Figure 8b) and good binding between PANi and titania was evidenced by small blue-shifts in positions of some peaks in FTIR spectrum attributed to PANi.

Importantly, the baseline resistance of the nanofiber sensor is only 1.3 kΩ, which is more than two orders of magnitude lower than that of stacked PANi/PANi-TiO₂ sensor.

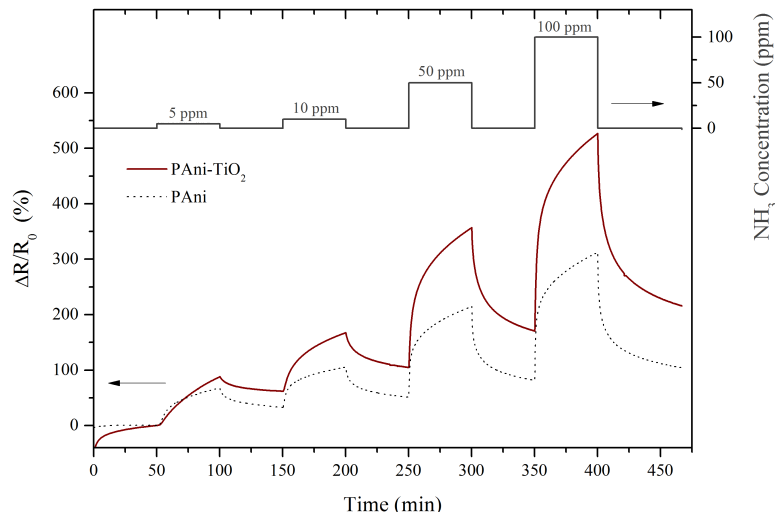


Figure 9 Comparison of dynamic responses of nanocomposite layer of PAni-TiO₂ nanofibers and reference titania-free sample.

Figure 9 shows the dynamic response of PAni-TiO₂ nanofibers to ammonia. Compared to titania-free nanofibers, the sensitivity of the sensor increased twofold to about 500 % at 100 ppm of NH₃. However, at NH₃ concentration as low as 10 ppm, there was only minor enhancement in response of the nanocomposite sensor. This implies that depletion regions at TiO₂-Pani interfaces take effect mostly at higher gas concentrations.

We have shown that electrochemical polymerization can be used to synthesize a sensitive element of a gas sensor *in-situ* in a colloidal suspension of nanoparticles. In the following part of this work we have focused on nanocolloids based on ILs. Nanoparticles of various materials and shapes can be synthesized in ILs by both chemical and physical synthesis. Common example of the latter is vacuum sputtering deposition on the surface of an IL [25]. Resulting colloids are extremely pure and do not contain any additional stabilizers (e.g. surfactants). Thus, nanoparticles synthesized in ILs show very good catalytic activity [26]. However, to the extent of our knowledge, there is not evidence yet on an application of IL-based colloids in synthesis of nanocomposites based on conducting polymers.

In this thesis we investigated two different methods to enhance the properties of PAni-based gas sensor by the nanoparticles dispersed in IL. First, we tried to replace the water-based electrolyte used in electrochemical polymerization of aniline by the IL. Using potentiostatic polymerization we synthesized PAni-TiO₂ nanocomposite (titania nanoparticle were dispersed in the IL prior the polymerization) so we could compare our results with those of nanocomposites prepared in aqueous electrolyte. Second, we used electrophoretic deposition (EPD) to immobilize catalytic nanoparticles of various metals onto the surface of thin PAni film.

4.4 Pani-TiO₂ Nanocomposite Synthesized in an Ionic Liquid

Ionic liquid [BMIM][BF₄] was used as an electrolyte in electrochemical synthesis of PANi-TiO₂ nanocomposite. Prior the synthesis, titania nanoparticles and aniline were added into the IL. PANi-TiO₂ nanocomposites were deposited onto the working electrode in potentiostatic regime at the electrode potential of 850 mV or 1700 mV. In the former case we observed only very slow polymerization rate. Extending the polymerization time (to several hours) we were able to deposit PANi-TiO₂ film with thickness comparable to that of the film synthesized in aqueous electrolyte. Nevertheless, bridging the gap between the interdigitated electrodes became an issue again. SEM micrographs revealed that PANi was deposited strictly onto the gold microelectrodes and SiO₂ in the gap between the digits remained clear suggesting that molecules of aniline radicals or PANi more strongly bond to each other than to the substrate (Volmer-Weber type of growth).

To bridge the gap between the digits we enhanced the polymerization rate by increasing the potential of the working electrode to 1700 mV. Compared to the previous case, the current through the electrochemical cell was more than fivefold and it increased during the polymerization (it doubled during the 50 minutes) indicating the increased surface area of the electrode. This was confirmed by the SEM images (Figure 10), which showed that PANi-TiO₂ covers also the gap between the digits. Moreover some seeds of PANi nanofibers with diameter around 180 nm appeared on the surface.

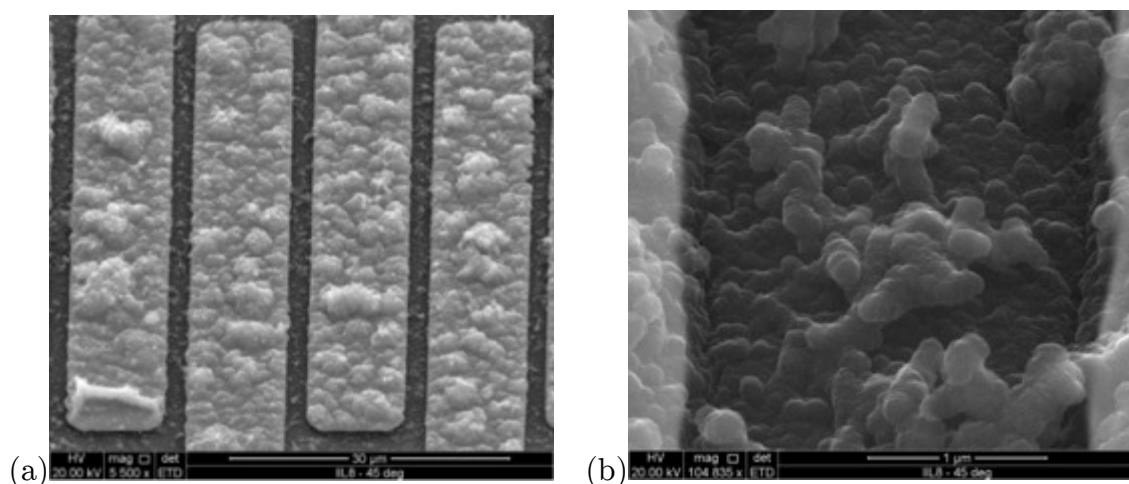


Figure 10 SEM micrographs (45° tilted view) of a PANi-TiO₂ nanocomposite deposited on interdigitated electrodes in [BMIM][BF₄] at a fixed potential of 1700 mV. View (b) shows a detail of the gap between the digits.

FTIR spectra of PANi-TiO₂ nanocomposite and [BMIM][BF₄] ionic liquid are shown in Figure 11. Some of the absorption peaks of [BMIM][BF₄] (at 1573 cm⁻¹, 1225 cm⁻¹ or at 1047 cm⁻¹) can be recognized in the spectrum of PANi-TiO₂ indicating the presence of ionic liquid in the nanocomposite film. FTIR spectrum of PANi-TiO₂ revealed that PANi is partially in the form

of protonated emeraldine. The conducting form of PANi is indicated by broad absorption band of charge carriers at wavenumbers higher than 2000 cm^{-1} as well as by the $-\text{NH}^+=$ vibration band (located around 1090 cm^{-1}) and absorption band of delocalized π -electrons (at 1298 cm^{-1}). Since there was no dopant (e.g. some protic acid) added into the polymerization solution, in our opinion IL itself is a dopant that causes the protonation of PANi. We proposed the possible mechanism of PANi-IL interaction that involves hydrogen bonding; similarly to PANi doping by camphorsulfonic acid [27]. Relatively strong absorption band that appeared at 3293 cm^{-1} implies the interaction through H-bonding.

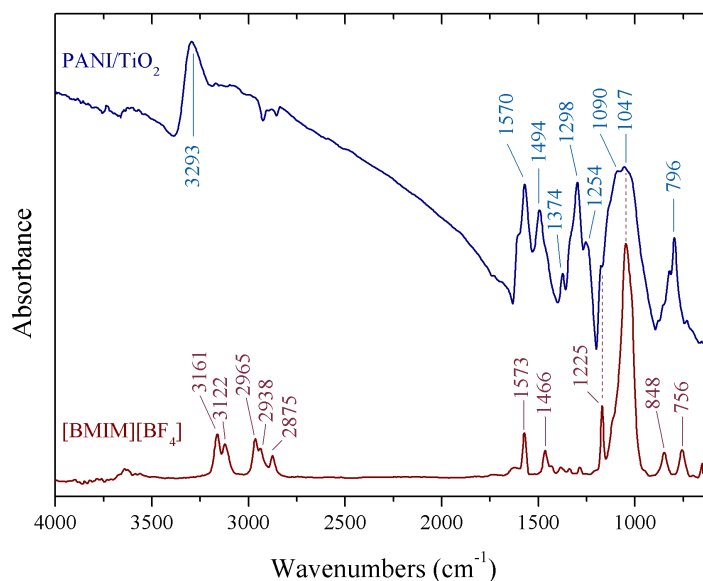


Figure 11 FTIR spectra of PANi-TiO₂ nanocomposite synthesized at 1700 mV and [BMIM][BF₄] ionic liquid.

Doping of PANi by an IL was not reported so far and we believe that it is an important finding since ILs are more stable dopants than typical inorganic acids (no dopant leakage during the sensor operation). Based on our experiments we assume that various ionic liquids show different performance as dopants and an important role is played also by the nature of anion. For example, polymerization resulted into insulating base form of PANi when BF₄ was replaced by triflate anion.

The ammonia response of the gas sensor based on IL-doped PANi (Figure 12) was much lower than that of the HCl doped PANi: the resistance increased only by about 60 % per 100 ppm of NH₃. However, the sensitivity increased several times with addition of titania nanoparticles. PANi-TiO₂ sensor showed response as high as 300 % at 100 ppm of ammonia. Electrochemical polymerization in ILs represents practically waste-free technology of nanocomposite synthesis. In addition to many different nanocolloid materials available, the electrochemical aspects of ILs – like wide electrochemical window or low solubility of oxygen [28] – bring certain advantages to the PANi synthesis.

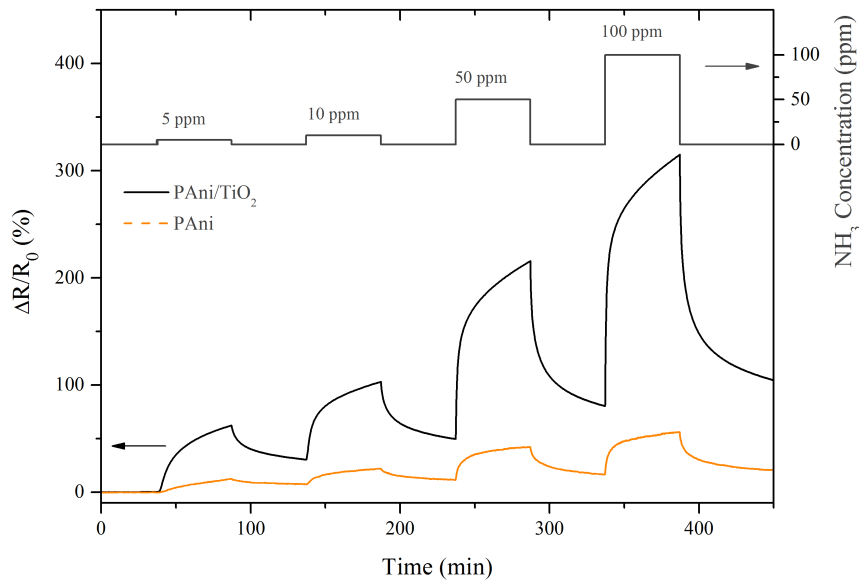


Figure 12 Responses of PANi and PANi-TiO₂ chemiresistors synthesized in [BMIM][BF₄] ionic liquid to 5, 10, 50 and 100 ppm of NH₃.

Although we studied only PANi-TiO₂ nanocomposite synthesized in IL, various nanoparticles can be dispersed or prepared in different ILs.

We have synthesized different metallic nanoparticles by sputtering deposition onto the surface of ILs. We expected that catalytic activity of nanoparticles on PANi surface (that are in direct contact with ambient gas) contributes the most to the properties of the sensor. Thus, rather than prepare nanocomposite (where relatively large amount of colloid is needed) we just functionalized the surface of PANi by immobilization of the nanoparticles.

4.5 Modification of a PANi Gas Sensor with Nanoparticles Synthesized in ILs

We investigated the possibility to use EPD to immobilize metal nanoparticles synthesized in ILs onto the surface of a gas sensor based on polyaniline (PANi). In common IL-based nanocolloids there is a preference in the polarity of ions adsorbed on the nanoparticle surface [29]. In case of metal nanoparticles, typically anions occur closer to the nanoparticles, thus negative surface charge is developed making the IL-based colloids processable by anodic electrophoretic deposition (EPD) (Figure 13). However, there are also some limitations, which stem from high viscosity of most of the ILs and high concentration of ions in the EPD solution. The viscosity of ILs originates from vigorous electrostatic interactions between the ions [30] and can be reduced by increasing the temperature [31] or by diluting the IL with a suitable solvent [32]. In our experiments, we used methanol to dilute the colloidal solutions of nanoparticles in ILs. The content of IL in the final solution was 2.5 vol% or 12.5 vol%.

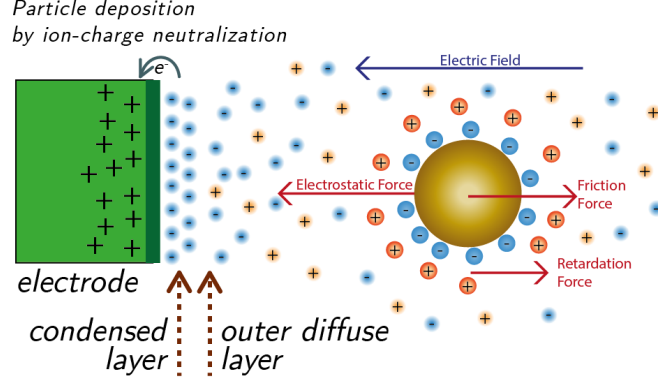


Figure 13 Migration of a particle in an electrolyte and main forces involved in electrophoretic movement.

Another limitation stems from accumulation of ions at the surface of the electrodes and formation of electrical double layers. Hence, the applied potential is confined into the thin double layers, which screen the intensity of electric field in the bulk of the electrolyte. We simulated such an ion distribution using the mean-field approximation based on Poisson equation,

$$-\nabla \cdot (\epsilon \nabla \psi) = \sum_i z_i e c_i \quad (2)$$

where $\epsilon = \epsilon_0 \epsilon_r$ is the permittivity of the solution and $z_i e$ is the charge of the ion i . In quasi-thermal equilibrium concentration of ions c_i generally obeys the Boltzmann distribution. In case of IL, Boltzmann distribution has to be corrected for steric effects due to the relatively large ions and high potential of the electrode. Corrected distribution is in the form,

$$c_i = c_0 \frac{e^{-\frac{z_i e \psi}{k_B T}}}{1 + c_0 a^3 \sum_i \left(e^{-\frac{z_i e \psi}{k_B T}} - 1 \right)}. \quad (3)$$

where c_0 is the reference concentration of ions in bulk of the IL, a^3 is the effective size of the ions and k_B is Boltzmann constant and T is temperature. Figure 14 shows the distribution of ions near the positively charged electrode in ionic liquid [BMIM][PF₆]. It is clearly seen that at voltages higher than 0.2 V density of anions at the electrode is limited by steric effects. Thus, condensed layer of crowded ions (where concentration is limited by effective ion size) is formed in addition to the diffuse layer (schematically depicted in Figure 13). Effective volume of [PF₆]⁻ anion was $a^3 = 0.122 \text{ nm}^3$.

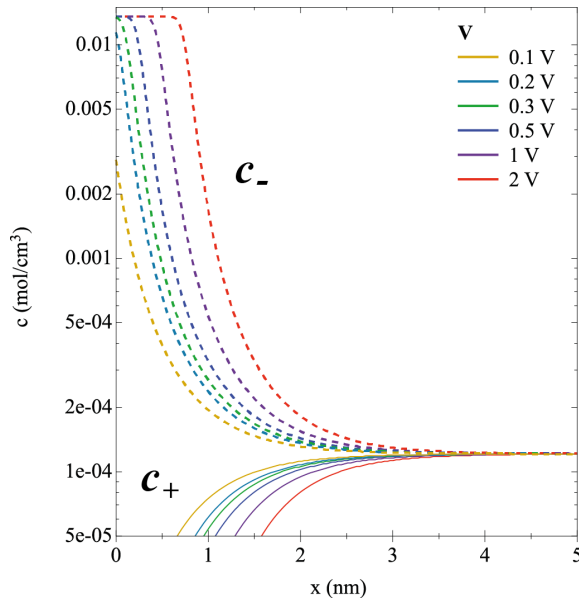


Figure 14 Spatial distribution of anions and cations(in $[BMIM][PF_6]$) near the positively charged electrode at different voltages.

Since the thicknesses of the condensed and diffuse layers are in the range of nanometres, electrode voltage of several volts leads to electric field intensity as high as tens of MV/cm. At such a high intensity, though lowered by finite size of ions, electrochemical reactions may occur at the electrode surface. To prevent the destruction of the PANi-based sensor by the electrochemical treatment we used **pulsed** DC voltage during the EPD of the nanoparticles. Nanoparticle immobilization took place in a small EPD cell (1 ml in volume) equipped with two electrodes: PANi film as an anode and Pt wire as a cathode, connected to positive and negative terminals of the voltage source, respectively (Figure 15). DC or periodic square pulsed voltage was applied between the electrodes. Widths of voltage pulses and gaps were equal (50 % duty cycle) and frequency of the square wave was 1 Hz (pulse width of 0.5 s).

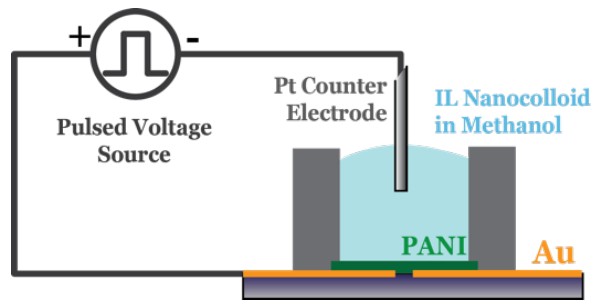


Figure 15 Schematic representation of the EPD experiment setup.

Electrical double layers at the electrodes are charged after the application of a voltage pulse and discharged during the gap between the discrete pulses (zero potential difference between the electrodes). Due to the displacement current related to charging of double layers the electrical intensity is non-zero across the whole EPD cell and drives the electrophoretic

migration of nanoparticles within the colloidal solution. As soon as double layers are charged, spatial redistribution of ions causes the shielding of the electrode potential.

At small amplitude of the pulsed voltage (up to 1 V), there was only displacement current that repeatedly charged and discharged the double layers and we did not observe any immobilized nanoparticles. Absence of conduction current suggests that electrodes are almost ideally polarizable and there is no charge transferred between the electrodes and electrolyte (no electrochemical reactions). One of the deposition mechanisms, which can be taken into account, is the neutralization of nanoparticle charge [33]. According to this mechanism, for successful EPD the charge of the ions surrounding a nanoparticle has to be neutralized by electron transfer between the electrolyte and electrode where nanoparticle is to be deposited (**Error! Reference source not found.**). Thus, beside the displacement current, at least small conduction current should be involved in the EPD, though it is connected with electrochemical reactions.

At pulse amplitude greater than 3 V we found some cracks in thin PANi film and it started to peel off the substrate after several minutes of EPD. Presumably, some ions can diffuse through the PANi film and electrochemical effects (i.e. anodic etching) occur also at the surface of underlying gold microelectrodes. In common EPD applications electrochemical reactions may influence the uniformity or other properties of the final deposit (e.g. by gas evolution due to the electrolyte decomposition) [34]. In our case the electrochemical reactions are even more pronounced as they may affect the properties of thin PANi film (e.g. its oxidation state and/or protonation). PANi represents the sensitive element of gas sensor and should remain in its conducting state to ensure proper operation of the sensor.

However there was an intermediate range of voltages from around 1.25 V to 2.25 V, that we considered the EPD window, where sensor structure can withstand the EPD process for sufficiently long time in order to immobilize nanoparticles without damaging the PANi film.

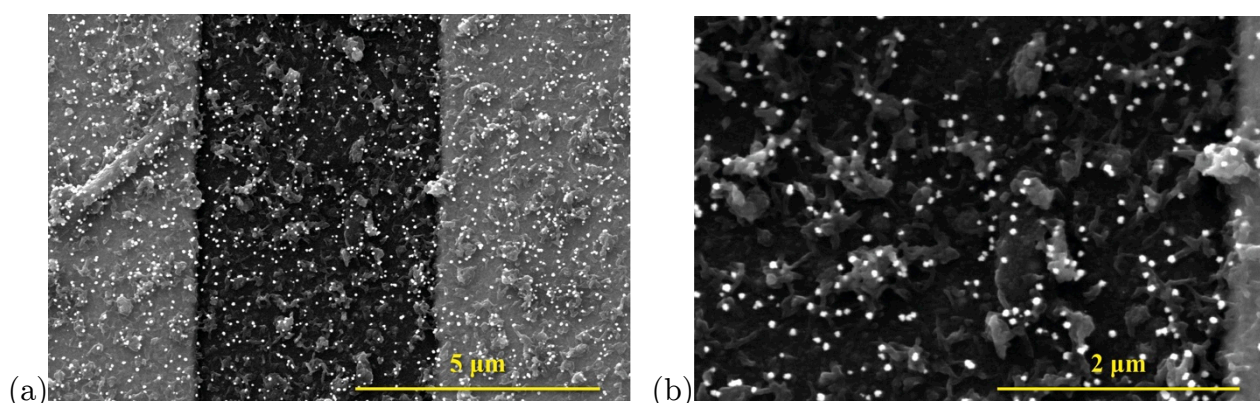


Figure 16 Surface of PANi film deposited onto gold interdigitated electrodes after 10 min of EPD deposition of Ni-Fe nanoparticles (bright dots) in 2.5 vol% solution of [BMIM][PF₆] in methanol.

Figure 16 shows the SEM micrographs of the surface of thin PANi film after immobilization of Ni-Fe nanoparticles. The content of [BMIM][PF₆] in the methanol solution was only 2.5 vol%, amplitude of the applied pulsed voltage was 1.75 V and duration of the EPD was 10 minutes. The surface of PANi seems to be uniformly covered with the nanoparticles. More detailed SEM inspection confirmed that they were actually clusters (around 50 nm in size) of few aggregated nanoparticles.

It can be expected that stability of nanoparticles relates to the content of IL in the solution. Figure 17 compares the surface of PANi after 10 and 30 minutes of deposition in a solution containing higher content of IL with colloidal nanoparticles (12.5 vol%). In spite the increased amount of nanoparticles, there were only very few nanoparticles immobilized after 10 minutes of EPD. However, PANi surface was successfully decorated by nanoparticles when deposition time was extended. Size of the immobilized nanoparticles was around 15 nm and almost no aggregation was observed.

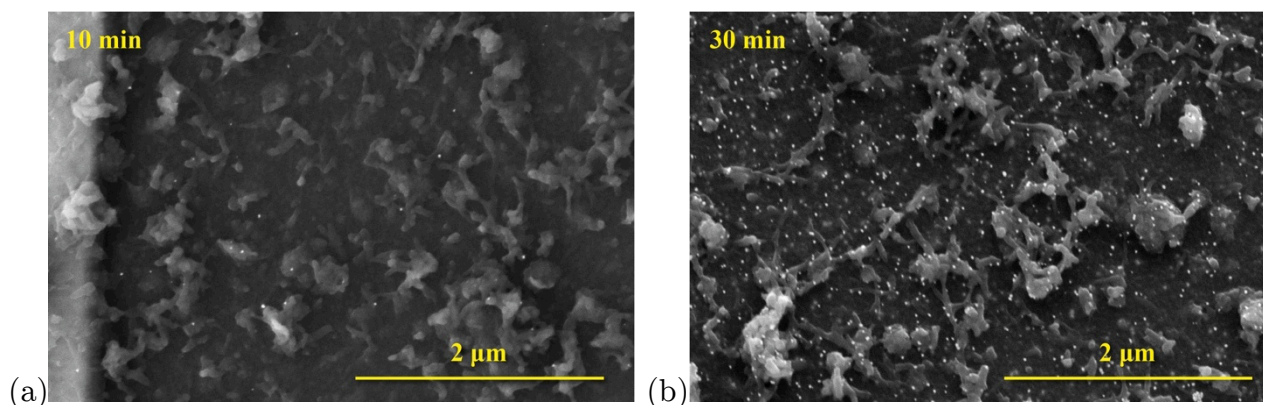


Figure 17 Surface of PANi film with immobilized Ni-Fe nanoparticles (bright dots) after (a) 10 min and (b) 30 min of pulsed EPD in 12.5 vol% solution of [BMIM][PF₆] in methanol.

Our experiments suggest that there is a trade-off between the amount of deposited nanoparticles (EPD efficiency) and their stability against aggregation. This trade-off depends on the content of IL in the solution. It can be argued that for successful immobilization of nanoparticles, the stabilization mechanism that prevents nanoparticles from aggregation has to be deteriorated at the electrode surface. This is done when ions adsorbed on a nanoparticle surface are oxidized at the electrode (i.e. their charge is neutralized). Microscopic observations were done after vigorous washing with a jet of acetone and isopropyl alcohol. The nanoparticles have remained attached to the surface of PANi indicating that they are rigidly fixed by van der Waals forces.

Figure 18 shows the ammonia response of three chemiresistive sensors based on PANi film decorated by Ag-Cu, Ni, and Ni-Fe nanoparticles. We have found that the sensitivity of the sensor decorated by Ag-Cu nanoparticles was almost twice (to ~ 560 % at 100 ppm of NH₃) the sensitivity PANi/Ni and PANi/Ni-Fe samples. It can be expected that also other gas-sensing properties of thin PANi film (especially its selectivity) can be tuned by its

functionalization with nanoparticles. Discrimination between the individual gases could be possible by using the several gas sensors based on the same PANi structure and functionalized with different nanoparticles (the principle of electronic nose).

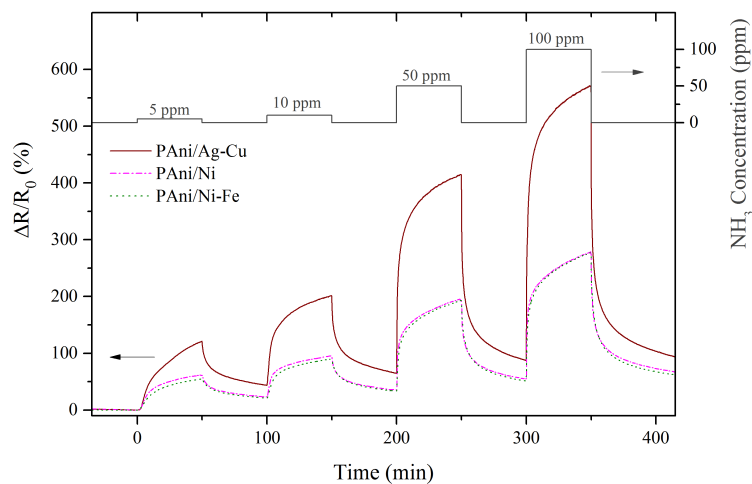


Figure 18 Comparison of dynamic responses of thin PANi films decorated with Ag-Cu, Ni and Ni-Fe nanoparticles to gaseous ammonia at room temperature.

5 Conclusions

In this thesis we investigated several novel methods to synthesize gas-sensing structure based on PANi film or PANi-based nanocomposite films. We tried to address the limitations of PANi as a sensitive material of a gas sensor by proposing novel techniques for synthesis and functionalization of PANi structures. We mostly used sensors based on thin film of PANi synthesized by chemical polymerization, which is a scalable, cheap and well reproducible process.

We have used, for the first time, the oxygen plasma as a suitable treatment of PANi film to modify its properties. We found substantial increase in its sensitivity to hydrogen. Also the response time of the sensor was shorter, due to the lower thickness of the film. This technology eventually became a subject of PCT patent application [35].

Then, we focused on nanocomposites of PANi and inorganic nanoparticles. We found electrochemical polymerization of PANi in colloidal solution of nanoparticles to be very versatile method of nanocomposite synthesis. Adjusting the parameters of synthesis we were able to prepare thin film or a mesh of nanofibers bridging the gap between the digits of the sensor's electrodes. For the first time we have used electrochemical polymerization to prepare PANi-based nanocomposite in an ionic liquid. We have found that PANi synthesized in [BMIM][BF₄] was in its conducting state without addition of any other dopant. This opens the way to prepare conducting PANi-based nanocomposites from various nanoparticles dispersed or synthesized in IL. Moreover, ILs are expected to be more stable dopants than majority inorganic acids.

Finally we have successfully used EPD to functionalize the surface of a PANi film by nanoparticles synthesized in different ILs. This pioneering application of EPD was achieved by precise tuning of parameters related to the colloidal solution and applied electric field. We have proposed the pulsed DC EPD to overcome the shielding of the electrodes (due to ions accumulated in electrical double layers) as well as to avoid degradation of PANi (by deprotonation) or electrodes of the sensor (by anodic etching). By adjusting the content of IL in the solution, stability of nanoparticles can be preserved while keeping the reasonable duration of the deposition.

Although we have demonstrated the immobilization of nanoparticles only onto thin PANi film, the EPD technique can be adopted to functionalize various much more complicated structures (e.g. nanofibers).

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