Concepts for low cost sensors based on molecularly imprinted polymers (MIP) for gas phase detection of explosives

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Abstract
Recent terrorist attacks such as the bombing in New York at 11.9.2001, suicide bombings in the middle east or e.g. in London Underground transportation systems in July 2005 show that the today used detection techniques for explosives (Imaging by X-ray, neutron activation techniques, IMS, NQR,) are inadequate and have to be improved as well as new counter-action / detection concepts have to be developed. In concerns with national security there are needs for inexpensive, rapid, high sensitive and selective sensors. In this respect, e.g. mass-sensitive devices coated with substance specific molecularly imprinted polymers (MIPs) look promising to achieve low-cost detection devices capable of detecting explosives traces fast, sensitive and reliable. ICT works on the development of molecularly imprinted polymers (MIPs) as specific sensing layer to detect explosives from the gas phase. Preliminary results and possible concepts for MIP-based low-cost sensors are presented.

1 Introduction

State of the art equipments used e.g. in airport portal systems or swapping technologies (Imaging by X-ray, NQR, neutron techniques, IMS) are expensive, big-sized, heavy and/or need high air-volumes or special swaps for detecting particulate explosives. X-ray techniques mainly detect metal-containments and igniters instead of the explosive substance itself. Moreover neutron and nuclear quadrupole resonance techniques have typically very high detection limits of several grams (e.g. 50 to 100 g for TNT).

Direct counter-action of suicide bombers will require the development of fast, sensitive and long-range specific detection techniques (> 10 to 100 m) in order to have a realistic chance to stop the suspect person before a bombing could occur. Techniques achieving such a performance currently are world-wide not available. Another way to proceed to counteract possible terrorist attacks would be to develop suitable self-reporting sensor networks able to detect explosives plumes of suspect persons or transported goods in a very sensitive and rapid way. Like nowadays everywhere installed fire / smoke sensors these sensors should be able to give information about the position and / or movement of suspected subjects or objects. Most challenging prerequisite for such self-reporting sensors / networks will be the necessity of suitable micro sensors that can detect targeted explosives components very rapid, sensitive and reliable preferably without the need for costly pattern recognition procedures / software modules as well as trapping devices for sample enrichment.

Instead of today used technologies e.g. mass-sensitive devices coated with molecularly imprinted polymers (MIP) seem to provide promising low-cost detection devices for use in self-reporting sensor networks for the surveillance of public areas or as on-line / in-line sensors in different vehicle transportation systems (cars, trucks, containers etc.) in order to directly detect and warn for possible terrorist threats by hazardous components. Objective of work at ICT is to develop molecularly imprinted polymers (MIP) having a high selectivity and sensitivity for relevant explosives commonly used by terrorists such as 2,4,6-TNT, 2,4-DNT or TATP. These substances exhibit vapour pressures in the ppb to percentage range, which in principle enables a possible detection of these substances via vapour trace

detection methods [1]. Preliminary results achieved for the synthesis of particulate MIPs capable of detecting 2,4,6-TNT or 2,4-DNT first results of the synthesis of MIPs directly on sensor surfaces will be presented as well as possible concepts for MIP-based low-cost sensors.

2 The technique of molecular imprinting

The technique of molecular imprinting allows the formation of specific recognition sites in macromolecules. In this process, functional and cross-linking monomers are copolymerised in the presence of a target analyte (template). The functional monomers form a complex with the imprint molecule and in the subsequent polymerisation the functional groups are held in position by the highly cross-linked structure. Subsequent removal of the template reveals binding sites that are complementary in size and shape to the analyte (figure 1). The complex between monomers and template can be formed via reversible covalent bonds [2] or via non-covalent interactions [3, 4, 5] such as hydrogen bonds.

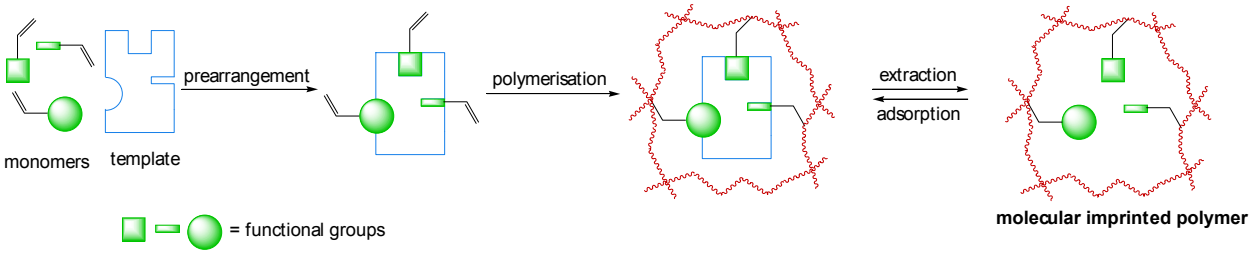

Figure 1: principle of molecular imprinting

For TNT or DNT as template it is not possible to use the covalent approach. Furthermore with the non-covalent approach we are able to use a large pool of functional monomers that are commonly used in the field of molecular imprinting. Because of the known problem that nitroaromatics are weak hydrogen bond acceptors [6], for the synthesis of the MIPs we used several acrylates with different functional groups as monomers (Figure 2) and ethylene glycol dimethacrylate (EGDMA) as cross linking agent.

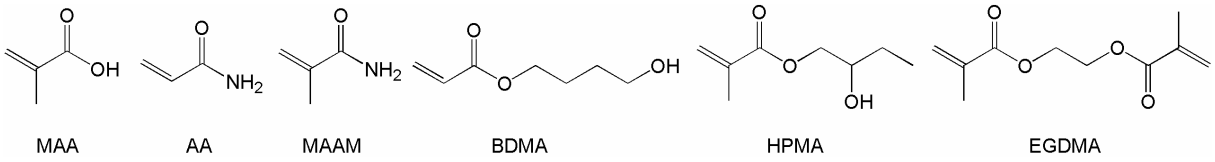

Figure 2: Tested monomers (MAA: Methacrylic acid, AA: Acrylamide, MAAM: Methacrylic amide, BDMA: Butandiolmonoacrylate, HPMA: 2-Hydroxypropylmethacrylate) and used cross linker EGDMA

3 Experimental

Synthesis of TNT- and DNT-specific particulate MIPs was achieved via suspension polymerisation [7] using AIBN as initiator for the 24 hours lasting radical polymerisation at 60 °C [10]. The microspheres were washed with water, chloroform, toluene and acetone and dried in vacuum. To remove the TNT and non reacted monomers the beads were Soxhlet extracted with Chloroform and subsequently extracted with supercritical carbon dioxide at 50°C and 150 bar. At least a removal of > 99,7% of the template was achieved. To test the performance of the synthesized polymer beads imprinted by 2,4,6-TNT or 2,4-DNT, the MIPs were exposed to a constant flow of these explosives accomplished in a special vapour generator [9]. The adsorbed amounts of explosives were measured via GC with mass-selective detection in combination with indirect solid phase micro extraction (SPME). To verify the enhanced uptake of the templates from the vapour stream, the imprinted polymer type was always tested against the non-imprinted correspondent.

Direct synthesis of TNT-imprinted MIPs as thin film coatings on so called quartz crystal micro balances, QCMs was performed via manual spray-coating with an art air-brush gun. In later experiments we used a nanoplotter for applying the MIP solution onto the sensor surface followed by UV polymerisation (UV starter Irgacure type) with a point lamp (Dymax) as for the spray coated ones. As porogenic solvents acetonitrile (ACN), chloroform (CH_3Cl) or dimethylformamide (DMF) were tested. To verify the enhanced uptake of TNT from the vapour stream, the imprinted polymer type was always tested against the non-imprinted correspondent using the mentioned TNT gas generator. In case of the thin film coatings the TNT uptake was directly measured via the decreasing QCM frequency of the treated MIP layers. As empirically found by Sauerbrey [8] the frequency of a QCM decreases linearly up to about 2 per cent of the quartz mass as a mass attachment occurs. For QCM measurements a commercial gaslab (ifak, Magdeburg) with quartzes having a ground frequency of 10 MHz were used.

4 Results and discussion

4.1 Performance of MIP beads

The synthesized porous beads were characterized by scanning electron microscopy and BET-adsorption tests using nitrogen physisorption for the determination of the specific surface area of the MIPs. As shown in figure 3 the synthesized MIPs have a diameter of about 10 to 20 µm. The specific surface area was typically about 200-400 m^2/g.

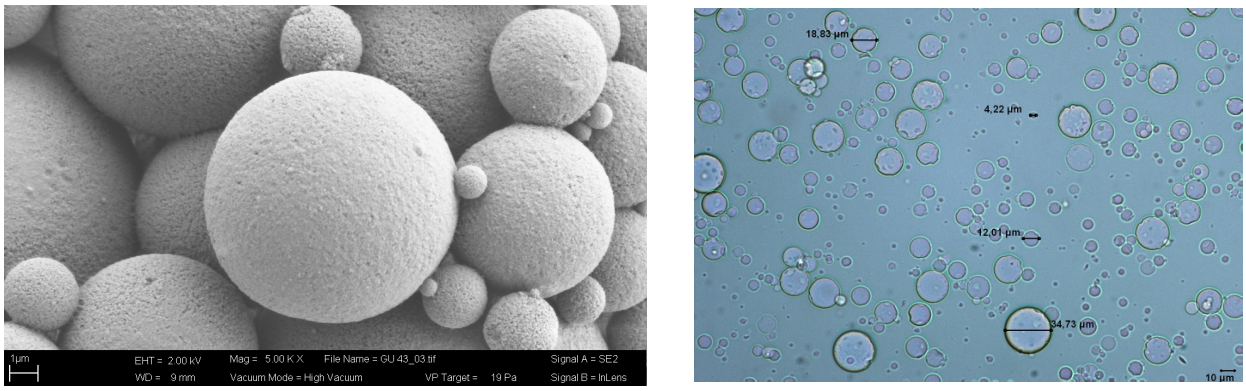

Figure 3: SEM and light microscopy of polymer beads

For some of the tested monomers we were able to detect a higher adsorption of the template by the imprinted than by the non-imprinted beads. As shown in figure 4, for TNT-imprinted polymers methacrylic acid and, to a lesser degree, the acrylamide monomer created a positive imprinting effect for 2,4,6-TNT. In comparison to the non-imprinted polymers, the imprinted MIPs show a higher tendency to adsorb / detect 2,4,6-TNT in the range of about 0,2-0,3 ng TNT/mg MIP (due to an extrapolation of the calibration curve evaluated for different amounts of solid TNT material).

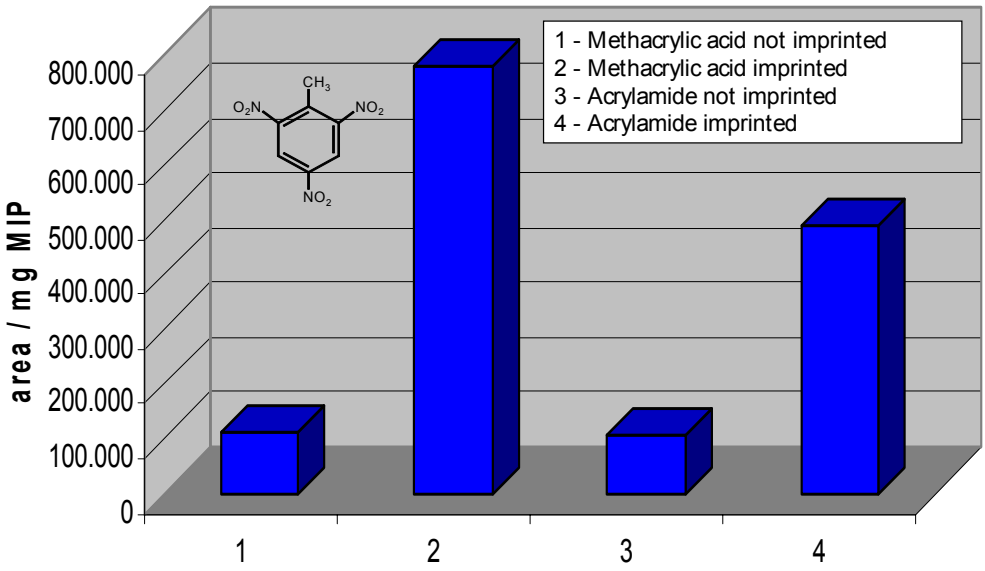

Figure 4: TNT-uptake of imprinted and non-imprinted MIP synthesized with methacrylic acid or acrylamide as measured by SPME-GC-MSD [peak areas per mg MIP]

As regards the synthesis of 2,4-DNT imprinted polymer beads, the methacrylamide monomer was demonstrated to have a positive imprint effect for the template (figure 5). Preliminary measurements with respect to the potential cross-sensitivity of TNT-imprinted MIPs using 2,4-DNT as test gas provided no measurable adsorption amounts as well as DNT-imprinted MIPs did not show measurable affinity for TNT. Despite the fact that nitroaromatics such as 2,4-DNT and 2,4,6-TNT are known to inhibit radical polymerisation reactions, the results show that suspension polymerisation achieved a positive imprinting effect for these explosives.

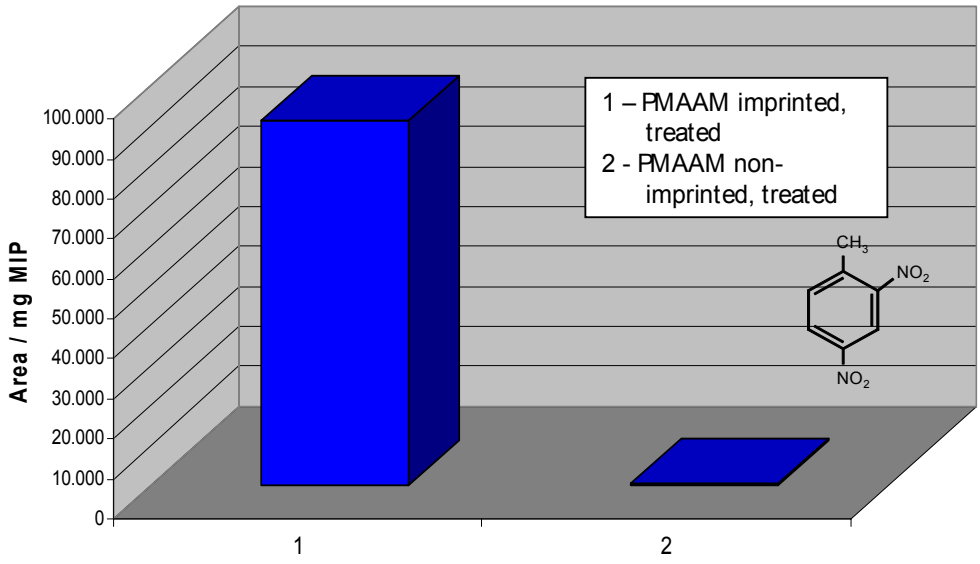

Figure 5: DNT-uptake of imprinted and non-imprinted PMAAM-MIP as measured by SPME-GC-MSD [peak areas per mg MIP]

4.2 Performance of spray-coated MIP layers on QCMs

Employment of MIPs as sensor materials is preferably possible as thin film coatings. Necessary or optimized coating thicknesses for the application of MIPs on mass sensitive sensors such as SAWs (surface acoustic wave) or micro cantilevers or workfunction-specific FETs (field effect transducers), will be in the range of some nanometers to about one micrometer. In principle thin films can be applied to the sensor surface by spray-coating, dipping or spotting followed by UV-polymerisation. In this study initially we tested manual spray-coating with a commercial artist spray gun.

After some adjustments of the synthesis conditions (N_2-atmosphere, distance of spray gun and UV-point-lamp to the QCM) typically treatment times under TNT vapour of one to two hours are sufficient to examine the performance of coated QCMs.The production of porous MIP materials with selective binding sites for the template depends amongst others on the used solvent due to e.g. different solubility of the contained components, the building tendency of a suitable pre-complex of the latter polymer structure as well as the evaporation of the solvent during the UV-curing of polymer coating. Therefore three different solvents ($CHCl_3$, ACN and DMF) were tested in this study.

As detected for the particulate MIPs independent of the used monomers the non-imprinted MIP coated QCMs show minor tendencies to adsorb TNT from loading vapour exemplarily shown in figure 6 for PAA, PMAA and PBDMA MIPs synthesized with DMF.

The different TNT-uptake of QCMs coated with imprinted MIPs synthesized with the three different solvents respectively is shown in figure 7. The highest sensitivity for TNT was regarded for the PAA-MIP which was synthesized in the presence of chloroform followed by that of DMF. Despite of the lower boiling point of acetonitrile in comparison to DMF the ACN-based PAA resulted to the lowest TNT sensitivity with an acrylamide polymer. Therefore not only the ability of a fast evaporation of the solvent during polymerisation is a driving force for producing higher MIP capacities but also the solubility and other parameters (e.g. polarity) may play a major / combined role.

Figure 7 also presents further results for different monomer types synthesized with the three solvents. In the case of PMAAM-MIPs the best TNT adsorption capacity was achieved using acetonitrile, the solvent having the medium boiling point and nearly the same polarity respectively solubility as DMF. Until now the monomers hydroxypropylmethacrylate (HPMA) and butandiolmonoacrylate (BDMA) have only been tested using DMF whereas the latter showed a considerable TNT adsorption tendency. In further synthesis these monomers should also be tested in combination with chloroform and acetonitrile.

As calculated via the decrease of the frequency of the coated QCMs, improved handling of the manual spray-coating technique led to reproducible film thicknesses in the range of some to about 500 nanometers and enhanced TNT-adsorption characteristics, nevertheless a “person factor” remained.

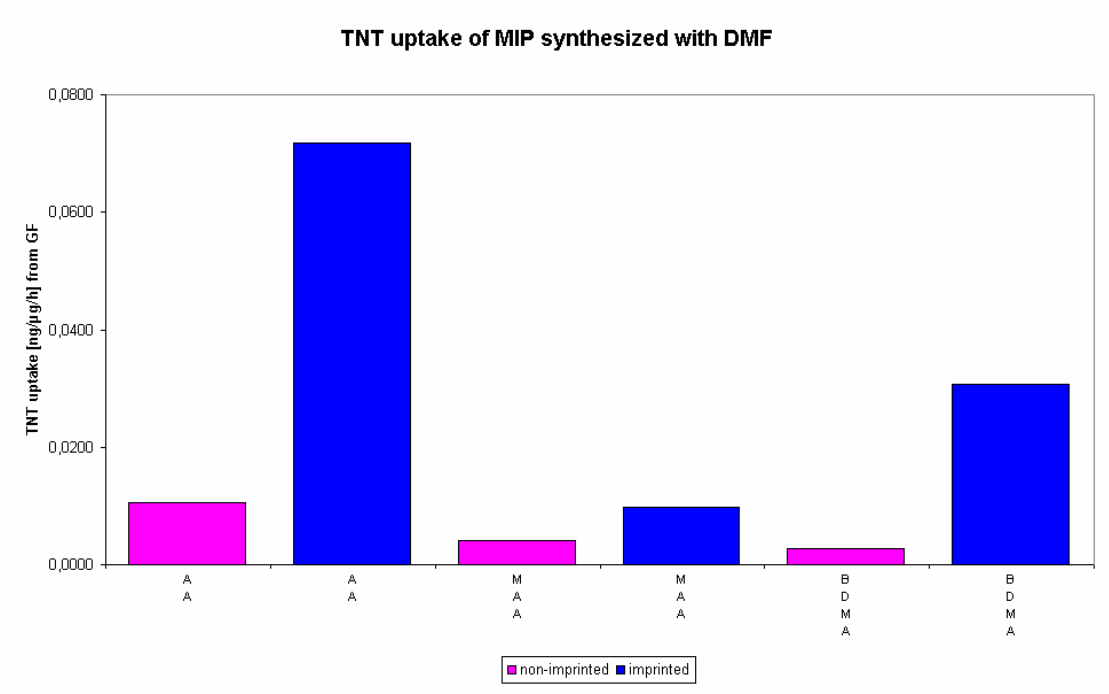

Figure 6: Comparison of TNT-uptake {ng/µg polymer/h] of different QCMs coated with imprinted or non-imprinted polymers (PAA, PMAA and PBDMA) using DMF

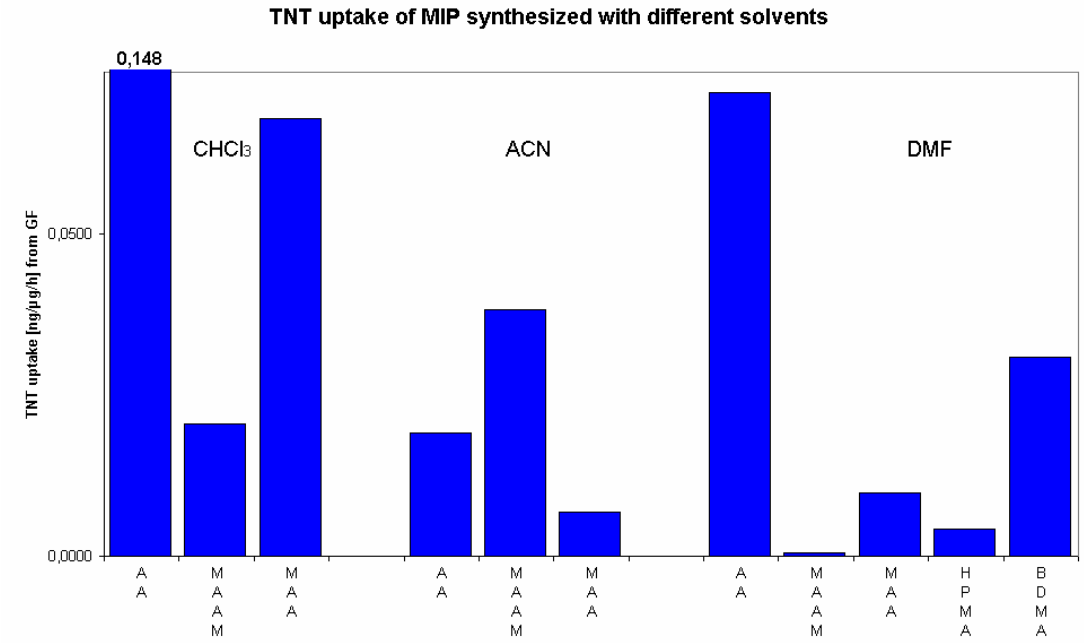

Figure 7: Comparison of TNT-uptake (normalized to ng TNT per µg polymer per hour) of different imprinted polymer types synthesized with different solvents

4.3 Layered MIPs after nanoplotting

In order to improve the coating process currently we are working with a computer controlled so called nanoplotter (GeSiM, Großerkmannsdorf) that can produce very accurately small drops in the size of 300 pl and put them onto surfaces (figure 8).

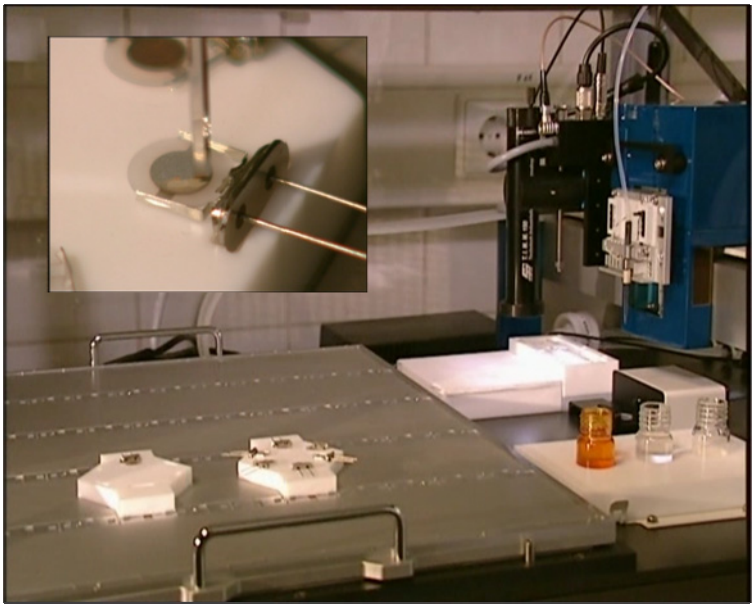

Figure 8: Coating of QCMs with a nanoplotter (Fa. GESIM)

We wrote and tested several print programs including different point raster applications with single or multiple drop applications to apply the MIP synthesis solution onto the circular QCM sensor electrode. Exemplarily figure 9 shows some raster electron microscopic pictures of different plotted and polymerised MIP film as well as an image of a cut into the MIP layer using a so called FIB technique (focused ion bombardment) for measuring the film thickness.

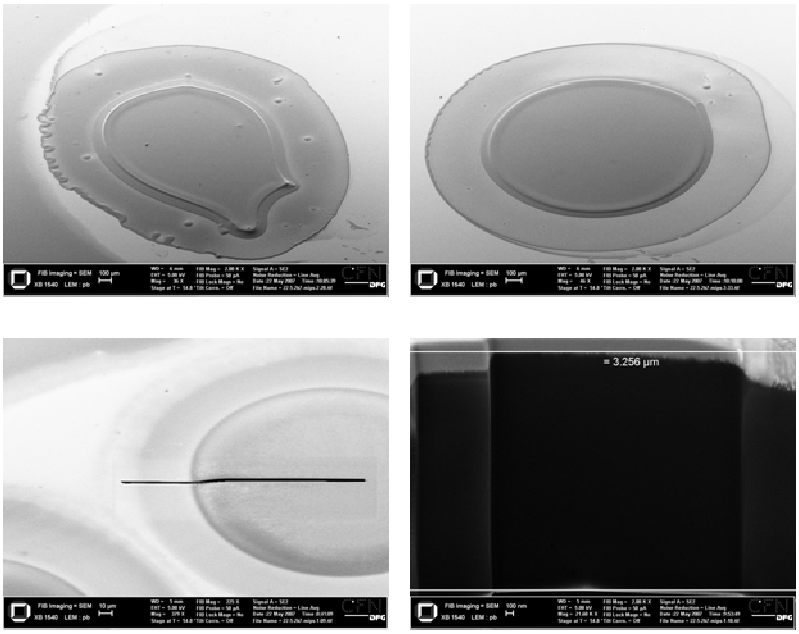

Figure 9: SEM pictures of MIP films nanoplotted on QCM electrodes using single-drop programs followed by UV polymerisation (above) and an image of a cut into a single MIP drop layer using a focused ion bombardment , FIB-beam (bottom: left side view onto the drop and right side perspective of the produced cut)

As shown in figure 9, nanoplotting yielded to very regular and closed films. At the edge of the circular film always a small so called “coffee drop” effect can be recognized. Via the FIB cutting technique the film thickness of a single drop was estimated to be 3,2 µm. The film thicknesses measured via the decrease of the QCM frequencies of uncoated to coated sensors were estimated to be in the range of 1 to 4 µm which is consistent with the FIB measurement. This is the ideal film thickness e.g. for field effect transistor sensors (FETs). In order to be able to coat sensors such as SAWs, which need very thin film thicknesses currently we are working on a concept for a spin-coater to further improve our MIP coating capabilities.

5 Summary and outlook

Low cost detection devices for detection of explosives are in high demand. In this respect low cost sensor platforms such as QCMs, SAWs, FETs or cantilevers combined with substance specific MIP coatings offer a suitable alternative to common high-priced explosive detection techniques. MIPs as substance specific coatings of low-cost detection devices look promising for use in self-reporting sensor networks for the surveillance of public areas or as on-line / in-line sensors in different vehicle transportation systems (cars, trucks, containers etc.) in order to directly detect and warn for possible terrorist threats by hazardous components.

Using suspension polymerisation we were able to produce some specific polymeric beads which showed increased binding properties for TNT respectively DNT in comparison to their non-imprinted correspondents. Furthermore DNT imprinted MIPs did not adsorb any TNT and vice versa meaning they showed no measurable cross-sensitivity.

Results received for the MIP layers on QCMs demonstrated that the used gaslab21 QCM module is suitable for a fast screening of MIP-coatings so that an improvement of the synthesis conditions could be started. The MIP layers produced via manual spray-coating have thicknesses in the range of some to about 500 nm matching the requirements of common mass-sensitive sensors. Nevertheless the reproducibility of the films should be improved. Best TNT sensitivity until now showed a PAA-MIP synthesized with chloroform. The response time reached with the quartz crystal microbalances, QCMs, is actually in the pg per minute range. Further improvement of MIP capacity will lead to shorter detection times (ca. one second).

Nanoplotting of MIPs leads to layers with very regular and closed films. Due to the basic operating parameters of the used nanoplotter as well as the viscosity of the applied MIP synthesis solutions the nanoplotter will be ideal e.g. for the coating of FET sensor surfaces.

Future experiments will address e.g. DNT as template and the cross-sensitivity of these MIP layers against TNT and vice versa. Also environmental conditions such as humidity and cross sensitivity / affinity to solvent vapours or other explosive components will be tested. In order to be able to achieve very thin MIP films we are working on a concept for a suitable spin-coating technology.

6 References

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