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Metalloporphyrin-functionalised diamond nano-particles as sensitive layer for nitroaromatic vapours detection at room-temperature

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Abstract

A new sensitive coating for surface acoustic wave (SAW) transducers based on diamond nano-particles functionalised with a zinc porphyrin complex is investigated for the detection of nitroaromatic vapours. The role of diamond nano-particles is to offer a stable sp³ carbon porous matrix onto which the metalloporphyrin receptor is immobilised. This functionalised matrix can then be deposited by a layer-by-layer deposition method homogeneously on the transducer surface while featuring a high surface area. Good repeatability was obtained from sensor to sensor. The resulting sensors show a very high sensitivity of typically 120 Hz ppb⁻¹ with a limit of detection (LOD) at 1 ppb level towards 2,4-dinitrotoluene (DNT) vapours, a tracer for explosive trinitrotoluene (TNT). The response is enhanced by more than a factor 10 when using diamond nano-particles as opposed to a transducer with only the metalloporphyrin complex deposited on the surface. The response time $t_{90\%}$ is approximately 4 min and the sensor response is fully reversible. The cross-sensitivity of the sensor is low when exposed to polar compounds such as ethanol or moisture. Those results are encouraging towards the development of low cost portable explosive vapour detectors. Furthermore, the carbon terminated surface of diamond nano-particles offers wide opportunities for grafting other types or receptors for chemical or biological gravimetric detection.

Keywords

Diamond nano-particles; SAW chemical sensors; Gas detection; DNT; Metalloporphyrins

1. Introduction

Rapid detection of explosives is important because it may help prevent terrorist attacks, or enable the location of unexploded ordnance such as land-mines. A number of explosive vapour sensing techniques have been reported in the literature, including ion mobility spectroscopy (IMS) [1], fluorescence [2], surface acoustic wave (SAW) [3], micromechanical cantilever [4] and immunochemical methods [5]. Such simple techniques are promising, because they can be incorporated into inexpensive and portable microelectronic devices.

Among those systems, SAW devices offer a good compromise between high sensitivity and low-cost since they can be manufactured on a large scale using Integrated Components (ICs) fabrication technology. The success of this technology has been demonstrated by the arrival of handheld portable warfare agents detectors based on the SAW sensors on the market [6]. Nevertheless the sensitive coating deposited on such transducers is generally a limiting element in terms of selectivity, sensor to sensor repeatability, reliability and long term stability [7], [8], [9]. Recently, a new sensitive coating for SAW sensors based on diamond nano-particles (DNPs) was investigated for the detection of volatile chemicals [10]. This study showed that homogeneous and reproducible coatings could be obtained by a layer-by-layer deposition of nano-particles and that sensitivities to target chemicals down to sub-ppm could be

achieved with fully reversible responses. There the surface of the DNPs was modified by simple hydrogenation or hydroxylation processes to demonstrate the tunability of the coatings.

The aim of the present work is to show that DNPs can also be functionalised with larger molecules selected for their high affinity with specific compounds that one may want to detect. In this context, this study focuses on metalloporphyrin-functionalised diamond nano-particles for detecting nitroaromatic vapours.

In the family of the nitroaromatic compounds, trinitrotoluene (TNT) is an inexpensive compound found in fifteen explosive compositions. For example, TNT is widely used in industrial explosives containing ammonium nitrate [11]. DNT is present in TNT samples as an impurity resulting from the manufacturing process [12]. Nevertheless, the equilibrium vapour pressure at 25 °C for DNT is significantly higher than for TNT, with values around 100 ppb against 5 ppb, respectively [13]. Therefore DNT is often used as a tracer for detecting the presence of TNT. For this reason DNT was chosen as target analyte in this work.

Metalloporphyrin is an aromatic system formed by four pyrrolic rings linked by methinic bridges with a transition metal atom at the central core and different possible lateral functional groups. Combinations of porphyrins obtained by metal and lateral functional groups offer a large variety of interaction mechanisms that can be exploited for chemical sensing. For instance, metalloporphyrins have been used in this field as artificial olfactory receptors [14]. Hydrogen bonds, polarization, polarity interactions and ligand properties are expected to take place between volatile compounds and the porphyrin. Also, the role of metal is of primary importance to determine the sensitivity and selectivity properties of this molecule [15], [16].

Metalloporphyrins are promising sensing materials for detecting compounds such as TNT or DNT, due to their high binding strength to nitroaromatic compounds [17], [18]. In particular, it appears that zinc-porphyrin (ZnTPP) was often used as sensing element for its strong affinity with nitroaromatic compounds [19], [20]. This motivated our choice to use zinc-porphyrin complex in this study.

Thus this paper shows that DNPs can be functionalised by a Zn-porphyrin complex and that the resulting particles can be deposited homogeneously over the surface of a SAW transducer to form the sensitive coating. The resulting sensor was evaluated in terms of performance towards the detection of DNT vapours at ppb levels.

2. Experimental

2.1. Materials and apparatus

The DNPs were supplied by the Institut Franco-Allemand de Recherches de Saint-Louis (ISL). They were prepared by detonation synthesis using a procedure described in Ref. [21]. The primary size of those particles is typically 5 nm.

Poly (diallyldimethyl-ammonium chloride) (PDDAC, MW = 200,000–350,000, 20% wt/wt in H₂O), poly (sodium 4-styrenesulfonate) (PSS, MW = 70,000), 2,4-dinitrotoluene (DNT, 97%) and zinc 5,10,15,20-tetra (4-pyridyl)-21H-23H-porphine tetrakis methochloride (ZnTMPy) were purchased from Aldrich (France) and used without further purification.

The SAW transducers were purchased from Forschungszentrum Karlsruhe and consisted of 433 MHz quartz resonators with gold IDT electrodes (InterDigital Transducers). Gas sensing measurements were performed using the SAGAS instrument developed by Forschungszentrum Karlsruhe [22], [23]. This instrument allows data acquisition from eight sensors simultaneously.

Images of the coated surfaces were obtained using a field emission gun scanning electron microscope (Hitachi S-4500 FEG-SEM).

Spectra of DNPs in KBr pellets were recorded using a Bomem MB 100 FTIR spectrometer equipped with InSb and MCT detectors, allowing spectra to be recorded in the 500–4000 cm^{-1} spectral range (4 cm^{-1} resolution).

The average size diameters (Z_{av}) of the diamond nanoparticles evaluated by dynamic light scattering (DLS) and the zeta potential (ZP) values of the diamond nanoparticles in solution were recorded on a Malvern ZetaSizer Nano. Instrumental calibration was carried out according to the manufacturer recommendations throughout all experiments.

2.2. DNP and porphyrin-functionalised DNP solution

The DNPs were dispersed in deionised water by intense ultrasonic treatment for 2 h to make a colloidal solution of concentration 0.1% wt/wt. The resulting DNPs dispersed in water have a zeta potential of typically -40 mV at pH = 6.5. This negative charge is attributed to carboxylic acid groups present at the diamond surface. Indeed FTIR analysis of the nano-particles indicates the presence of carboxylic acid and acid anhydride groups with a broad band centred at 1775 cm^{-1} (C=O stretching bond).

The presence of negative charges at the DNP surface was used for bonding porphyrin on DNP using a non-covalent method. The principle consists of attracting electrostatically positively charged metalloporphyrin molecules onto the negatively charged DNP nano-particles. ZnTMPy was selected for this purpose because it contains a cationic functional group (Fig. 1).

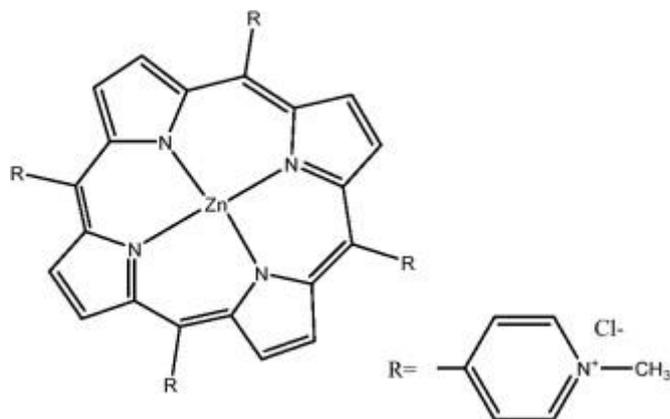


Fig. 1. Formula of porphyrin material ZnTMPy (zinc 5,10,15,20-tetra (4-pyridyl)-21H-23H-porphine tetrakis methochloride).

Thus ZnTMPy was added into 4 mL of the 0.1% wt/wt aqueous DNP colloidal solution to obtain a ZnTMPy concentration of 0.1 mM in solution. The mixture was agitated for 4 h and then sonicated using an ultrasonic sonotrode for an additional 2 h at room temperature. Then, five rinsing cycles were carried out in order to remove the excess of porphyrin not attached to the DNP surface. Each cycle consisted in centrifugating the solution at $14,000 \times g$ for 30 min, separating the solvent from the precipitate, and then re-dispersing the precipitated DNPs in freshly deionised water by sonification for another 15 min. After the fourth centrifugation, the solvent appeared colourless. It was separated from the precipitate and analyzed by UV/visible spectroscopy using an Ocean optics USB2000 spectrophotometer to check that no more porphyrin was present in solution. The concentration of porphyrin in the solvent was found to be less than 10^{-7} M and therefore negligible. After re-dispersion of the later DNP precipitate in water, the solution appeared green, whereas the original DNP dispersion was brown in colour, suggesting that ZnTMPy was indeed immobilised onto the DNPs surface (Fig. 2).

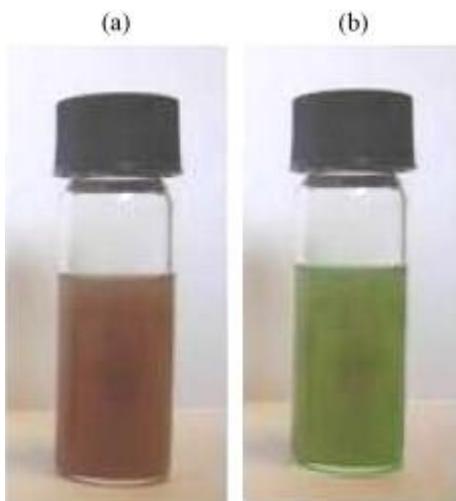


Fig. 2. Solution of nano powders, before (a) and after (b) porphyrin treatment respectively in water.

2.3. Diamond nanoparticles coatings

A strict control of the sensitive coating thickness and uniformity is crucial in order to obtain reliable SAW sensor performances. In a previous study we showed that a layer-by-layer deposition method using a polyelectrolyte was suitable for high quality DNP coating on SAW sensors [10]. Therefore the same approach was used in this study. Measurement of the zeta potential of the DNPs in aqueous solution showed that it becomes positive with typical value of +40 mV at pH = 6.5 when ZnTMPy is immobilised on their surface. This may be explained by the presence of four positively charged sites on the each metalloporphyrin molecule. Even though some of the positive charges contribute to electrostatic attachment through the negative charges present on the DNT surface, it is likely that an excess of positive charges remains which account for the overall positive charge of the functionalised particles.

In brief, the deposition principle hereby consists of attracting by electrostatic interactions the positively charged ZnTMPy–DNP onto a substrate coated with the anionic polymer PSS. Prior to DNP coating, the SAW transducers were individually washed thoroughly in acetone, iso-propanol, and deionised water for several times. Finally the SAW sensors were rinsed with deionised water and dried under nitrogen flow. Then each SAW sensor was dipped into an aqueous 10^{-2} M PSS polymer solution for 10 min. The SAW sensors were subsequently rinsed with deionised water and dried under nitrogen flow. This process is assumed to leave a thin polymer film on the substrate despite its solubility in water, as demonstrated for PDDAC in Ref. [24]. Then the SAW sensors were immersed into the ZnTMPy–DNP colloidal solution for another 10 min and finally rinsed with deionised water and dried under nitrogen flow. Unless specified, this procedure was repeated three times in order to obtain three quasi monolayers of nanoparticles onto the surface. Finally, the SAW sensors were washed with deionised water and dried under gentle nitrogen flow.

For comparison purpose, SAW sensors were also coated with as-received DNPs. The deposition procedure was similar to above, except that this time since the zeta potential of the particles is negative at neutral pH (–40 mV), the cationic polymer PDDAC (10^{-3} M in deionised water) was used. SAW sensors were also coated with ZnTMPy without DNP by repeating the same process with the PSS solution and using an aqueous solution of 10^{-3} M ZnTMPy. This method has already been reported as successful to assemble porphyrins layers on sensor surfaces [25].

2.4. Gas sensor characterisation

The experimental gas rig used for the characterisation of the modified DNP coated SAW sensors is depicted in Fig. 3. The sensors were tested against different vapours generated either from diffusion tube placed in a permeation oven (Calibrage, France) under flow and temperature control the case of DNT, or at saturated vapour pressure ethanol. The diffusion tubes were purchased from Calibrage, France. The vapour sources were calibrated gravimetrically after a five days stabilisation period in the diffusion ovens by weighting the mass loss of the diffusion tube every four days, using a micro-scale with 0.001 mg readability (Mettler Toledo MX5) over a period of twenty days. The experimental conditions used for DNT vapour generation by diffusion are: oven temperature: 25 °C, flow rate in oven: 330 sccm, diffusion rate: $598 \pm 55 \text{ ng min}^{-1}$, concentration reached: 240 ppb. Ethanol vapours were generated by passing a nitrogen flow of 330 sccm above a volume of ethanol kept constant at 25 °C. The temperature within the gas cell containing the sensors was measured by using a thermocouple when cycling between clean nitrogen and contaminated nitrogen passing through the permeation ovens. No significant temperature variation was measured. Nevertheless, to compensate for any possible temperature variation within the gas cell, the temperature of the sensors was kept constant at 23.4 °C using a Peltier element located underneath the sensors. Dry nitrogen was used as the reference and carrier gas to transport the single volatile chemical compounds through the gas cell containing the sensors. The total flow rate above the sensors was kept constant at 330 sccm throughout all experiments. Data acquisition was carried out every 1 s using the SAGAS instrument. For all tests a raw SAW transducer resonating at 433.9 MHz and isolated from the gas cell was used for reference measurements to compensate for eventual temperature variation.

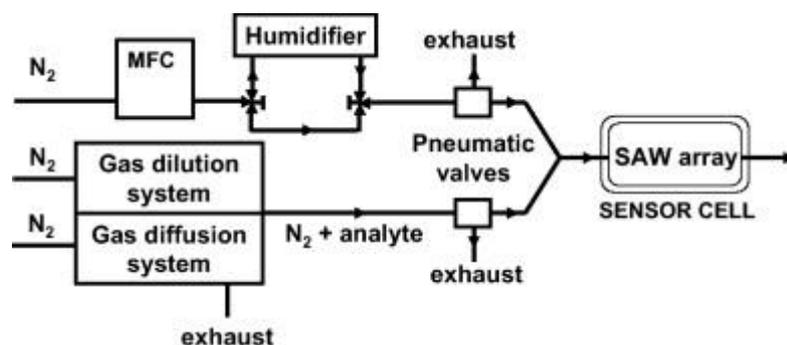


Fig. 3. Experimental setup used for gas sensing measurements.

Additionally, the resonators operating frequencies before or after DNP deposition were checked using a networks analyzer (Rohde and Schwarz[®] ZVB20).

3. Results and discussion

3.1. Characterisation of the ZnTMPy–DNP

FTIR spectra of DNP, ZnTMPy and ZnTMPy–DNP were recorded in KBr pellets and are shown in Fig. 4. For DNP, the bands are generally broad since the absorbance frequencies are dependant upon the size of the particles. The band centred at 1780 cm^{-1} is characteristic of C=O stretching from carboxylic acid attached to diamond surface [26] and appears both on the DNP and ZnTMPy–DNP spectra. For DNP, the bands centred around 1000 cm^{-1} , 1400 cm^{-1} and 3400 cm^{-1} are arising from water adsorption on the DNP surface. Similarly, the band centred at 3400 cm^{-1} in the spectrum of ZnTMPy is assigned to O–H stretching mode of water molecules bound to the cationic porphyrin [27]. This later band is also visible in the ZnTMPy–DNP spectrum. Furthermore, some of the weak and medium bands in the region $1600\text{--}680 \text{ cm}^{-1}$ due to the vibrational modes of the porphyrin ring and to the substituted pyridyl moieties also

appear on the ZnTMPy–DNP spectrum, confirming the presence of the metalloporphyrin complex on the DNP surface. Amongst those bands one can notice the strong bands centred at 791 cm^{-1} and 988 cm^{-1} assigned to C–C and C–N stretching modes [28], as well as the band centred at 1632 cm^{-1} ascribed to the C=N stretching mode of the pyridinium group [26].

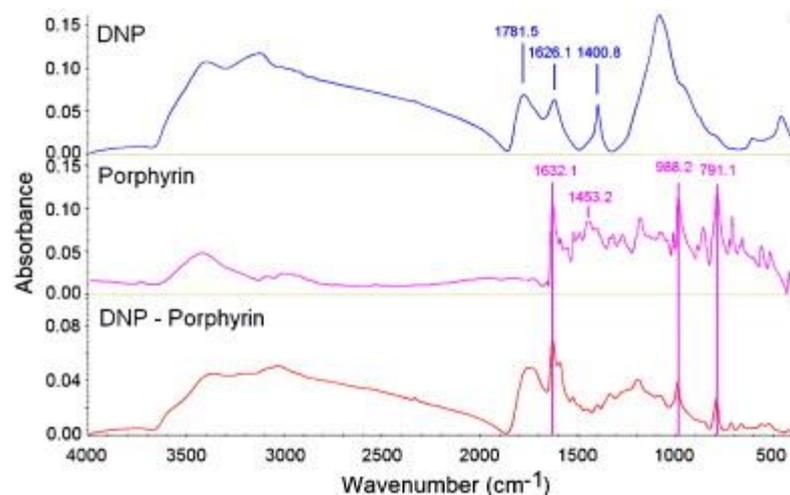


Fig. 4. FTIR spectra of DNP, ZnTMPy and ZnTMPy–DNP in KBr pellets.

3.2. Characterisation of DNP coatings

The operating frequency of the resonator was measured before and after the deposition of three layers of ZnTMPy–DNP and was found to be equal to 332.5 MHz and 332.2 MHz , respectively (Fig. 5). This shift towards lower the frequencies was accompanied by a slight increase in attenuation, from -9.8 dB to -15.1 dB in Fig. 5. This behaviour of the resonator is attributed mainly to mass loading on the transducer. The same coating was repeated on 4 sensors. Less than 10% difference in Δf from sensor to sensor was measured, which suggests that the deposition method is very reproducible in terms of mass added onto the various transducers. The homogeneity of the coating was confirmed by SEM imaging (Fig. 6) as uniform both on quartz and on the gold electrodes. This is an important result since the presence of such defects would be likely to disturb the propagation of the acoustic wave across the surface and consequently affects considerably the sensor response. The thickness of coatings made of three layers ZnTMPy–DNP was assessed to be in the order of $40\text{--}60\text{ nm}$, based on SEM observation.

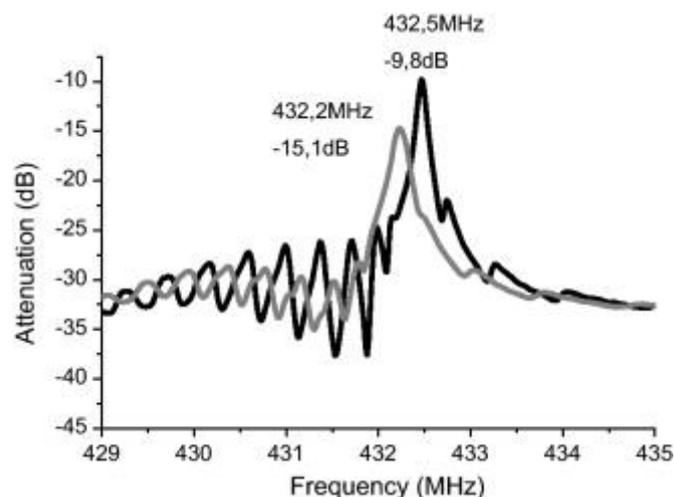


Fig. 5. Example of frequency shift response of a raw SAW transducer (dashed black curve), after three layers of ZnTMPy–DNP coating (dark gray curve).

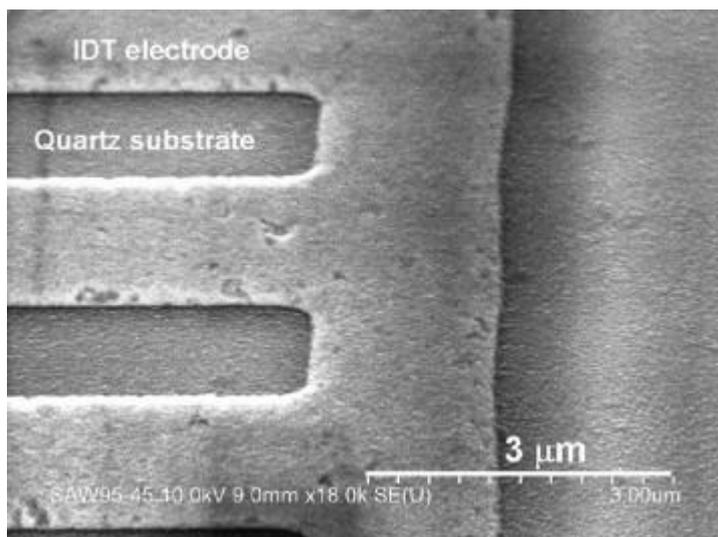


Fig. 6. SEM image of a SAW sensor after three layers of ZnTMPy–DNP.

3.3. Sensing performances

3.3.1. Response to DNT

The ZnTMPy–DNP SAW sensors characterised throughout all vapours measurements were made of three layers of ZnTMPy–DNP. Firstly the responsivity of the ZnTMPy–DNP sensors was compared to that of DNP sensors as well as ZnTMPy sensors. The later sensors were also prepared by depositing three layers of DNP and three layers of ZnTMPy on the SAW transducers, respectively. The three types of sensors were exposed to cyclic exposures to 140 ppb then 240 ppb DNT vapours. Exposure time was set to 120 s. Fig. 7 shows typical responses of two ZnTMPy–DNP, two DNP sensors and one ZnTMPy sensor to DNT vapours. All sensors are sensitive to DNT vapours and the response is almost reversible. The slight drift observed for some sensors is mostly explained by the low desorption rate of the analytes off the sensor surface. Sensors with the ZnTMPy–DNP coating on are the most sensitive ones, showing a frequency shift of approximately 29,000 Hz against the resonant frequency in reference gas after 120 s exposure to 240 ppbv DNT. In contrast the signal intensity of the DNP sensors and the ZnTMPy sensor was 7200 Hz and 2200 Hz, respectively, after the same vapour exposure. The delocalized π -electron system associated with the highly conjugated porphyrin molecule can interact with electronegative species (electron acceptors), and the strong tendency to form coordinate bonding between the metalloporphyrin molecule and the nitrogroup is well known [29]. It has been shown on a similar nitroaromatic compound that the zinc ion plays an important role in stabilising the complex [30]. This high affinity of DNT with the metalloporphyrin explains the high responsivity of the sensors functionalised with ZnTMPy. It is clear from those measurements that the responsivity of the sensor is largely enhanced when ZnTMPy is immobilised on the DNP. It is thought that when ZnTMPy is deposited directly onto the sensor surface, very few active sites are available to interact with the DNT molecules. This is partly due to the low surface area of the sensing layer since only three layers of metalloporphyrin is deposited onto the flat sensor surface. Also, because of the aromatic character of the metalloporphyrin, π - π interactions are likely to lead to a very closely packed porphyrin thin film with low diffusion coefficient, as described extensively in the literature [31], [32]. This reduces considerably the access to pyrrole nitrogens and zinc ions available that contributes to binding with the nitro aromatic ligand [32], [33]; hence the sensitivity of the sensor is poor. In the case of the DNP-sensors, the surface area of the sensitive coating is increased significantly by the presence of three layers of DNPs, which could explain that the responsivity is also increased significantly compared to the ZnTMPy-sensors. Here the detection mechanism is mainly driven by non-specific adsorption of DNT

on the DNPs surface, in particular via the acid groups present on the DNP surface. The affinity of DNT with the DNP surface is not particularly high thus the sensors response remains fairly low. In contrast, the ZnTMPy–DNP sensors combined both the high surface area and high affinity of DNT with ZnTMPy. The sensor response is much improved. The fact that the response of the ZnTMPy–DNP sensor is so much higher than the other two types of sensors suggest that pi-staking may not occur between metalloporphyrin molecules. Two hypotheses may be drawn from this result. On the one hand, the four methylpyridinium ions of the porphyrin are electrostatically attached to the DNP surface. In this case, the metalloporphyrin plane is parallel to the DNP surface, and adjacent porphyrin cannot stack on their neighbouring molecule. On the other hand, it is possible that only one methylpyridinium ion of each porphyrin molecule is responsible for immobilisation onto the DNP surface. In this case, pi-stacking will probably not occur provided that adjacent molecules are far from one another, or in other words if the surface immobilisation coverage is poor. More surface analysis would be necessary to validate those hypotheses.

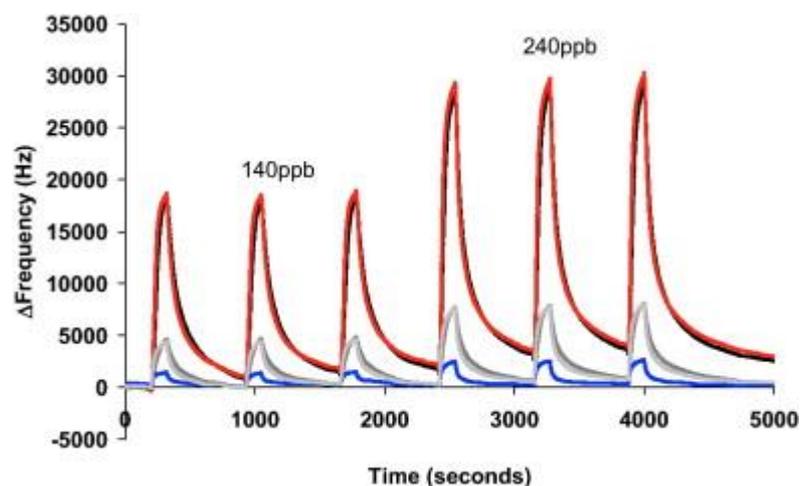


Fig. 7. Typical response of two ZnTMPy–DNP coated sensors (red curve and black curve), two DNP coated sensors (dark gray curve and gray curve) and one ZnTMPy coated sensor (blue curve) to three successive exposures to 140 ppbv then 240 ppbv DNT, respectively.

The first measurements above also showed that after 120 s exposure to DNT vapours, the sensors response does not reach the steady state. Therefore a ZnTMPy–DNP sensor was exposed for a longer time to 240 ppb DNT vapours (Fig. 8). It was found that complete thermodynamic equilibrium was still not reached after 2000 s exposure to DNT. The time required to reach 90% of the signal measured after 33 min exposure to DNT was typically 250 s. Moreover, the recovery is also not complete after 4000 s in dry nitrogen. The recovery time after 2000 s exposure to DNT vapours was found to be approximately 4000 s, with a T90% recovery of 1600 s. We believe that the response kinetic is mainly driven by adsorption/desorption onto coating surface. However, since the recovery time is significantly longer than exposure time, it is clear that this is not the only physico-chemical mechanism involved, and perhaps diffusion through the diamond nanoparticles takes also a major role in the detection kinetic.

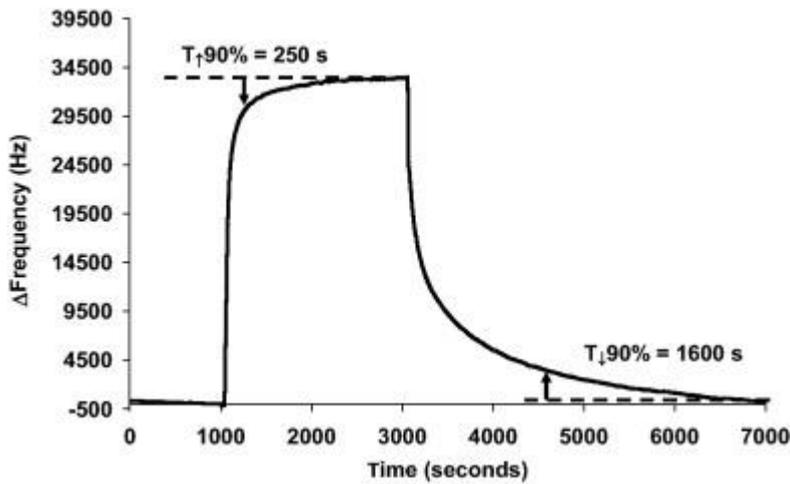


Fig. 8. Long exposure time of 2000 s to 240 ppb DNT gas with a ZnTMPy–DNP coated sensor until reaching thermodynamic equilibrium.

Fig. 9 shows a typical transient response of ZnTMPy–DNP SAW sensor exposed to increasing then decreasing concentrations of DNT vapours in the range 11–240 ppb in dry nitrogen. For each concentration, 3 exposures were repeated consecutively. It is clear that the sensor signal increases as expected with increasing concentrations. The signal increase is mostly attributed to mass loading on the transducer but also to acousto-electric effects. Indeed delocalised π -electron system associated with the highly conjugated metalloporphyrin molecule induces a significant conductivity of the coating that varies upon interaction with the target molecules [34]. For each concentration, the signal intensity is approximately the same, both upon increasing concentrations and decreasing concentrations. After each cycle, the sensor signal does not return to the baseline. This is mostly because the sensor was not given enough time to fully recover.

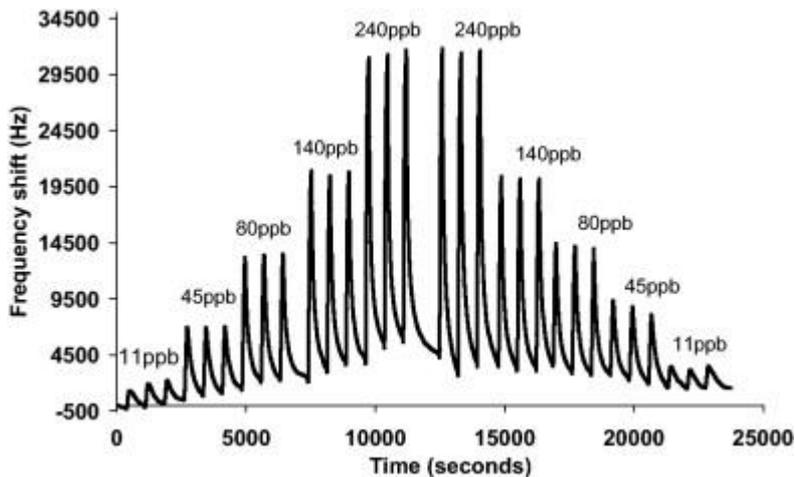


Fig. 9. Transient response of SAW sensor coated by ZnTMPy–DNP, at room temperature, to different concentrations of DNT.

One requirement of explosive vapour detectors is the fast response time, since the information to as the presence of explosive or not in a probe area may result in emergency actions to be undertaken immediately. For most applications, response times typically above 2 min are generally not acceptable. Fig. 10 shows a calibration curve obtained from four separate SAW sensors prepared with three layers of ZnTMPy–DNP, three layers of DNP and three layers of ZnTMPy. Data points were recorded 6 times for each concentration, each time after 120 s exposure to DNT in dry nitrogen. A quasi linear dependency of frequency shift versus DNT concentration was obtained in each case. If taking the slope

of the linear approximation of the calibration curve, the sensitivity of the ZnTMPy–DNP sensors was found to be in the order of 120 Hz ppb^{-1} . This is typically 13 times higher than for the ZnTMPy-sensor. Furthermore, the limit of detection (LOD), defined as the smallest DNT concentration giving rise to signal intensity three times higher than the noise level of the measuring equipment, was assessed to be in the order of 1 ppb.

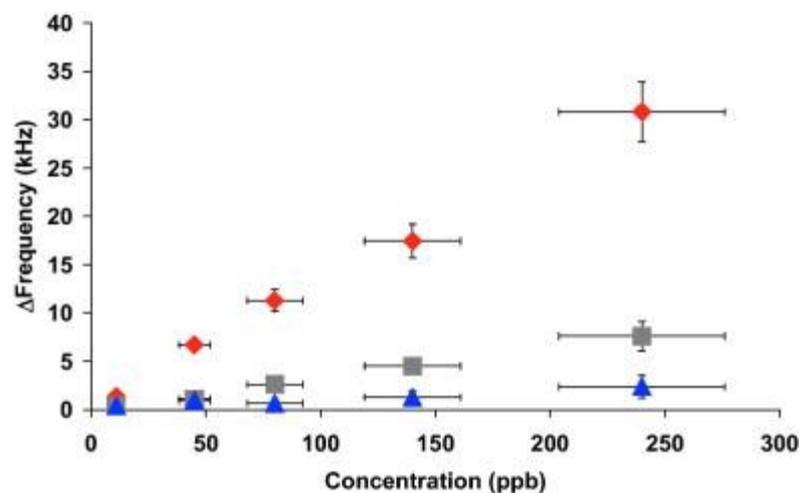


Fig. 10. Calibration curve obtained from four separate SAW sensors prepared with three layers of ZnTMPy–DNP (red curve), three layers of DNP (gray curve) and three layers of ZnTMPy (blue curve) to DNT gas at room temperature.

3.3.2. Effect of ethanol or moisture on sensor response

The ZnTMPy–DNP sensors were also exposed to ethanol vapours in order to assess the sensor response to a common polar interfering volatile compound. Fig. 11 shows that the response to 5% ethanol vapour in dry nitrogen gas generates a signal typically 7 times weaker than that given when the sensor is exposed to 240 ppb of DNT in nitrogen gas. Hence it is anticipated that the sensor will be highly selective to DNT vapours in the presence of low levels of ethanol vapours below the ppm level.

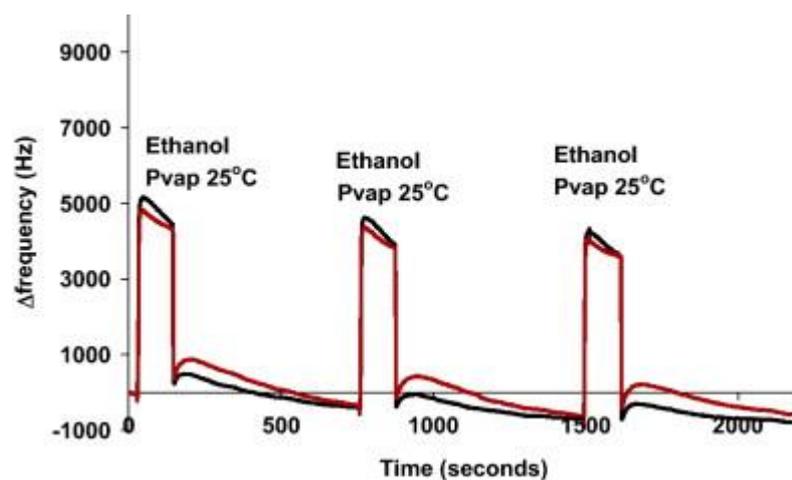


Fig. 11. Typical response of two ZnTMPy–DNP coated sensors (brown curve and black curve) to three successive exposures to 5% ethanol in nitrogen gas.

Finally, two ZnTMPy–DNP SAW sensors as well as a DNP SAW sensor, both coated also with three layers of nano-particles, were exposed successively twice to 70% RH nitrogen, then three times to 140 ppb DNT in 70% RH nitrogen and then twice 140 ppb DNT in 2% RH nitrogen, in order to investigate assess the effect of humidity on the sensor response to DNT vapours. Each exposure was

carried out for 120 s. The response curves are plotted in Fig. 12. It appears from the response that the ZnTMPy–DNP coated sensors are approximately ten times less sensitive to relative humidity than the DNP sensor. The ZnTMPy–DNP sensors response to DNT vapour seem to be insignificantly affected by relative humidity variation from 70% to 2%. The signal intensity at both %RH values is comparable to the value obtained during calibration in dry nitrogen (Fig. 10). In contrast, since the DNP sensor is sensitive to %RH, its response to DNT vapours is also significantly affected when varying the ambient moisture level. The sensitivity of the DNP sensor to humidity is partly attributed to the presence of carboxylic acid groups at the DNP surface, which enable the formation of hydrogen bonds between the DNP surface and water molecules. On the other hand, the fact that the ZnTMPy–DNP sensors are poorly sensitive to ethanol vapours as well as moisture suggests strongly that hydrogen bonding is not a predominant interaction mechanism with incoming analytes.

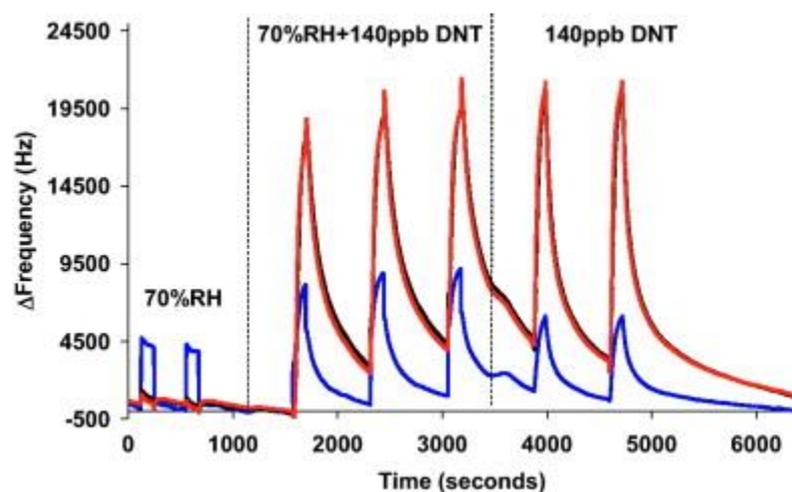


Fig. 12. Typical response of two ZnTMPy–DNP coated sensors (red curve and black curve) and one DNP coated sensor (gray curve) to two successive exposure to 70% HR in nitrogen then three times to 140 ppbv DNT in 70% HR in nitrogen and then twice 140 ppb DNT in 2% RH in nitrogen, respectively. Each exposition was carried out for 120 s.

4. Conclusion

Herein, we provided a new sensitive coating based on functionalised diamond nano-particles to use with surface acoustic wave transducers for the detection of nitroaromatic compounds at room temperature in the gas phase. A zinc-complex porphyrin was chosen for its high affinity with nitroaromatic compounds and was immobilised successfully on the diamond-nanoparticle surface. The modified DNP were then deposited on the SAW transducer surface. The resulting sensor was very sensitive to DNT vapours (120 Hz ppb^{-1}), with a limit of detection at 1 ppb level. The diamond nano-particles enhanced the sensitivity by more than a 10-fold factor when compared to a zinc-porphyrin sensitive film alone. Diamond nano-particles offers several advantages for this type of application: their sp^3 carbon nature makes them intrinsically very stable, but at the same time their carbon terminated surface offers wide opportunities for grafting (covalently or not) a large number of receptors selected for their affinity with analytes of interest. The modified DNP can then be deposited homogeneously onto a SAW transducer surface, as demonstrated through the current example, to achieve high sensing performances at room temperature.

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