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

E. Chevallier[a], E. Scorsone[a,*], H.A. Girard[a,b], V. Pichot[c], D. Spitzer[c], P. Bergonzo[a]

[a] CEA, LIST, Diamond Sensors Laboratory, F-91191 Gif-sur-Yvette, France
[b] Laboratoire de Physique de la Matière Condensée (PMC), CNRS–Ecole Polytechnique, F-91128 Palaiseau cedex, France
[c] NS3E, ISL-UMR 3208, Institut franco-allemand de recherches de Saint-Louis, France

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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 sp^3 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.

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 [7–9]. 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 methynic bridges with a transition metal atom at the central core and different possible lateral functional groups.

* Corresponding author. Fax: +33 0 1 69 08 69 34.
E-mail address: emmanuel.scorsone@cea.fr (E. Scorsone).

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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 H_2O), 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 (Zav) 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).

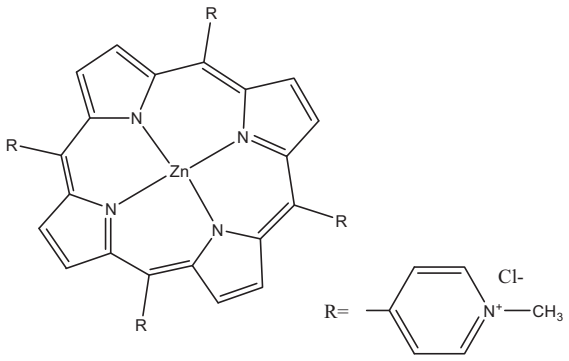

Fig. 1. Formula of porphyrin material ZnTMPy (zinc 5,10,15,20-tetra (4-pyridyl)-21H-23H-porphine tetrakis methochloride).

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).

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 × *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 forth 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).

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

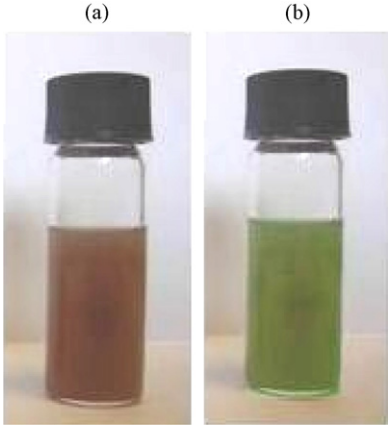

Fig. 2. Solution of nano powders, before (a) and after (b) porphyrin treatment respectively in water.