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Bio-inspired explosive sensors and specific signatures

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Abstract

The low vapor pressure of explosives makes the gaseous detection challenging and drives even the particle detection. There is a need to provide easy portable systems, highly spreadable. A bio-inspired concept was developed to detect explosive vapors with unprecedented sensitivities. Vertically aligned TiO₂ nanotubes were grown on a cantilever. The sensors successfully detected trinitrotoluene (TNT) and pentaerythritol tetranitrate (PETN) with a minimum threshold concentration down to 0.8 ppt. This work describes also the investigations undertaken to develop the characterization of explosives by nanocalorimetry, which is able to identify explosives in form of single particles.

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1. Introduction: two approaches

The detection of explosives remains a facing challenge and this for different reasons. One main reason, inherent to explosives, is their very low vapor pressure at room temperature. These weak vapor pressures are so small that at room temperature (between 20 and 25 °C) only a very small number of molecules are really present in the gaseous state. As a result, all the detection systems to be developed should attain extremely high sensitivities. They should also be very specific to the numerous explosives and formulations to be potentially detected. The second reason, inherent to detection, is that the places where explosives have to be detected, became very numerous in the recent years and are now largely beyond the battlefields because explosives are potentially present in every public places

such as railway stations, airports, and other places where the population concentration is high. This second aspect enhances drastically the difficulty, as it asks to develop portable systems extremely sensitive and very cheap to permit their necessary high dissemination. Furthermore, the detection of explosives in public places requires being fast, which is not necessarily possible with the use of complicated analytical laboratory techniques that even requires additional sample preparation. Coming back to the extreme sensitivity required to detect explosives in the gas phase, an alternatively developed approach is even to abandon the detection of gaseous products and to focus the investigation on particle detection. This second view, which joins ultimately the first one when one particle is one molecule, is currently also intensively studied. The present work describes the investigation for both approaches. Although the gaseous one was more extensively studied, the particle detection is also justified by the need of powerful characterization techniques for explosive nanoparticle engineering [1]. The current paper describes the genesis of these both approaches that are meant to join in the future. The gaseous vision is bio-inspired from the bombyx mori silkmoth and its powerful pheromone detection [2]. The nanocalorimetric vision is derived from a technique introduced in 1993 by L.H. Allen et al. [3], which was at first essentially used to characterize phase transitions in polymers on the local scale. Its potential to quantify thermal parameters for very small explosive amounts was recently demonstrate by N. Piazzon et al. [4]. In the forthcoming parts, we show the concept and first important results obtained by the bio-inspired detection of explosives in the gas phase. Secondly, the nanocalorimetry is highlighted and some important results are shown.

2. The bio-inspired vapor detection

2.1. The Bombyx mori silkmoth detection

Natural species work with structures that are quite simple in their elementary composition. In most of the cases, essentially atoms with low mass such as H, C, O, N, are present in their structures with which they are able to make movement, protection from light, from temperatures and from other hazards. It is shown that this simplicity is even at the origin of the powerful behavior of many structures, like the butterfly wings used by the species to protect them from light and heat by colors of structural origin [5]. Similarly, the Bombyx mori silkmoth, due to its highly developed antenna system, is able to detect a single pheromone molecule [6]. This detection system, based on a micron-structured antenna/sensilla sensor, is very powerful as it combines an extreme sensitivity WITH an extreme selectivity, two aspects that represent the Grail of detection. The sensitivity is very high because the Bombyx mori is able to detect single pheromone molecules reaching thereby a mass sensitivity of 10^{-21} gram! The selectivity of this system is even so impressive because the recognition takes specifically place on one single pheromone molecule type (Fig. 1).

The silkmoth pheromone detection system is not just able to catch the pheromone molecules but also to sense and recognize them via a very efficient transducing system. The proteins on sensillas are the receptors and the signal is transmitted to the brain via a transducing system that includes the nerve endings and the sensory neuronal network of the specie. Using this concept, the objective was to find out two artificial systems or supports able to play these respective roles of the receptor and the transducer.



Fig. 1. (left) *Bombyx mori* (copyright CSIRO); (right) Sensing system of the silkmoth *Bombyx mori* showing micrometer-sized sensillas grafted to antennae (courtesy from ref. [6]).

2.2. The bio-inspired cantilever based explosive sensor

Since the invention of the Atomic Force Microscope (AFM) by G. Binnig et al. [7], a tremendous multidisciplinary work has been made by combining the principle of this technique and the human imagination to make progress on various domains. One impressive aspect of atomic force microscopy is its extremely high sensitivity to control very small forces of only some pico Newtons. AFM can be operated in different modes such as contact or intermittent contact. In this last mode a small silicon or silicon nitride cantilever oscillates at or near its resonant frequency, which looks like with some imagination to the movement of butterfly small antennae. The chosen receptor was therefore the cantilever and the transducing system is the control of its vibration or its bending. Atomic force cantilevers were used in the past for the detection of different products. Here are only cited the different works essentially dedicated to the detection of explosives. In this way, Thundat and Pinnaduwa et al. showed some ten years ago, that a non functionalized oscillating silicon or silicon nitride cantilever was able to detect up to 70 picograms of explosive [8-11]. The high sensitivity of such a system should not hide two important shortcomings especially for non functionalized beams: the very small geometrical size of a simple cantilever and its extreme sensitivity to many or even any products without discrimination.

2.3. The TiO_2 nanotubes functionalized sensing cantilever

The functionalization of the cantilever was undertaken to enhance drastically the “capture” surface of the pristine cantilever. A classical silicon or silicon nitride cantilever has a too small geometrical size for the aim to detect molecules. With a length of 225 microns and a width of 28 microns, its geometrical surface is rather small. So the idea was to enhance the surface by nanostructuring aligned nanotubes perpendicularly oriented to the beam. First calculations show that depending on the dimensions of the nanotubes (inner and outer diameters, and length), it was possible to enhance the capture surface of the cantilever by a factor of 10 to 1000. The second step was to define the nature of the sensing material. Different studies conducted in the past, showed that materials like tungsten oxide and titanium oxide have a high affinity to different explosives such as nitroaromatics and nitrate esters and even nitramines [12]. As the higher affinity towards TNT was obtained for the titanium oxide, this last material was chosen to be nanostructured into nanotubes on one side of the cantilever to permit the optical readout on the other side.

The used technique was the classically employed anodization synthesis to nanostructure parallel, aligned nanotubes on centimeter sized macroscopic silicon wafers [13-14]. Our laboratories have successfully transferred this technique from a centimetric wafer to a micrometric cantilever [2, 15]. This two steps growth technique comprises first the deposition, by a magnetron sputtering method, of one micrometer thick titanium layer onto the silicon beam. For this step, a coating speed of 2.65 Å/s had to be adjusted to obtain afterwards, well shaped open TiO₂ nanotubes (Fig. 2). For the second step, which is the anodization, another important factor was to adjust the temperature and the electrolyte composition to optimize the oxidation of titanium into titania and to induce in the mean time a controlled dissolution of the oxide in order to obtain well shaped titania nanotubes. A precise regulation of all these parameters (Tab. 1) permitted to obtain well shaped titania nanotubes while overcoming the principal difficulties of delaminating (Fig. 2c), curved cantilevers by remaining stress in the titanium coating and the silicon cantilever dissolution inherent to too acidic conditions (Fig. 2d).

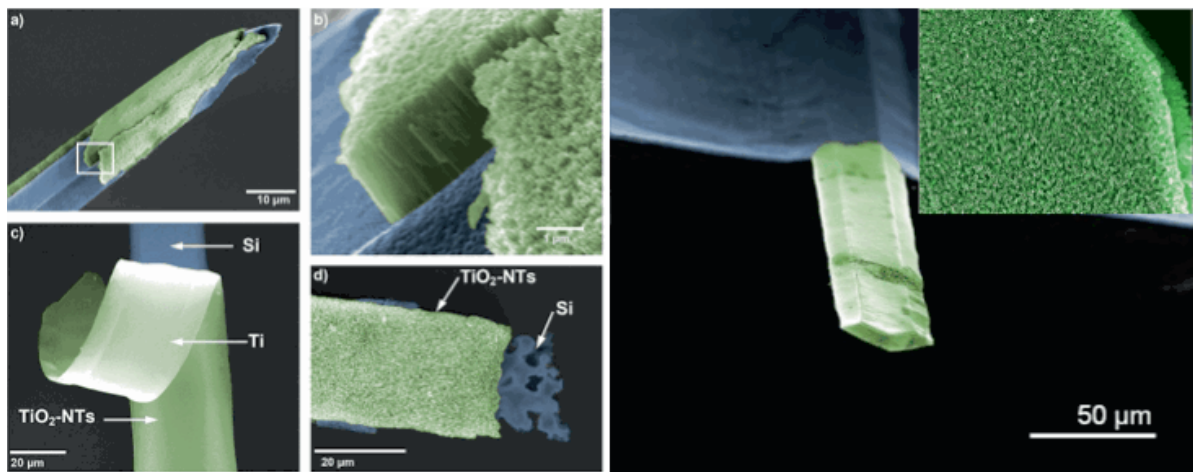


Fig. 2. (left mosaic figure) a)-b) removing of the titania nanotubes due to imperfect anodization, c) delamination coming from residual stress in the titanium coating, d) silicon dissolution due to too acidic conditions; (right) optimized nanostructured microcantilever covered by TiO₂ nanotubes.

Table 1. Parameters of the optimized cantilever functionalization.

Parameter	
Ti deposition thickness	1 micron
Ti deposition speed	2,65 Å/s
Electrolyte type	Glycerol based (5% v/v H ₂ O, 0,5%w/w NH ₄ F)
Electrolyte temperature	27 ± 1 °C
Anodization duration	120 minutes
Cantilever	TL-FM Nanosensors, t=3±1, l=225±10, w=28±8 μm
TiO ₂ -NTs dimensions	Φ _{int} = 60, Φ _{ext} =120±5, L=1700±30 nm
TiO ₂ -NTs density	8,1.10 ⁹ ±0,1 NT.cm ⁻²
Surface enhancement	72±1
Remaining Ti thickness	300 nm

2.4. The explosive sensing

Sensing experiments were undertaken with the TiO_2 nanotubes functionalized cantilevers with the objective to sense several explosive types among three molecules families being the nitroaromatics, the nitramines, the nitrate esters, and the peroxides. We chose for the above mentioned explosive families, TNT, cyclomethyltrinitramine (RDX) and PETN respectively. Among these explosives, the TiO_2 bio-inspired sensing cantilever was essentially able to detect or to sense TNT and PETN (Fig. 3). These products, generated by a nanocalorimetric heating element were detected with a detection threshold that could be brought down to 0.8 ppt (part per trillion, or one molecule of explosive in 10^{12} molecules of “equivalent” air). A resonant frequency decrease of about 250 Hz was obtained in about 3 minutes of explosive generating (red curve on Fig. 3). The experience was conducted by generating successive explosive pulses at a fixed concentration, and by measuring the cantilever frequency shift during the explosive adsorption. An important aspect was that at each time, the sensing cantilever was put at a temperature slightly higher (50°C) than the temperature at which the explosive was generated (47°C) to prevent the explosive sensing only due to condensation of the product onto the beam. It could so be proved that no adsorption of TNT occurred on a non functionalized cantilever (black curve on Fig. 3) and that the frequency shift obtained in the case of functionalized cantilevers was really due to affinity between the titania nanotubes and the explosive. Another experiment was conducted with the titanium coated cantilever obtained by the magnetron sputtering, more exactly without the nanotubes. This showed a low frequency shift just due to the adsorption of the explosive onto the TiO_2 natural coating that appeared on the cantilever after some time in air (blue curve on Fig. 3).

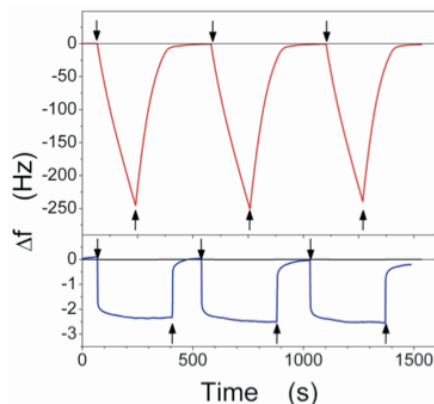


Fig. 3. Resonant frequency shift measurement during TNT generation (↓ TNT generation; ↑ TNT generation stop).

The detection of different other molecules was investigated with TiO_2 based cantilevers, which showed that only TNT and PETN were successfully detected. Explosives such as RDX were not detected.

2.5. Current and future new steps

Different new steps are undertaken currently. The first is the synthesis of other oxides able to detect explosives like RDX in order to detect all kind of explosives, which can be a possible threat. So the current work is oriented to the growth of oxides such as CuO and ZnO onto silicon microcantilevers. A second important consideration is to avoid the development of a sensor with too many sensing cantilevers. This important consideration will drive the necessity to obtain sensing microcantilevers that are rather universal, for this, the research is going on to find and to use features common to explosives.

3. The nanocalorimetric analysis of explosives

As before depicted, the detection of explosives in the gaseous form, is a quite challenging perspective. The complementary idea to detect and to characterize small explosive amounts is to use nanocalorimetry on single micrometric sized explosive particles. This technique consists in heating at very fast rates (heating ramps up to one million degree per second) a silicon nitride thin membrane to record the thermal signature of an explosive [4] (Fig. 4). As an example, we show here the explosives Hexanitrohexaazaisowurtzitane (CL-20) and RDX, for which it is possible, with only 10 to 15 ng of sample amount to obtain a characteristic thermal curve. This important result shows that it is possible to obtain the identification of explosives with real small quantities.

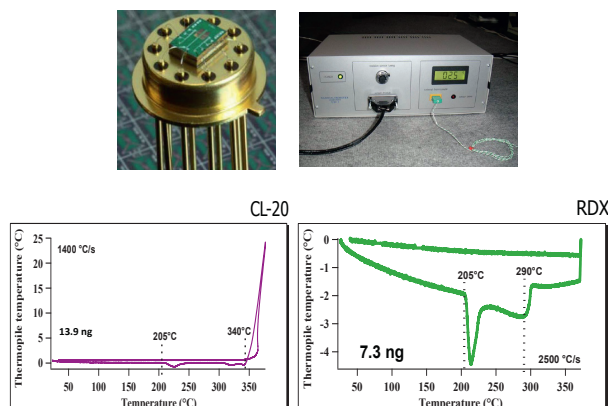


Fig. 4. (upper part, from left to right) nanocalorimetry sensing membrane and control unit, (bottom part, from left to right) nanocalorimetric trace for CL-20 and RDX.

4. Conclusion

This work describes two different approaches for one main aim: the detection of very small explosive amounts or concentrations. It was shown that both approaches are interesting as they are able to detect explosives in small amounts and also that for the moment, they each do not fully respond to all the specifications of a universal explosive sensor.

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