# Nanosensors for trace explosive detection

Selective and sensitive detection of explosives is very important in countering terrorist threats. Detecting trace explosives has become a very complex and expensive endeavor because of a number of factors, such as the wide variety of materials that can be used as explosives, the lack of easily detectable signatures, the vast number of avenues by which these weapons can be deployed, and the lack of inexpensive sensors with high sensitivity and selectivity. High sensitivity and selectivity, combined with the ability to lower the deployment cost of sensors using mass production, is essential in winning the war on explosives-based terrorism. Nanosensors have the potential to satisfy all the requirements for an effective platform for the trace detection of explosives.

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**We discuss the potential of nanosensors as a platform for trace explosive detection with an emphasis on nanomechanical sensors for achieving high sensitivity and selectivity. Nanomechanical sensors, because of their versatility, can be used for receptor-based as well as receptor-free detection, and integrate well into a multiplexed multimodal sensor system.**

## The need for explosive trace detectors

In recent years, explosive-based terrorism has grown enormously because explosive-based weapons are simple, easy to deploy, and can cause enormous damage[1–3]. Detecting explosives is a challenging task because of a number of issues, such as the low vapor pressures of most explosives, frequent introduction of novel explosive compositions, and concealment and weapon delivery schemes. Trace detection of explosives typically involves collecting vapor or particulate samples and analyzing them with a sensitive sensor system. Currently, many different techniques exist for detecting trace explosives[4–9]. The most common include ion mobility spectrometry (IMS), mass spectrometry (MS), and gas chromatography (GC) followed by detection using a sensitive sensor. Most of these devices are, however, rather bulky, expensive, and require time-consuming procedures. Because of these limitations, such systems are sparsely deployed at strategic locations such as airports and government buildings. Further complications arise when one considers not only airports, where there is a reasonably controllable environment for sensing and detection, but also the virtually uncontrollable entry points to public places, transportation

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networks, infrastructures, and road networks with unpredictable vehicular and pedestrian traffic. Protecting against explosive-based terrorism can thus only be accomplished by mass deployment of miniature sensors that are sufficiently sensitive and selective, inexpensive, and amenable for mass production.

For optimum sensitivity in explosive trace detection in air, the proven strategy is:

1. Collect air and particulate samples from around or on the suspected object;
2. Preconcentrate the explosive molecules on a sorbant material;
3. Adsorb the released molecules from the preconcentrator on a signal transduction sensor element for detection; and
4. Analyze, characterize, and report the data.

Central to detection is chemical recognition using a selective agent and signal transduction. In an integrated system, the signal is then processed for reporting. The most important performance characteristics of trace explosive sensors include high sensitivity, selectivity, reversibility, and real-time operation. Table 1 shows commonly used sensor performance characteristics. Trace explosive detection requires extremely high sensitivity and low limits of detection (LODs) because of the relatively small number of molecules that can be collected as a result of their very low vapor pressures. High selectivity is essential in order to have an acceptable rate of false positives. To facilitate continuous operation, the sensor should be readily reversible at room temperature. These sensors should also have fast detection and regeneration times for efficient operation. Finally, the sensors should have the capability for mass deployment because of the breadth of terrorist threats involving explosives. Currently available sensor platforms are unable to meet these stringent requirements. Sensors based on nanoscience, however, offer a clear path to the development of trace explosive sensors that satisfy these criteria.

### Table 1 Definition of performance parameters for sensors

| Performance parameter | Definition |
|---|---|
| Sensitivity | The slope of a calibration curve or change in unit sensor response with change in unit analyte concentration. |
| Limit of detection (LOD) | Lowest analyte concentration value that can be detected. |
| Resolution | Smallest concentration variation that can be detected when the concentration is continuously changed. |
| Dynamic range | The analyte concentration from LOD to maximum concentration that can be reliably detected. |
| Selectivity | The ability to detect a specific analyte in the presence of other interfering molecules. |
| Reversibility | The ability of the sensor to return back to its original value when the analyte is removed. |
| Response time | The time required to respond from zero analyte concentration to a step in the concentration. |
| Linearity | The range where the sensor response is in direct proportion to the analyte concentration. |
| Hysteresis | The difference in sensor characteristics for increasing and decreasing analyte concentrations. |

## Properties of explosives

Before we discuss trace explosive detection, it is important to understand the physical and chemical properties of explosives. Explosives are chemical compounds that can be initiated to undergo self-propagating decomposition resulting in the sudden release of heat and pressure. Explosives are classified as low or high explosives based on their burn rates. Low explosives that burn at low rates (centimeters per second) include propellants, black powder, etc. High explosives, which detonate at velocities of kilometers per second, are further divided into primary and secondary explosives based on their stability. Primary explosives, such as lead azide, are extremely sensitive to external stimuli such as friction and thermal or electrical sparks for initiating explosion. Secondary explosives, such as 2,4,6-trinitrotoluene (TNT) and hexogen (RDX), are very stable and require primary explosives to initiate explosion.

Many commonly used explosives are organic compounds and can be classified into six broad classes based on their chemistry[10–13]:

1. Aliphatic nitro compounds, such as nitromethane, hydrazine nitrate;
2. Nitroaromatic compounds, such as TNT, dinitrobenzene (DNB), hexanitrostilbene, picric acid;
3. Nitramines or nitrosamines, such as octogen (HMX) or RDX;
4. Nitrate esters, such as pentrite (PETN), ethylene glycol dinitrate (EDGN), nitroglycerine, and nitroguanidine (NQ);
5. Acid salts, such as ammonium nitrate; and
6. Organic peroxides, such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD).

Explosives from the last group, known as home-made explosives (HMEs), have very high vapor pressures because of the presence of volatile organic compounds (VOCs) such as acetone. Recently, HME-based terrorism has grown rapidly because of the ease with which they can be manufactured. However, HMEs are extremely unstable and require special handling to avoid detonation.

Most common explosives have extremely low vapor pressures at ambient temperature. Table 2 shows the vapor pressures of common explosives[8]. The very low vapor pressures indicate that these molecules are extremely sticky and tend to adsorb to surfaces very easily. It should be noted that the vapor pressures of explosives increase rapidly with temperature. Explosive vapors created by heating a sample condense rapidly on cooler surfaces. Adsorption will be higher on surfaces with a high surface energy such as metals, metal oxides, etc.

**Table 2 Vapor pressures and molecular weights of some explosives**

| Explosive | Molecular weight (g/mol) | Vapor pressure at 20°C (Torr) |
|---|---|---|
| Ethylene glycol dinitrate (EGDN) | 152.1 | $5.2 \times 10^{-2}$ |
| 2,4,6-trinitrotoluene (TNT) | 227.1 | $4.8 \times 10^{-6}$ |
| Pentaerythritol tetranitrate (PETN) | 316.1 | $6.2 \times 10^{-8}$ |
| 2,4,6-trinitrophenol (picric acid) | 229.1 | $3.1 \times 10^{-8}$ |
| Tetranitro-triazacyclohexane (RDX) | 222.3 | $8.3 \times 10^{-10}$ |
| Tetranitro-N-methylamine (Tetryl) | 287.1 | $3.7 \times 10^{-10}$ |

compared with low surface energy materials such as polymers, plastics, etc. The sticky nature of explosive molecules on surfaces at room temperature also causes condensation of the molecules in delivery lines into sensor systems. Therefore, trace sampling of these families of explosives with very low vapor pressures is a challenging problem because of the small number of molecules in a sampling volume.

## Sample collection and preconcentration

Sample collection is the front end of any integrated sensor system, and for trace explosive detection it is the most challenging task. Since vapor pressures of most explosives are extremely low, a large amount of air must be sampled in order to obtain enough molecules of a particulate for detection by the sensor element. The higher the sensitivity of the sensor, the smaller the number of molecules that need to be collected for analysis. Often the sensitivity of sensors is insufficient to detect trace explosive vapors in realtime and, therefore, preconcentrators are essential for detecting explosives. Typically, a large volume of air, which is a mixture of many molecules including very low concentrations of explosives, is collected using a pump, and explosives and particulates are trapped using special materials. The trapping material is then heated to desorb the trapped molecules. The mechanism of trapping is based on the adsorption phenomena on large-area surfaces.

Conventional preconcentrators are bulky, require large amounts of power, and have slow response times. Recent advances in microfabrication have allowed the development of miniature preconcentrators that can be heated rapidly because of their low thermal mass. The microfabricated preconcentrators are coated with high affinity materials that can withstand temperature cycling and can have potentially higher efficiency than their bulky predecessors in collecting explosive molecules[14–17]. Recently, researchers at the US Naval Research Laboratory (NRL) have developed a sorbent-coated microfabricated preconcentrator device where the temperature of the device can increase to 180°C in 40 ms[17]. The adsorbed molecules, including explosive, desorb very fast during this heat cycling. Since the sorbent material is designed to have a high partition coefficient for explosives, all the explosive molecules collected over a period of time can be desorbed in 40 ms for detection by a sensing unit. The NRL preconcentrator is based on a suspended array of micro hot plates designed using complementary metal-oxide-semiconductor (CMOS) technology and coated with a thin polymer layer that selectively adsorbs the explosive molecules.

## Signal transduction using nanosensors

Nanoscale effects provide unprecedented opportunities for developing ideal trace explosive sensors that satisfy all the requirements outlined above. Here we define 'nano' in a more general sense, where reduction in size results in effects that cannot be observed with macroscale materials or provides the ability to achieve disproportionately higher sensitivity[18–22]. Nanoscale dimensions can, in certain cases, enhance physical and chemical properties, and this enhancement can originate from various sources such as increased surface area, confinement effects, etc. Recent advances in top-down fabrication techniques have spurred both micro- and nanotechnologies. Micro and nanoelectromechanical systems (MEMS and NEMS) are fabricated using similar top-down processes. As fabrication leads to smaller and smaller dimensions, better physical performance can be expected for certain types of signal transduction. For example, an increase in sensitivity can be achieved by making the sensor dimension smaller. However, increasing the detection sensitivity alone cannot satisfy all the ideal sensor requirements. The sensor also needs to have high chemical recognition capability. Despite their high sensitivity, many nanosensor platforms suffer from poor selectivity. However, the development of materials with nanoscale effects that can provide chemical speciation is still in its infancy. An example is the use of polymer particles and nanoparticles that, when bound to an explosive molecule, change one of their measurable properties providing high specificity detection (see section on receptor-free detection below). Sensor platforms that use nanoscale effects to enhance physical properties such as electrical, magnetic, mechanical, and optical properties, however, are abundant. By combining the high sensitivity offered by nanosensors with the chemical selectivity provided by some receptors, it is possible to develop miniature sensors that are highly selective, sensitive, and reversible.

In the nano arena, various bottom-up approaches have been developed using individual atoms and molecules to build useful structures, such as nanoparticles and nanowires, and functional groups for molecular recognition and self-assembly. These functional groups are then combined with micro- and nanodevices to achieve sensors with better performance characteristics, as well as signal transduction to the real world. The combination of micro/nanoscale top-down and nanoscale bottom-up processes is paving a clear path to the development of nanosensors by combing a wide variety of old and new concepts.

A large number of sensing elements/platforms exist that can be considered nanosensor platforms. This includes micro- and nanofabricated structures, quantum dots, nanowires, nanotubes, nanobelts, etc. These sensors are based on surfaces that undergo physical changes as a result of molecular adsorption. For example, micro- and nanofabricated resonant devices for mass detection undergo a variation in their resonance frequency after the adsorption of molecules. Nanosensors, however, suffer from some serious drawbacks. First, receptor-based sensors often have poor selectivity[23,24]. Second, since the sensors are extremely small physically, they do not have a large enough cross section to collect molecules on a reasonable time scale[25]. Sensors with large surface area are better for collecting explosive molecules than miniature ones. The enhanced sensitivity is thus offset by a lack of sufficient molecules for rapid detection. Also, nanosensors based on adsorption generally do not have a very large dynamic range because of the limited number of adsorption sites in the sensor.

## Receptor-based trace explosive detection

We can categorize nanosensors as receptor-based or receptor-free. Receptor-free nanosensors are based on detecting physical properties of explosives, e.g. thermodynamic, chemical, or optical properties. Receptor-based sensing achieves selectivity through the specific interaction between the receptor molecule and the explosive analyte. A change in a measurable property, such as mass, conductivity, or absorbance, is then used to quantify the interaction. However, since there are no reversible receptors that are specific for explosives yet, an array of different reversible receptors is used in an electronic nose format for speciation.

Chemical selectivity in explosive detection based on receptors originates from the chemical interaction between the explosive molecules and the receptor molecules. For reversible detection, explosive molecules must bind to the receptors with weak chemical bonds that can be broken at room temperature, for example, van der Waals interactions, hydrogen bonding, etc. Chemical selectivity based on weak interactions is very unselective and, therefore, should be used in an array format such as an electronic nose. There are a number of coatings that can be used for imparting partial selectivity, such as self-assembled monolayers (SAMs), polymers, metal oxides, single-stranded DNA, etc. The choice of coating has to take into account the response time and the recovery time.

An example of a partially selective coating for explosives is a SAM of 4-mercaptobenzoic acid (4-MBA; also known as thiosalicylic acid)[26]. SAMs of 4-MBA provide carboxyl end groups for acid-base reactions with explosive molecules. A 4-MBA SAM immobilized on Au-coated nanosensor surfaces has a $pK_a$ in the range of 5–7 and binds strongly with basic groups such as nitro-substituted molecules of explosive vapors. Recently, Zuo *et al.*[27] reported the use of 6-mercaptonicotinic acid (6-MNA) monolayers to increase the sensitivity of TNT detection. There are also many polymers with high partition coefficients for explosives[28]. Molecularly imprinted polymers (MIPs) are another way of obtaining chemical speciation. MIPs for explosives are specially generated via the interaction of functional monomers, explosive molecule templates, and a cross-linking agent. The templates are then removed prior to sensing. Only the molecules that match the template shape and properties can occupy the cavity, providing high selectivity. MIPs that are very specific for TNT have been developed and demonstrated[29,30].

## Electronic nose approach

Since most reversible receptors for explosives are not very selective, it is possible to use them in an array format for creating a response pattern similar to an artificial olfaction system[31–33]. A wide variety of highly sensitive physical sensor platforms are available for developing such an electronic nose concept. The responses from the array are analyzed with pattern recognition algorithms. However, each receptor group in the array must provide a unique signal for the pattern recognition to work. At present, an array format with a pattern recognition algorithm can identify a single chemical with certainty. However, the confidence level of the pattern recognition goes down with binary mixtures, and totally fails for mixtures of three or more components. Simply increasing the size of the array will not increase the selectivity. This is mostly because of the limited number of interactions that can serve as the basis for a given interaction. It is, therefore, doubtful that any method based on sensor arrays and pattern recognition will achieve selectivity when relying on simple interactions for speciation of small molecules, especially explosives. Concentrated efforts are presently underway to develop receptors with high selectivity.

As described above, coatings that can identify explosive molecules with no interference do not exist at the present time. This would require the use of partially selective coatings on arrays able to provide responses that are orthogonal or close to orthogonal (see section on nanomechanical sensor platforms). For each analyte vapor (explosives as well as interfering molecules), an ideal detector array would produce a unique chemical response signature[34,35]. A catalog of these signatures may be produced for a large number of analytes of interest and may then be used for the identification of unknown vapors. For single component analytes, this task is relatively straightforward, but for mixtures of several different analytes a sophisticated computational algorithm is required.

## Nanowire platform

Nanostructures such as nanowires and nanocrystals offer a highly sensitive platform for the detection of molecular adsorption on their surfaces[36–40]. Nanowires such as carbon nanotubes have diameters in the nanometer range. Inorganic nanowires and nanocrystals have unique electrical and optical properties that can be exploited for highly

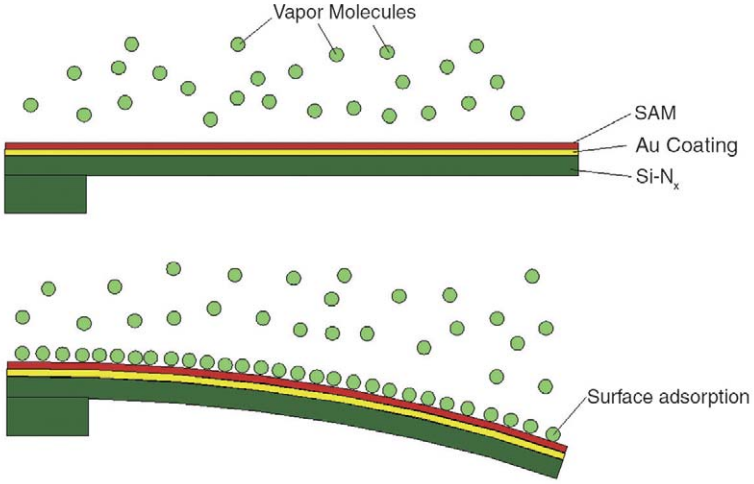

*Fig. 1 Diagram showing molecular-adsorption-induced bending of a cantilever beam arising from differential adsorption. Differential adsorption is obtained by immobilizing a selective layer on one side of the cantilever. The adsorption decreases the free energy, which changes the surface stress.*

sensitive molecular adsorption detection. The optical properties of nanocrystals can be modulated by molecular adsorption. Electrical conduction in a nanowire changes drastically through field effects induced by molecular adsorption. Snow *et al.*[41] have demonstrated an interdigitated electrode capacitor modified with single-walled carbon nanotubes (SWNTs) that can detect classes of chemical vapors with high sensitivity. When an electrical potential is applied, the huge electric field radiating from the SWNTs changes the polarization of the adsorbed molecules, which affects the measured capacitance. The change in capacitance depends on the class of molecule and can provide partial selectivity. By coating the SWNTs with chemically selective layers, however, it is possible to achieve even higher selectivity. Nanowires can be grown from many different materials such as Si, ZnO, etc., thus providing different surface properties for chemical sensing and modification with functional groups[42–45].

## Nanomechanical sensor platform

Molecular-adsorption-induced nanomechanical effects offer unprecedented opportunities for trace explosive detection. Nanomechanical sensors such as cantilever beams have many modes of operation[46–55]. For example, the resonance frequency of a cantilever beam varies with mass adsorption. The sensitivity of detection depends on the resonance frequency of the cantilever. Cantilevers with very high resonance frequencies – nanocantilevers – show very high sensitivity to mass adsorption[56]. If molecular adsorption is restricted to one side of the cantilever, the beam undergoes bending because of adsorption forces. Cantilevers with very low spring constants (low resonance frequency) show high sensitivity for bending mode operation. Fig. 1 shows the bending mechanism of a cantilever sensor. The force causing the cantilever to bend is independent of the adsorbed mass and depends solely on the binding energy of the adsorbate-surface interaction.

Cantilevers are usually microfabricated from Si using conventional photomasking and etching techniques. Typical dimensions of a cantilever can vary from 200 μm to a few microns in length, depending on the mode of operation. For miniature sensor systems, detecting cantilever response using variation in piezoresistance is very attractive[57]. In piezoresistive cantilevers, any change in deflection of the cantilever results in a variation of the cantilever resistance. The Si piezoresistive cantilever fabrication technique developed by Boisen's group[58] produces cantilevers with high sensitivity, low electronic noise, and very small drift. Fig. 2 shows a scanning electron micrograph of a piezoresistive cantilever array. The piezoresistive readout technique is miniature and compatible with electronic packaging. Fig. 3 shows the differential bending response of a piezoresistive cantilever beam coated with 4-MBA with respect to an uncoated cantilever when exposed to TNT vapors. A reference cantilever (uncoated) makes it possible to collect the response signal in common mode rejection.

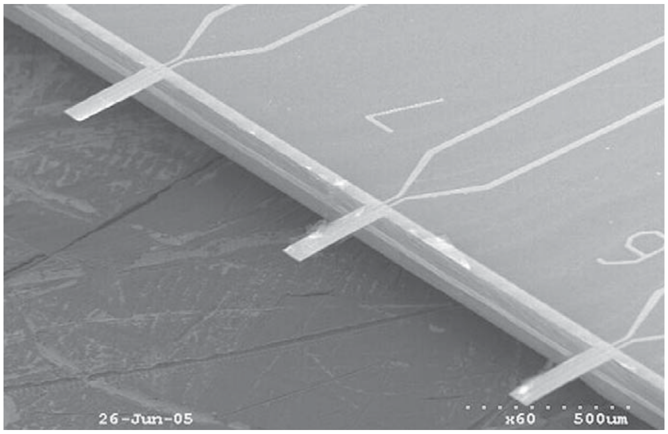

*Fig. 2 Scanning electron micrograph of a piezoresistive microcantilever array. The electrical resistance of the cantilever changes with bending. Cantilever bending from submonolayer coverage of adsorbed molecules can be detected.*

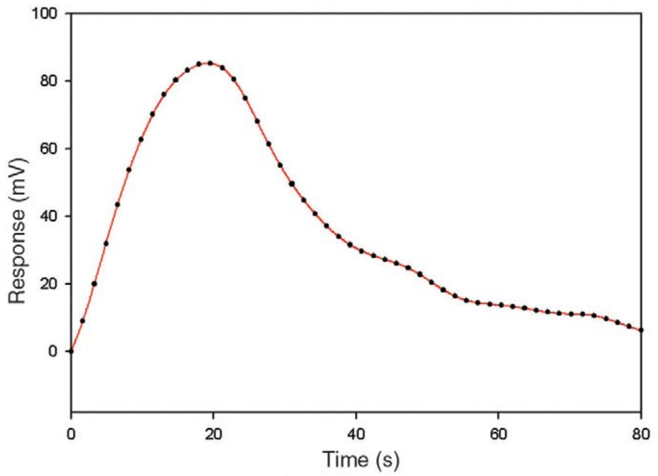

*Fig. 3 Differential bending response of a piezoresistive cantilever coated with a 4-MBA functional layer with respect to an identical but uncoated cantilever when exposed to TNT vapors. The cantilever is exposed to the TNT vapor for 20 s, followed by a 60 s desorption period where it is flushed with dry nitrogen only. As the TNT desorbs from the cantilever surface, the bending returns to the original baseline value and the device is ready for another exposure.*

This makes it possible to reject environmental interference, such as temperature fluctuations, that would otherwise show up in the signal. The device is exposed to TNT for a short period followed by a flow of dry nitrogen. This produces the response peak shown in Fig. 3 followed by a desorption period during which the adsorbed material is removed by the nitrogen, leaving the device ready to detect a new analyte. Since the cantilever coatings are only partially selective, an array where each cantilever is coated with a different selective coating is needed for speciation. Fig. 4 shows the response from an array of cantilevers coated with different partially selective coatings. The exposure of the array to all analytes is conducted in the same manner as described above for TNT. The weak bonding between the analytes and the cantilever coatings makes it possible to desorb the analytes with a flow of nitrogen, thus regenerating the detector. The array response patterns can then be analyzed with pattern recognition algorithms to provide speciation of the analytes.

## Receptor-free trace explosive detection

A cantilever platform offers the possibility of detection methods based on thermal processes because of its low thermal mass[59–61]. When a microcantilever with adsorbed explosives is heated rapidly at a rate of $10^5$ °C/s, the explosive undergoes thermally induced decomposition/deflagration. Heating a cantilever at such a high rate is accomplished by passing a current pulse through the cantilever (10 V, 10 ms). During heating, the temperature of the cantilever increases from room temperature to close to 500°C. Differential cantilever bending with and without adsorbed explosives shows a deflagration response of adsorbed TNT (Fig. 5). A sensitivity of 40 pg is demonstrated for deflagration-based cantilever sensors. In this technique, the cantilever cleans itself at the end of each heat cycle. The technique has the potential of being miniaturized.

Another approach using the very high thermal sensitivity of a cantilever beam is photothermal deflection spectroscopy[62–65]. Bimaterial cantilevers have been demonstrated to have very high sensitivity to changes in temperature. A bimaterial cantilever undergoes bending because of the changes in temperature resulting

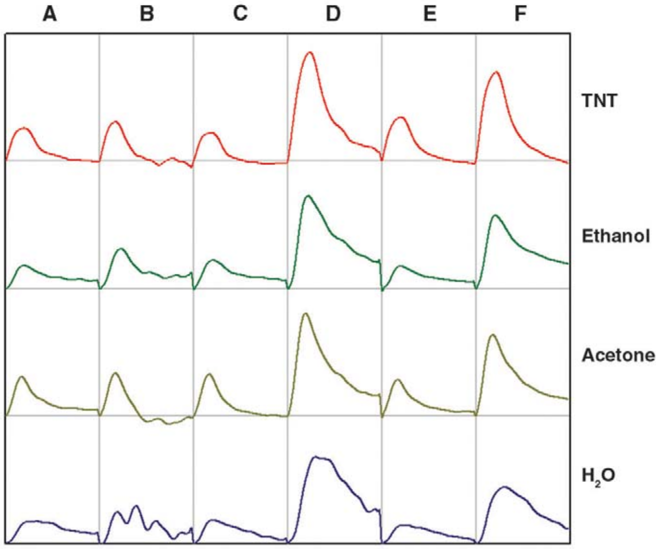

*Fig. 4 Response patterns of an array of six cantilevers each coated with a different SAM (columns A-F) when exposed to vapors of TNT, ethanol, acetone, and water. Each column shows the 80 s bending response (see Fig. 3) of one cantilever/coating (A-F) when exposed to each of the four analytes. The rows in the figure are produced by placing all six responses to one analyte side by side to produce a response pattern that is unique to the analyte. These response patterns are then analyzed with a pattern recognition algorithm for speciation.*

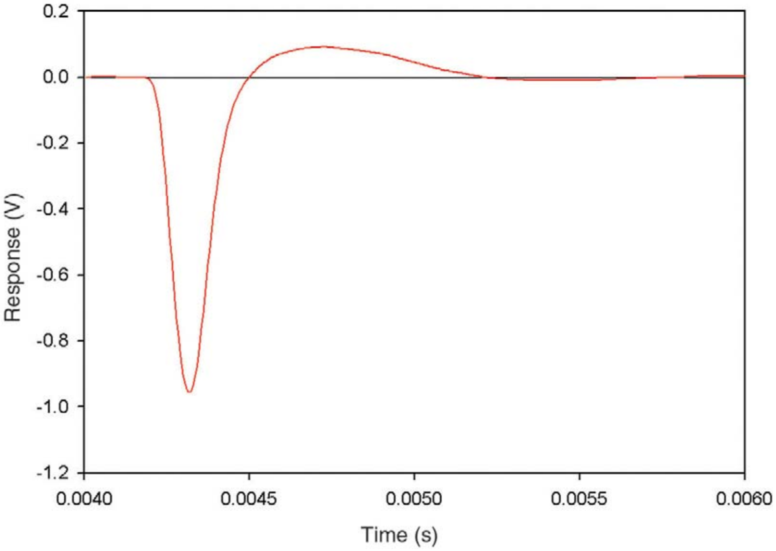

*Fig. 5 Deflagration response. As the cantilever exposed to an explosive is heated, its temperature first lags behind the temperature of the reference cantilever (no explosives) because of the increased thermal load. Then as the explosive reaches the deflagration temperature, the exothermic process causes the temperature of the loaded cantilever to increase and exceed that of the reference cantilever. As the explosive leaves the cantilever, the temperature returns to that of the reference cantilever.*

from, for example, adsorption of infrared (IR) energy by the cantilever or adsorbed molecules. Resonant absorption of IR radiation by a monolayer of adsorbed explosive molecules results in bimaterial cantilever bending caused by the nonradiative de-excitation of the molecules. A mechanical IR spectrum of the adsorbed explosives can be obtained by sequentially exposing the cantilever to IR radiation from a monochromator. The bending of the cantilever as a function of illuminating wavelength reveals the IR absorption spectrum of the molecules adsorbed on the cantilever surface. This photothermal deflection signal depends on the temperature changes arising from absorption of IR energy, and is directly related to the vibrational modes of the adsorbates and to the heat capacity and thermal conductivity of the cantilever beam. Fig. 6 shows the mechanical photothermal deflection spectrum of TNT adsorbed on a cantilever. The observed photothermal spectrum corresponds to the excitation of various vibration modes of the explosive. The thermal energy is then transferred to the bimaterial substrate causing cantilever bending. The extent of bending is proportional to the released thermal energy. Almost all of the peaks observed in the photothermal spectra match very well with the conventional IR absorption spectra. For example, the

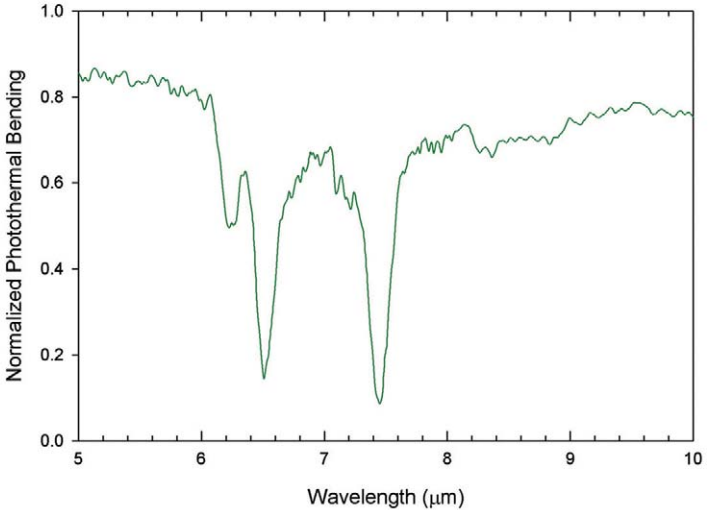

*Fig. 6 Photothermal deflection spectroscopy of adsorbed TNT on a cantilever. When a bimaterial cantilever that is exposed to TNT is sequentially illuminated with infrared (IR) radiation, the cantilever bends as the adsorbed TNT molecules absorb the energy. The plot of the bending as a function of the IR wavelength creates a mechanical IR absorption spectrum of TNT.*

symmetric stretching vibrations of the C–$NO_2$ bonds cause the peak at around 7.5 μm, while the 6.5 μm peak is caused by the asymmetric stretching vibration of the same bonds. However, the relative intensities of the peaks are slightly different for the photothermal spectrum compared with conventional IR spectra because of surface effects. The extent of bending is directly proportional to the adsorbed explosives, the impinging power of the IR radiation, the absorption mode, and the thermal sensitivity of the cantilever. The disadvantage, however, is the need to incorporate a tunable IR source.

Another highly successful platform for trace explosive detection is based on amplifying fluorescence polymers (AFP)[66–69]. These polymer fluorescence characteristics change when TNT molecules are adsorbed on the polymer. The AFP fluoresces when continuously excited by an ultraviolet light source. However, when a single molecule of TNT adsorbs on the polymer, the fluorescence is quenched. A chain of such conjugated polymer quenches is observed when TNT molecules adsorb anywhere on the molecular wire. The fluorescence can be detected with simple optical components. The AFP signal transduction is highly selective and very sensitive for TNT vapor detection. A commercial version of this sensor is marketed by Noamdics, which uses thin films of AFP. Many variations of the fluorescence platform exist[70–72]. For example, nanocomposite films, such as silica doped with nitrogen-containing macrocyclic molecules (porphyrins), show fluorescence quenching in response to explosive molecule adsorption[73].

Receptor-free detection of nitroaromatic explosives can be carried out using electrochemical techniques that make use of redox properties[74–76]. However, these methods are useful only if the explosives can be first dissolved in a solution. Most explosives are not very soluble in aqueous media. Pulsed voltammetry has been demonstrated for the detection of TNT in a marine environment. In this method, nitroaromatic groups are first reduced into hydroxylamines followed by conversion of the hydroxylamines into amines. In electrochemical methods, the reduction potential with respect to a reference electrode is unique and thus provides selectivity in detection. Variations of electrochemical techniques can be miniaturized. The technique is very simple and easy to use. Electrochemical detection has limitations, however, for example the explosives must be in an electrolyte for detection. Electrochemical techniques also have limited sensitivity.

## Combined platforms

It is possible to achieve true chemical selectivity for explosive molecule detection by combining different sensor platforms, or different operational modes of the same sensor platform, to obtain orthogonal signals. For example, the mass, stress, and thermal signals of explosives measured with cantilevers are truly independent of one another and can provide orthogonal signals for pattern recognition. In addition, the ability to heat cantilevers to well above room temperature allows the use of coatings that bind explosive molecules with higher energies (for example, Lewis donor-acceptor, Bronsted acid-base, and charge transfer interactions that have enthalpies ($H$) in the range 100–400 kJ/mol). Although these binding mechanisms are irreversible at room temperature, sensor regeneration can be accomplished by heating the cantilever by passing an electrical current through it. The temperature at which these analytes desorb also carries selectivity information. Selectivity and sensitivity can also be accomplished by combining different platforms into a single sensor unit for measuring different chemical and physical properties. For example, the electrical polarization effects of adsorbed explosives can be measured as changes in capacitance of a SWNT sensor with mass and stress measurements made using cantilever arrays. It is also possible to combine some of these ultrasensitive platforms with separation methods, such as gas chromatography, to obtain chemical selectivity. However, separation methods can increase the detection time. Fast micro-GCs are under development that, in combination with ultrasensitive sensors, can detect explosives vapors.

## Challenges in moving toward practical application

Creating a sensor that is both sensitive and selective is only the first part of the challenge. The second part involves bringing explosives from the environment to the sensor element. The practical application of nanosensors for trace explosive detection will require integrating nanosensor elements into a system that includes vapor collection and preconcentration.

The integration requires many challenges to be overcome. Extremely low vapor pressures limit the number of explosive molecules that can be collected in a reasonable detection time. Also, the concentration of the explosives decreases exponentially as a function of distance from the source. Very low concentrations of explosive molecules can increase the false positive rate. Effective techniques for sample collection and preconcentration are, therefore, very important in developing practical sensor systems.

The preconcentration step will increase the detection time. Since explosive molecules stick to surfaces, delivery lines and other components need to be maintained at a higher temperature. Operating at higher temperatures decreases sensitivity. However, a decrease in sensitivity is preferable to sacrificing selectivity, especially when using receptor-based signal transduction that depends on low-energy molecular interactions. For example, water molecules that occur at orders of magnitude higher concentrations than explosives can severely restrict the selectivity when certain receptors are used. Techniques based on arrays can provide partial selectivity. However, a multimodal array approach, where a combination of receptor-based and receptor-free techniques is used for detection, can lead to high selectivity and sensitivity in practical explosive detection. Nanosensors offer the freedom of multimodal detection, and therefore make an ideal platform for trace explosive detection.

## Conclusions

Trace explosive detection with high sensitivity and selectivity is a formidable challenge because of a number of operational factors, such as the acute dearth of explosive molecules that can be collected in a reasonable time, lack of selectivity because of interference from other molecules, and the breadth of chemical compounds and combinations that can be used as explosives. However, nanoscale effects can be exploited to offer the possibility of sensors that satisfy all the requirements for trace explosive detection. Nanosensors with increased sensitivity and selectivity and the ability to operate in a multimodal platform offer a potential paradigm for deploying a large number of sensors for detection. We have shown that nanosensors have potential as highly sensitive and very selective signal transduction platforms for an integrated explosive sensor system.

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