

Overview of nano enabled sensor for analysis of explosive substances

Sandeep K Vaishnav *, HS Bhawara and Rajesh Mishra

State Forensic Science Laboratory, Police Line Campus, Tikrapara, Raipur, Chhattisgarh, India.

Abstract

Threats of armed conflict and terrorist attacks present difficult challenges for defense agencies around the world and are an increasing source of worry for the public and security-conscious policymakers. The environmental monitoring of residue or discarded explosives in soil, as well as the detection of ultra-low levels of explosive compounds in remote areas or under extreme conditions for anti-terrorist activities, continue to pose significant challenges. Most explosives produce very little vapors, making it difficult to detect them with common techniques for other compounds. Due to a number of factors, including the large variety of explosives substances, the enormous number of deployment methods, and the dearth of low-cost sensors with high sensitivity and selectivity makes explosive detection very complicated and expensive task. To defeat explosives-based terrorism, sensors must have high sensitivity and selectivity as well as the capacity to produce and deploy them at lower costs. Nanotechnology-based sensors have an excellent possibility of meeting all the criteria for a successful approach to explosive trace detection. The design and analytical capabilities of explosive detection systems employing nanomaterial as signal transducers are covered in this overview. The review article also discusses the importance of nano-enabled technologies for the explosive detection in security applications, gives background on the technology, and identifies other issues that need to be resolved.

Keywords: Nanoprobes; Nanosensor; Nanomaterials; Nano-enabled; Multifunctional nanomaterial; Explosive substances

1. Introduction

Forensics, environmental monitoring, as well as the production and storage of explosives, all require the ability to detect minute quantities of explosives. Explosives continue to pose a threat to national and global security. Recent occurrences [1-3] have highlighted the significance of explosive trace detection (ETD) technologies. The use of homemade explosives (HMEs) in terrorist operations is a particular cause for concern because of their devastating potency, ease of acquisition, and accessibility to online tutorials for production and use. Therefore, there is a constant need to enhance current ETD technology and maintain initiatives to find new strategies. This review's objective is to inform readers of the nano technological advancements in important ETD technology.

There are different types of explosives, which can be classified according to their structure and composition (Figure 1). The use of nitroaromatic explosives i.e. TNT, DNT in ammunition raises environmental concerns. [4] Organic peroxides that are sensitive to heat, shock, and friction are frequently employed in HMEs. Several Nitrate esters are liquids, and they are used in the military as plastic explosives, detonators, and propellants. Ammonium nitrate/fuel oil (ANFO) and urea nitrate (UN) are two of the most commonly used explosive precursors for improvised explosive devices (IEDs). The different chemical and physical properties of explosives make sample collection and explosive trace detection a challenging task. The majority of particulate sampling is achieved through use of sampling wands so direction, pressure and technique are important factors for successful collection of material. Vapour sampling is even more challenging since many explosives have very low vapour pressures. Many explosives are also considered "sticky" and will adhere to

* Corresponding author: Sandeep K Vaishnav

a range of surfaces which result in accumulation of explosive particles, thus limiting the number of analyte molecules per volume of sample. Furthermore, screening baggage poses logistical and operational challenges. Cargo is usually wrapped in protective materials which may restrict efficient sampling. In all cases, there will be interference from benign materials which could cause false positive alarms. Therefore, deployment of new detection technologies requires careful consideration of the regulatory (threats, sensitivity, selectivity), operational, civilian and financial requirements.

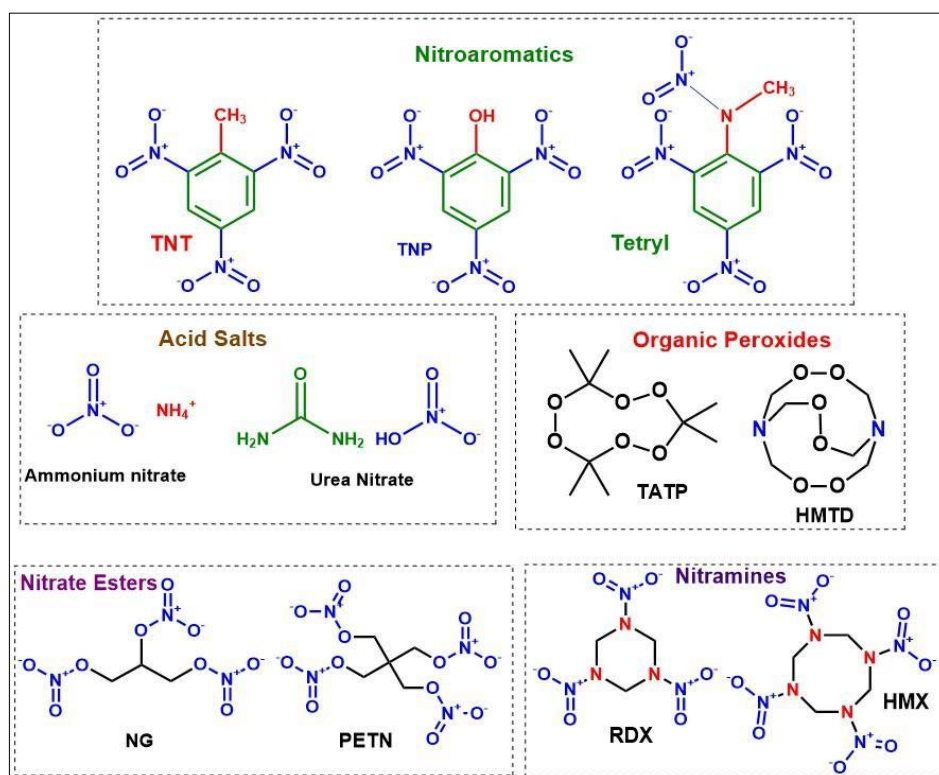


Figure 1 Classification of Explosives by Chemical Group

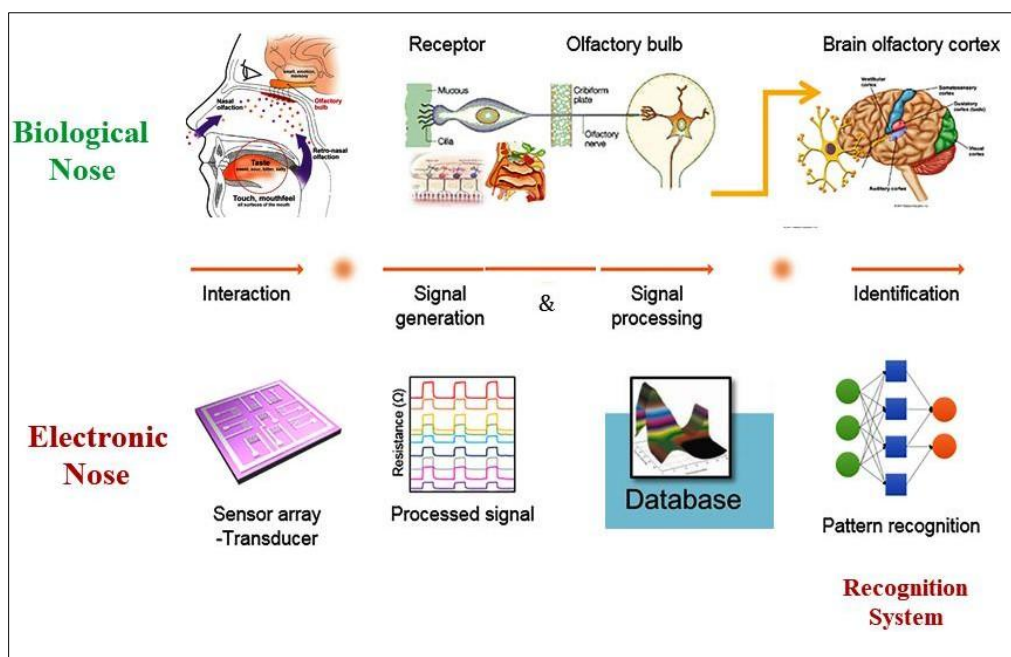


Figure 2 Electronic Nose Concept

The research and development studies in the area of nanomaterials have demonstrated the ability of nanostructures to function as sensors of various chemical and biological compounds including explosives. Ultra-small devices with high sensing capabilities are among the key promises of the nanosensor domain. Electronic noses, nanowire/ nanotube and nanomechanical devices are nanosensor concepts with the strongest potential to form viable technological platforms for trace explosive detection. The electronic nose technique can mimic the bomb-sniffing dogs without their drawbacks. An electronic nose device is composed of a chemical sensing system, sampling system and pattern-recognition system, such as an artificial neural network (Figure 2). [5] The current review highlights such kind of nanoenabled techniques for detection of trace amount of explosive.

2. Nano-Enabled Technologies for Explosives Detection

The area of nanotechnology is developing quickly, and as nanomaterials are controllable, they are ideal for use in sensor arrays. Utilizing the high surface areas that nanostructured materials offer for detection as well as their distinct electrical, optical, catalytic, magnetic, and mechanical features, selectivity can be attained. There are numerous ways of categorizing nanomaterials, and Table 1 provides some possibilities based on chemical composition.

Table 1 Different classes of nanomaterial sensor used for the detection of explosive

Type	Detection method	Detection Method	LOD	Ref.
Plasmonic	Au nanoparticles functionalised with 4-Aminothiophenol and N-(1-Naphthyl)-ethylenediamine dichloride (NED)	PETN	0.15 mg L ⁻¹	6
	Electrochemical sensor consisting of Ag nanoparticles on carbon fiber electrodes	TATP, HMTD	200 ppb, 250 ppb	7
	Cu nanoparticle-incorporated polyfurfural film electrochemical sensor	TNT	41.6 ppb	8
Semiconductors	TiO ₂ sensor contained within a quartz crystal Microbalance	NG	1-10 ppm	9
	Optoelectronic sensor using polyoxometalatedoped TiO ₂	TATP	50 ppb	10
	In ₂ O ₃ amperometric sensor	TATP	2.9 ppb	11
Quantum dots	WO ₃ and chromium titanium oxide gas sensor	Ammonia, nitromethane, NO ₂	2.8 ppm	12
	Fluorescent silicon nanodots	TNP	0.92 nM	13
	L-cysteine-coated CdS quantum dots	TNP	39 ngML ⁻¹	14
	Electrochemiluminescence (ECL) resonance energy transfer (RET) sensor using CdTe quantum dots	TNT	0.65 ppm	15
Carbon based	Electrochemical sensor using MIP cast on multi-walled carbon nanotube (MWCNT)	RDX	20 pmol L ⁻¹	16
	SWCNT	TNT	772 ppb	17
Hybrid Composite Nanomaterial	Porphyrin-functionalized grapheme	DNT, TNT, DNB, and TNB	0.5 ppb, 1ppb	18
	Mesoporous silica nanoparticles (MSNs) encapsulating poly (p-phenylenevinylene) (PPV)	TNT	1.3 x 10 ⁻⁷ M	19

2.1. Inorganic Semiconductors Based ETD Sensors

Low manufacturing costs, simplicity of usage, and high levels of thermal, chemical, and electrical stability makes Metal Oxide (MOx) semiconductors attractive materials for sensing applications. [20] These characteristics have led to a variety of applications, such as the monitoring of hazardous and volatile organic compound emissions as well as environmental pollutants. [21, 22] Electron transition energies in the UV/visible range of the electromagnetic spectrum are characteristic of MOx semiconductors, which also have high band gaps (> 2 eV). A wide customizable spectral range can also be used to increase sensitivity and selectivity. This is advantageous for electronic and optoelectronic sensors. The most popular type of gas sensor is a resistive one, and it works by measuring the conductance change that occurs when a target molecule binds to it. [23] In natural environment, oxygen ions are created when O_2 adsorbs on the MOx surface. The MOx sensor's conductivity is influenced by the target gas's oxidative/reductive state and the type of charge carrier, which can be either electrons or holes in n- or p-type semiconductors, respectively. TiO_2 , ZnO, [24], [25], Sn_2O , [26] and Cu_2O are only a few of the n- and p-type semiconductor materials that have been employed for explosives detection. The conducting glasses ITO and FTO were coated with TiO_2 nanostructures that were produced by Tang et al. With detection being possible at ppb levels, the photoresponse to TATP was maximum for TiO_2 -FTO homojunction complexes. The authors discovered that the sort of nanostructures generated during the production of TiO_2 depended on the placement of the conducting glass. [27]

A chemiresistive sensor for the detection of ammonium nitrate was created by Bastatas et al. using ZnO-coated silica nanosprings (AN). Improved charge carrier activation, easier analyte desorption, and easier sensor reuse were all made possible by UV irradiation. TNT, DNT, TNP, RDX, and AN may all be detected using a chemiresistive sensor array that was created by Qu et al. [28] To enhance the adsorption of explosives onto the MOx surface and sensor responsiveness, the scientists doped ZnO with Co, Ni, and Fe to form p-type semiconductor films. Response periods of 12 seconds were required for detection to occur at ppb-ppt values. The scientists explain the quick response of the doped sensors by a decrease in the charge transfer distance between the charge reservoir layer and the MOx nanoparticles' surface defect centers [29] (Figure 3). A promising advance, not only in terms of decreased energy usage but also in terms of decreased potential risks for use in an operational environment, is the capacity of some MOx sensors to function (as demonstrated by Bastatas and Qu) at low temperatures. The working temperature change, sensor arrays and composite materials can be used to increase the selectivity of MOx semiconductors towards particular explosives. Oxygen is charged and adsorbed onto the MOx surface at different rates depending on temperature variation. So, it is possible to profile particular gases using sensor response. The information from many sensors with various operating temperatures can be combined to increase selectivity. [20, 30] It is possible to create composite MOx structures in which each material is selected with preference for a certain gas analyte. [31] To find TATP and DADP, Warmer et al. employed SnO_2 and WO_3 . The authors observe that the oxidising and reducing actions of organic peroxides are temperature-dependent and take advantage of this property to increase the selectivity of WO_3 films toward TATP by varying the temperature. The LOD for the sensor was in the ppb range. [32]



Figure 3 Fe-doped ZnO chemiresistive sensor (A and C) Models showing the charge transfer mechanism of undoped and doped ZnO (B) Schematic representation of the gas sensor array composed of three doped sensor; Fe-ZnO, Co-ZnO and Ni-ZnO, (D) Schematic representation of the gas sensor array composed of four sensor; ZnO, Fe-ZnO, Co-ZnO and Ni-ZnO.[29]

Tracense Systems has created an E-nose using SiNW-FETs, or silicon nanowire field effect transistors. Explosives that contain nitro or peroxide group can be selectively bound by silicon nanowire arrays that have undergone chemical modification. Explosives can be detected by observing how the conductance changes when they are adhered to the arrays. TNT and the peroxide explosives TATP and HMTD both demonstrated parts-per-quadrillion (ppq)-ppt detection. [33, 34] Yang et al. created an array of Schottky optoelectronic sensors using SiNWs that were combined with TiO₂ and reduced graphene oxide. For a variety of nitro-based explosives, limit of detection were reported to range from 0.05 ppq to 74 ppb. [35] By substituting ZnO for TiO₂, the same group was able to differentiate among urea, black powder, and nitrate- and nitro-explosives. [36] Utilizing catalytic properties of some metal oxides as thermodynamic sensors allows for the attainment of selectivity. In this instance, a common setup entails scanning two microheaters, one of which has the catalytic material coated in it. Thermodynamic data pertaining to the catalytic activity unique to the analyte can be gathered by comparing the electrical energy necessary to keep both heaters at a constant temperature. Amani et al employed [37] SnO₂-x and ZnO in this manner to detect TATP at ppm levels. [38] Similar technology created by Rossi et al. enhanced detection to ppb levels by employing sensors with smaller thermal masses. Additionally, it was shown that SnO > ZnO > CuO was the order in which metal oxide catalysts were most sensitive to TATP. According to the authors, the catalyst undergoes catalytic oxidation or reduction as a result of the breakdown of TATP. [24] Additional enhancements to this system included the installation of a conductometric platform to gather both the thermodynamic response and the electrical resistance of the catalytic MOx sensor. [39]

2.2. Organic Semiconductors Based ETD Sensors

In most conjugated polymers, the polymer chain alternates between single and double bonds, resulting in a conjugated structure and a persistent delocalized electron system. Unique photoconductive, photoluminescent, and mechanical traits result from these characteristics. Research on conjugated polymers has mostly concentrated on adjusting their fluorescence characteristics to increase sensitivity and selectivity for explosives detection. Later in the study, examples of these materials are discussed. This section will discuss research on conducting polymers, a subset of conjugated polymers and a group of materials known as organic semiconductors. [40, 41] Tunable electrical characteristics and mechanical plasticity are two appealing characteristics of semiconducting polymers. Additionally, a variety of simple deposition techniques are available, which makes them perfect for composite sensors in E-noses. [42, 43] Diketopyrrolopyrrole and metal organic framework were used as the sensing elements in the development of an organic field effect transistor (OFET) sensor by Surya et al. In this system, the thienylenevinylene-thienylene (PDPP-TVT) semiconducting polymer served as the channel material, and the Cd(II) MOF served as the receptor and pre-concentrator. TNT and RDX were found by the system at ppb and ppt concentrations, respectively. [44] Loch et al. created semiconducting poly (dendrimers) customized with fluorine and carbazole as fluorophore moieties for the sensing of DNT and the explosive taggant DMNB. [45] For the purpose of detecting the vapour of explosive precursors based on nitro and peroxide, Blue et al. developed polymer-based microsensors. The conductive polymer PRODOT (3,4-Propylenedioxythiophene) was used as the starting material by the authors to create copolymers. The final copolymers were electrochemically coated onto interdigitated electrodes (IDEs), and sensing was accomplished by determining the change in capacitance upon target vapour adsorption. For nitrobenzene and 2-nitrotoluene, detection thresholds of 200 ppb were reached; for peroxide vapours, ppm values were attained. [46]

2.3. Graphene and Carbon Nanotubes Based ETD Sensors

Due to their advantageous electrical, mechanical, and chemical properties over inorganic counterparts, carbon-based semiconductors like grapheme and carbon nanotubes (CNTs) have received substantial attention as sensing materials. These materials can be chemically functionalized, and many of them are printable using inexpensive techniques. [47] The high surface area to volume ratio of graphene's 2D structure and the sp² network's ability to enable interactions make it ideal for the detection of explosives that lack electrons in the nitroaromatic family. [48, 49] The addition of oxygen containing functional groups, either chemically as graphene oxide [50] or during the manufacturing process [51], can enhance sensitivity further via van der Waals interactions with the NO₂ groups. Peptide modifications, nanoparticles, doping, [52] organic polymers, and peptide modifications are examples of techniques used to increase the selectivity of graphene materials for ETD. [53, 54] With the majority of investigations concentrating on nitroaromatic materials, the high conductivity of single walled (SW) and multi-walled (MW) carbon nanotubes has also been examined for explosives detection (Figure 4). According to research by Woods and Star, the interactions involving CNTs and nitroaromatic explosives entail both charge-transfer and stacking effects. [55, 56]

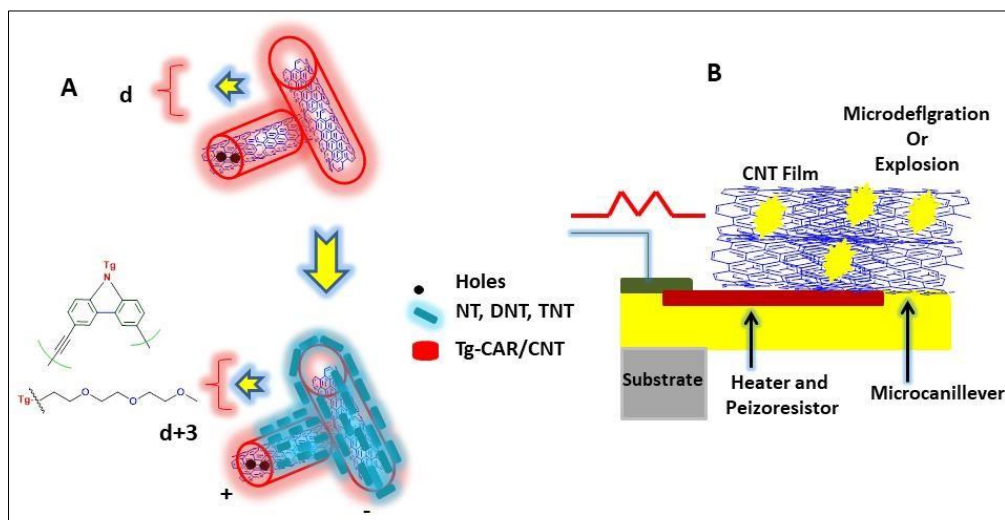


Figure 4 Sensing of Nitroaromatic explosive using Carbon nanotubes (A) using single walled CNT modified with Tg-Car/CNTs. (B) Piezoelectric microcantilever sensor coated in CNT Film. [57]

On the same footnotes a high performance chemiresistive sensors for trace vapor detection of nitroaromatic explosives by employing a porous thin film of single-walled carbon nanotubes (CNTs) coated with a carbazolyethynylene (Tg-Car) oligomer. The sensors detect up low quantities of 2, 4, 6-trinitrotoluene (TNT), 4, nitrotoluene (NT), and 2, 4-nitrotoluene (DNT) vapours at ppb to ppt levels. At substantially greater vapour concentrations, the sensors also exhibit remarkable selectivity to NT from other typical organic reagents. (Figure 4) [57] Stefano et al. examined the performance of a TNT electrochemical sensor utilizing electrodes coated with pure and acid-treated CNT. The study discovered that due to catalytic effects and enhanced electrode surface roughness, residual metallic impurities in pure CNTs can enhance the electrochemical response for TNT. [58] Due to their fluorescent characteristics and chemical inertness, carbon dots another nanoform of carbon employed in ETD have interesting uses for sensors. For the selective detection of TNT, Ran et al. employed carbon dots that had been modified with nitrogen and the macrocyclic structure pillar[6]arene. The electrochemical sensor reached a 0.95 nM detection limit. [59] Wang et al. created a magnetic carbon dot-based MIP composite for the sensing of TNP with a LOD of 0.5 nM. [60] O-phenylenediamine and chloroform were used in a straightforward solvothermal process by Ju et al. to create carbon dots. The LOD on the colorimetric sensor was 2 μ M. The carbon dots were immobilised on normal filter paper to show the practical use of this technique. [61]

2.4. Quantum Dots Based ETD Sensors

The quantum confinement effects of quantum dots (QDs), which are nanocrystalline semiconductor materials, give them outstanding fluorescence capabilities. In addition, QDs have broad excitation spectra, narrow emission spectra, and great stability, all of which make them suitable as colorimetric probes. The peculiar optical features of QDs result from their small size, which ranges from 2 to 10 nm. Semiconductor crystals are the same size as the Bohr radius and, thus, the distance between an electron hole pair at these dimensions. At these distances, the semiconductor material's conduction band divides into sub-bands with distinct energy levels, and the bandgap changes in relation to the crystal's size [62, 63]. With emission wavelengths attainable from UV to near-IR, this significantly boosts the tunability of QDs. Based on their semiconductor components, QDs can be divided into four categories, with the majority of advancements occurring in groups II–IV and IV. [64–66] Graphene QDs and carbon QDs, both of which have previously been discussed, are examples of carbon nanostructures that can be included in [67, 68] QDs. Additionally, semiconductor QDs can be divided into core-type, core-shell, and alloyed categories based on their chemical make-up. Fluorescence resonance energy transfer (FRET) and photo-induced electron transfer (PET), which are both frequently employed to produce such sensing, can be utilized to detect nitroaromatic explosives due to the electron-rich nature of QDs (Figure 5). [69, 70] Khan et al. employed a FRET-based sensor made of co-doped N and S carbon QDs to detect TNP. The greatest fluorescence emission of the developing donor QDs was observed at 300 nm, which was reduced in the influence of TNP. [71] CdS QDs and diphenylamine were utilized by Ganiga et al. to detect RDX and PETN. The luminous CdS QDs served as the acceptor in this system and were quenched by the diphenylamine. Explosives and diphenylamine interact electrostatically, forming a complex and restoring fluorescence with a maximum emission at 355 nm. [72] For the purpose of detecting TNP, Gong et al. synthesized QDs made of core-shell CdSe/silica that had been functionalized with NH₃. [73] Peveler et al. created a fluorescent sensor array using modified core-shell CdSe/ZnS QDs with calixarene, cyclodextrin -OH, and -OMe surface modifications. Fluorescence quenching of the QDs results through interactions involving explosive targets and surface receptors that results from host-guest binding, electrostatics, and stacking

(Figure 5). At ppb levels, the system was able to distinguish among DNT, TNT, tetryl, RDX, and PETN. The use of machine intelligence also produced effective classification outcomes. [74, 75] A chemical sensor for TNT has been reported by Komikawa et al. employing TNT-binding peptides coupled to CdTe/CdS quantum dots. Fluorescence quenching is used to detect the presence of TNT. [76] Using SiO₂ spheres with a 3-mercaptopropionic acid capped and L-cysteine-capped CdTe quantum dots, Qian et al. created a two-component composite sensor (QDs). The Meisenheimer complexes formed between TNT and the amine moiety of cysteine were used to detect TNT. By comparing the ratio of the fluorescence intensities of the two probes, a correlation between TNT concentration and fluorescence emission was found. A reported limit of detection was found to be 3.3 nM. [77] Molecular-imprinted polymers (MIPs) and doping are further methods to increase the selectivity of QDs towards explosives. [60, 78]

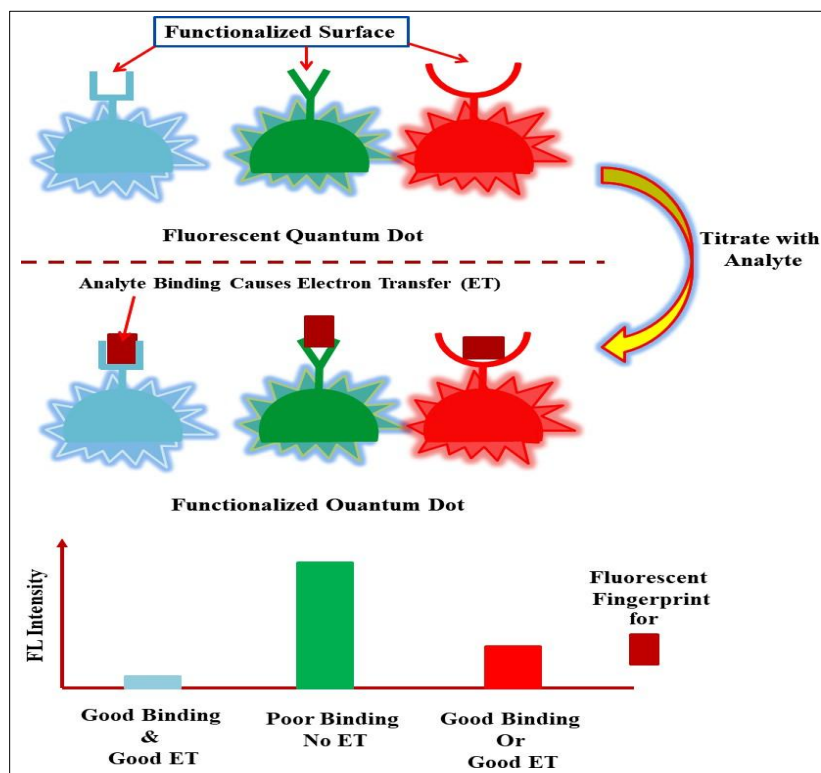


Figure 5 Fluorescent assays consisting of modified CdO/ZnS quantum dots (QDs): Schematic representation showing sensing mechanism using the QD system

2.5. Metal Nanomaterial Based ETD Sensor

Due to their increased surface areas, catalytic effects, and improved electrical conductivity, metal-based nanoparticles (such as gold, titanium, platinum, and others) have been used for explosives detection because they can result in enhanced sensitivities, particularly in electrochemical systems and in optical sensors. Below is a summary of the various nanoparticles that have been used to electrochemically detect trace explosives. The use of modified carbon electrodes with mesoporous titanium dioxide, which serves as a support with deposited nanoparticles of ruthenium, platinum, or gold for TNT detection, has been described by Filanovsky et al. [79]. The benefits of using TiO₂-PtNP and TiO₂-AuNP electrodes in this work included well-separated TNT and oxygen reduction signals, high sensitivity, and good linearity between peak currents and TNT concentration. In a different study, Willner et al. employed gold nanoparticles to increase the sensitivity of TNT detection electrochemically [80]. A functionalized electrode for detecting TNT at parts per trillion (ppt) concentrations was produced by aggregating AuNPs on the Au electrode and bridging them with oligoaniline units. By adjusting the donor-acceptor interactions between TNT and donor-crosslinked AuNPs, this was accomplished. Moreover, by imprinting molecular recognition sites into the donor oligoaniline-cross-linked AuNPs, the sensitivity was increased to TNT concentration of 200 pM. The colorimetric sensing of TNT at picomolar levels was made possible by Jiang et al. [81] utilising a simplified technique using gold nanoparticles. The procedure was based on the colour shift of AuNPs brought about by the donor-acceptor (D-A) interaction between TNT and primary amines, in this case cysteamine, which serves as both a primary amine and a stabilizer for the AuNPs. As shown in Figure 6, the addition of TNT to the aqueous solution causes the cysteamine-stabilized AuNPs to aggregate, changing their hue from red to violet blue (Figure 6). Jiang group noticed that the solution's hue, which could be seen with the unaided eye, altered after the addition of 114 pg L⁻¹ of TNT. Trace explosives were detected using Surface Enhanced Raman

Spectroscopy (SERS), one of the sensitive methods for molecular detection [82]. In order to recognise TNT at a 2 pico molar (pM) level in aqueous solution, Dasary et al. showed that gold nanoparticles modified with cysteine can serve as SERS probes [83]. TNT causes gold nanoparticles to assemble as a result of the Meisenheimer complex that forms between TNT and cysteine. It thus created hot patches and significantly increased the Raman signal's strength. For the SERS method of TNT detection, Yang et al. employed silver nanoparticles functionalized with p-aminothiophenol (PATP) encapsulated on silver molybdate nanowires [84]. PATP molecules bound on silver nanoparticles undergo a catalytic coupling reaction to provide DMAB, which can produce imprint molecule sites that constitute SERS "hot spots." The Raman signal strength is markedly increased when the TNT analyte is anchored at the hot regions. The detection limit (LOD) for TNT was about 10^{-12} M.

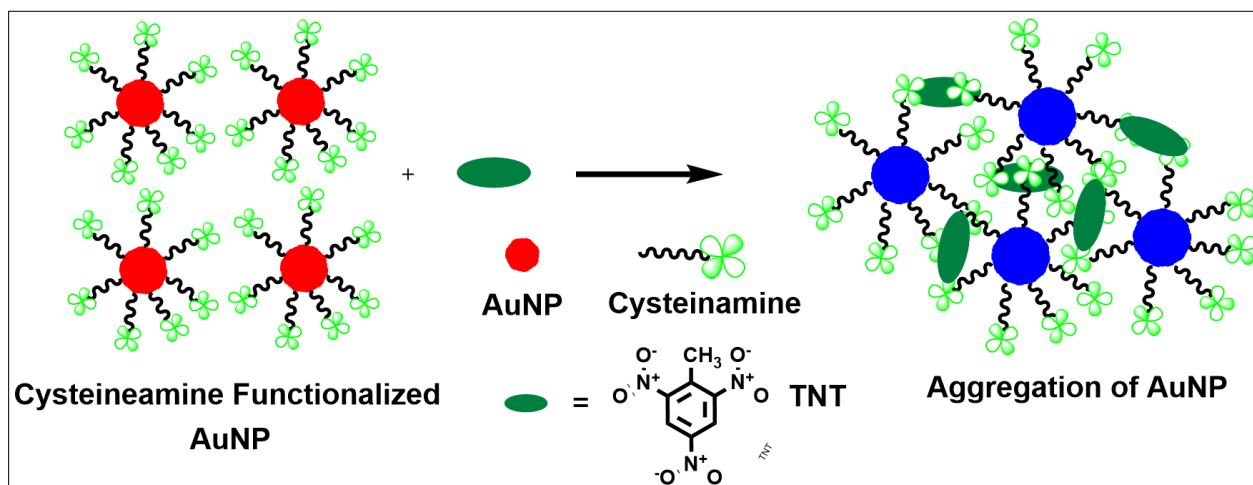


Figure 6 Schematic representation of direct colorimetric detection of TNT based on the electronic interaction between cysteamine and TNT. [81]

2.6. Hybrid Nanomaterials Based ETD Sensor

In addition to the earlier discussed nanomaterials, hybrids of these materials are also employed for the detection of nitroaromatic explosives. It has been reported that Pt nanoparticles combined with a graphene hybrid nanosheet (PNEGHNs) can detect TNT [85]. Due to conductivity, small size, and uniform distribution of Pt nanoparticles, PNEGHNs demonstrated advantages over graphene nanosheets, including excellent conductivity and attractive electrocatalytic behaviour. Adsorptive stripping voltammetry (ASV) was used at the modified GCE of PNEGHN and demonstrated a broad linear range with a limit detection of roughly 0.3 ppm for TNT. TNT detection also uses a hybrid electrode made of graphene and ionic liquid [86]. Ionic liquid and a 3D graphene material were combined to create the ionic liquid-graphene-hybrid composite, which has a significant mesoporosity and a huge specific surface area. For the purpose of TNT detection, the ionic liquid-graphene hybrid electrodes were contrasted with an anionic liquid-carbon nanotube (IL-CNT) and an ionic liquid-graphite (IL-graphite) paste electrode. When used for voltammetry, this sensor has a low detection limit of 0.5 ppb and a sensitivity of $1.65 \mu\text{Acm}^{-2}$ per ppb. Guo et al. demonstrated porphyrin-functionalized graphene for accurate electrochemical detection of DNT, TNT, DNB, and TNB in a different study [87]. The porphyrin/graphene sensor demonstrated ultra-trace detection of 1,3,5-trinitrobenzene, 1,4-dinitrotoluene, 0.5 ppb 2,4,6-trinitrotoluene, and 1 ppb 1,3-dinitrobenzene at low concentrations. The great sensitivity of this sensor was attributed to porphyrin's particular and effective adsorptive characteristics, graphene's enormous electroactive surface area, and the latter's quick charge transfer (Figure 7).

It is reported that metallic nanoparticles and carbon nanotubes can both be used to detect nitroaromatic explosives. In a Nafion matrix, Hrapovic et al. developed SWCNT and MWCNT composites containing Pt, Au, and Cu nanoparticles (NP). With cyclic voltammetry and ASV, these sensors demonstrated steady, repeatable, and low background current. Control trials at the MWCNT-modified GCE and the NP-modified GCE revealed no response for TNT reduction. In tap water, river water, and cleaned contaminated soil samples, a detection limit of $1 \mu\text{g L}^{-1}$ was reported [88]. The combination of nanomaterials with electrochemical devices, as discussed in this section, presents an exciting possibility for the development of novel and effective sensors for the trace identification of nitroaromatic explosives. It has also been observed that fluorescent tags, such as quantum dots [89], fluorescent dyes, and conjugated polymers [90], can change GO through covalent or non-covalent interactions. The mesoporous silica nanoparticles (MSNs) encapsulating poly (p-phenylenevinylene) (PPV) were presented by the Zhang group as water-soluble GO functionalized by amine-modified MSNs [19]. They observed that there is a considerable distance between the PPV and GO because the fluorescent PPV

macromolecules are contained within MSNs. Therefore, the electron transfer could be stopped and PPV@MSN could still exhibit fluorescence in aqueous solution. The creation of GO-PPV@MSN-TNT complexes in the presence of TNT reduces the distance between fluorescent PPV and TNT by interacting with the amino groups on PPV@MSN. As a result, the TNT derivatives can strongly absorb the photoluminescence emission of GO-PPV@MSN, leading to the FRET-based quenching of the fluorescence. With a detection limit of approximately 1.3×10^{-7} M, this sensor exhibited a linear relation to the Stern-Volmer equation for TNT in the concentration range of 0 – 2.4×10^{-6} M.

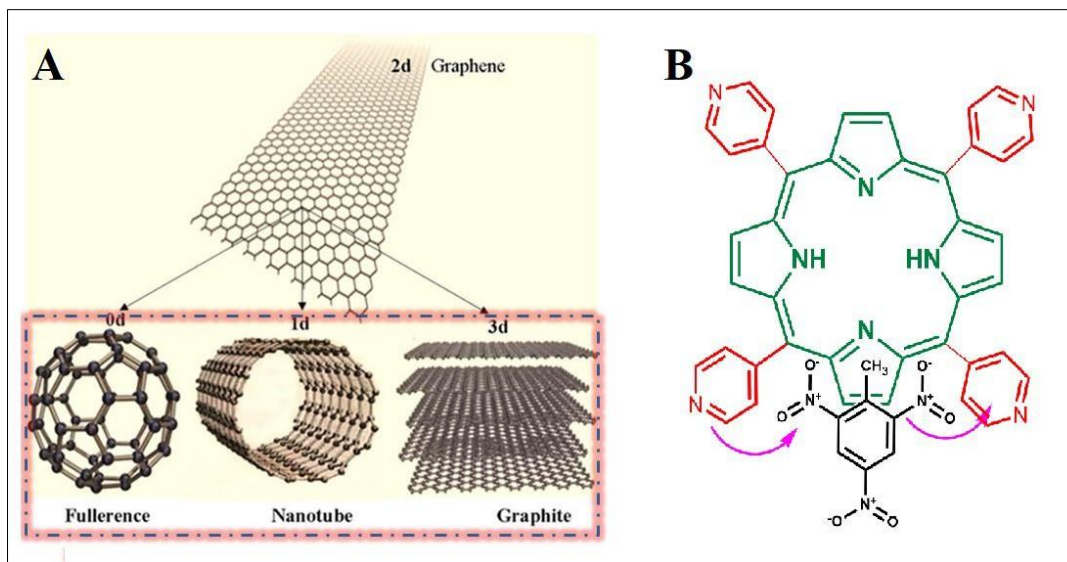


Figure 7 (A) Structure of Graphene Fullerene nanotube and Graphite (B) Interaction between porphyrin and TNT. [87]

3. Conclusion

High sensitive and selective detection of trace explosives often comes with certain issues because of interference from other molecules or the difficulty to use expensive and massive instruments for on-site detections. When some current approaches are used, the unique optical and electrical properties of nanoscale materials, which are frequently present, could improve the sensitivity and selectivity. Analytical chemistry is able to use new nanomaterials that have particular properties as they develop to further analytical needs. With some systems being able to detect many types of explosives at low concentrations, there have been major advancements achieved in gas sensing technologies like graphene and quantum dots. SERS is still a hot topic thanks to advancements in nanoparticle characteristics, both plasmonic and non-plasmonic. The creation of quick, sensitive, selective, and low cost sensors is the main motivation behind efforts to build new sensors. Regarding their inherent qualities, nanomaterials could hasten the achievement of these objectives. Analytical effectiveness of nanomaterial-based sensors can be increased and its deficiency to identify nitroaromatic explosives overcomes by using data processing techniques like chemometrics. Therefore, it is expected that the development of future explosive detection technologies will heavily rely on nanomaterials.

Compliance with ethical standards

Acknowledgments

We are thankful to Dr. Manmohan L. Satnami, Associate Professor School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur for providing valuable guidance for the preparation of review article.

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] Al-Hajj S, Dhaini HR, Mondello S, Kaafarani H, Kobeissy F, DePalma RG. Beirut ammonium nitrate blast: analysis, review, and recommendations. *Frontiers in Public Health*. 2021 Jun 4;9:657996.
- [2] Independent - London Attack. <http://www.independent.co.uk/news/uk/crime/silent-bomber-mohammedrehman-and-wife-sana-ahmed-khansentenced-to-life-in-prison-for-londonterror-a6790741.html>
- [3] BBC News-Istanbul: Six dead, dozens wounded in Turkey explosion. <https://www.bbc.com/news/uk-england-manchester-40008389>
- [4] Dutta P, Chakravarty S, Sarma NS. Detection of nitroaromatic explosives using π -electron rich luminescent polymeric nanocomposites. *RSC advances*. 2016;6(5):3680-9.
- [5] Guill JV. The Nose Knows: Developing Advanced Chemical Sensors for the Remote Detection of Improvised Explosive Devices in 2030. AIR COMMAND AND STAFF COLL MAXWELL AFB AL; 2009 Apr 1.
- [6] Üzer A, Yalçın U, Can Z, Erçağ E, Apak R. Indirect determination of pentaerythritol tetranitrate (PETN) with a gold nanoparticles- based colorimetric sensor. *Talanta*. 2017 Dec 1;175:243-9.
- [7] Krivitsky V, Filanovsky B, Naddaka V, Patolsky F. Direct and Selective Electrochemical Vapor Trace Detection of Organic Peroxide Explosives via Surface Decoration. *Analytical chemistry*. 2019 Mar 20;91(8):5323-30.
- [8] Zhang Y, Ma Y, Wang L. Simple Copper Nanoparticle/Polyfurfural Film Modified Electrode for the Determination of 2, 4, 6-Trinitrotoluene (TNT). *Analytical Letters*. 2020 Nov 1;53(16):2671-84.
- [9] Procek M, Stolarczyk A, Pustelny T, Maciak E. A study of a QCM sensor based on TiO₂ nanostructures for the detection of NO₂ and explosives vapours in air. *Sensors*. 2015 Apr 22;15(4):9563-81.
- [10] Lü X, Hao P, Xie G, Duan J, Gao L, Liu B. A sensor array realized by a single flexible TiO₂/POMs film to contactless detection of triacetone triperoxide. *Sensors*. 2019 Feb 21;19(4):915.
- [11] Zhang WH, Zhang WD, Chen LY. Highly sensitive detection of explosive triacetone triperoxide by an In₂O₃ sensor. *Nanotechnology*. 2010 Jul 15;21(31):315502.
- [12] Horsfall LA, Pugh DC, Blackman CS, Parkin IP. An array of WO₃ and CTO heterojunction semiconducting metal oxide gas sensors used as a tool for explosive detection. *Journal of Materials Chemistry A*. 2017;5(5):2172-9.
- [13] Qi W, He H, Fu Y, Zhao M, Qi L, Hu L, Liu C, Li R. Water-dispersed fluorescent silicon nanodots as probes for fluorometric determination of picric acid via energy transfer. *Microchimica Acta*. 2019 Jan;186(1):1-7.
- [14] Wang H, Chen C, Liu Y, Wu Y, Yuan Y, Zhou Q. A highly sensitive and selective chemosensor for 2, 4, 6-trinitrophenol based on L-cysteine-coated cadmium sulfide quantum dots. *Talanta*. 2019 Jun 1;198:242-8.
- [15] Li Z, Zhou Y, Yan D, Wei M. Electrochemiluminescence resonance energy transfer (ERET) towards trinitrotoluene sensor based on layer-by-layer assembly of luminol-layered double hydroxides and CdTe quantum dots. *Journal of Materials Chemistry C*. 2017;5(14):3473-9.
- [16] Alizadeh T, Atashi F, Ganjali MR. Molecularly imprinted polymer nano-sphere/multi-walled carbon nanotube coated glassy carbon electrode as an ultra-sensitive voltammetric sensor for picomolar level determination of RDX. *Talanta*. 2019 Mar 1;194:415-21.
- [17] Wang J, Du S, Onodera T, Yatabe R, Tanaka M, Okochi M, Toko K. An SPR sensor chip based on peptide-modified single-walled carbon nanotubes with enhanced sensitivity and selectivity in the detection of 2, 4, 6-trinitrotoluene explosives. *Sensors*. 2018 Dec 17;18(12):4461.
- [18] Guo CX, Lei Y, Li CM. Porphyrin functionalized graphene for sensitive electrochemical detection of ultratrace explosives. *Electroanalysis*. 2011 Apr;23(4):885-93.
- [19] Zhang H, Feng L, Liu B, Tong C, Lü C. Conjugation of PPV functionalized mesoporous silica nanoparticles with graphene oxide for facile and sensitive fluorescence detection of TNT in water through FRET. *Dyes and Pigments*. 2014 Feb 1;101:122-9.
- [20] Li Z, Li H, Wu Z, Wang M, Luo J, Torun H, Hu P, Yang C, Grundmann M, Liu X, Fu Y. Advances in designs and mechanisms of semiconducting metal oxide nanostructures for high-precision gas sensors operated at room temperature. *Materials Horizons*. 2019;6(3):470-506.
- [21] Mirzaei A, Janghorban K, Hashemi B, Neri G. Metal-core@ metal oxide-shell nanomaterials for gas-sensing applications: a review. *Journal of Nanoparticle Research*. 2015 Sep;17(9):1-36.

- [22] Wang X, Chen X, editors. Novel nanomaterials for biomedical, environmental and energy applications. Elsevier; 2018 Nov 16.
- [23] Ji H, Zeng W, Li Y. Gas sensing mechanisms of metal oxide semiconductors: a focus review. *Nanoscale*. 2019;11(47):22664-84.
- [24] Rossi AS, Ricci P, Gregory OJ. Trace detection of explosives using metal oxide catalysts. *IEEE sensors journal*. 2019 Mar 11;19(13):4773-80.
- [25] Cao Y, Zou X, Wang X, Qian J, Bai N, Li GD. Effective detection of trace amount of explosive nitro-compounds by ZnO nanofibers with hollow structure. *Sensors and Actuators B: Chemical*. 2016 Sep 1;232:564-70.
- [26] Omijeh B, Machiavelli AO. Optimizing a Sensor to Detect Ammonium Nitrate Based IEDS in Vehicles Using Artificial Neural Networks. *American Journal of Neural Networks and Applications*. 2019;5(1):1-6.
- [27] Tang Y, Zhang Y, Xie G, Zheng Y, Yu J, Gao L, Liu B. Construction of Rutile-TiO₂ Nanoarray Homo Junction for Non-Contact Sensing of TATP under Natural Light. *Coatings*. 2020 Apr 20;10(4):409.
- [28] Bastatas LD, Wagle P, Echeverria E, Austin AJ, McIlroy DN. The Effect of UV Illumination on the room temperature detection of vaporized ammonium nitrate by a ZnO coated nanospring-based sensor. *Materials*. 2019 Jan 18;12(2):302.
- [29] Qu J, Ge Y, Zu B, Li Y, Dou X. Transition-Metal-Doped p-Type ZnO Nanoparticle-Based Sensory Array for Instant Discrimination of Explosive Vapors. *Small*. 2016 Mar;12(10):1369-77.
- [30] Bochenkov VE, Sergeev GB. Sensitivity, selectivity, and stability of gas-sensitive metal-oxide nanostructures. *Metal oxide nanostructures and their applications*. 2010 Mar;3:31-52.
- [31] Marchisio A, Tulliani JM. Semiconducting metal oxides nanocomposites for enhanced detection of explosive vapors. *Ceramics*. 2018 Jun 25;1(1):98-119.
- [32] Warmer J, Wagner P, Schöning MJ, Kaul P. Detection of triacetone triperoxide using temperature cycled metal-oxide semiconductor gas sensors. *physica status solidi (a)*. 2015 Jun;212(6):1289-98.
- [33] Patolsky F, Shacham R, Lichtenstein A, Havivi E, Modiln, H. Systems and Methods for Identifying Explosives. Patent number WO 2014111944 A8. 24 July 2014.
- [34] Tracense - explosives detection. <https://www.tracense.com/technology/vapors/>
- [35] Yang Z, Dou X, Zhang S, Guo L, Zu B, Wu Z, Zeng H. A High-Performance Nitro-Explosives Schottky Sensor Boosted by Interface Modulation. *Advanced Functional Materials*. 2015 Jul;25(26):4039-48.
- [36] Guo L, Yang Z, Dou X. Artificial olfactory system for trace identification of explosive vapors realized by optoelectronic Schottky sensing. *Advanced materials (Deerfield Beach, Fla.)*. 2017 Feb;29(5).
- [37] Caron Z, Mallin D, Champlin M, Gregory O. A pre-concentrator for explosive vapor detection. *ECS Transactions*. 2015 Jul 27;66(38):59.
- [38] Amani M, Chu Y, Waterman KL, Hurley CM, Platek MJ, Gregory OJ. Detection of triacetone triperoxide (TATP) using a thermodynamic based gas sensor. *Sensors and Actuators B: Chemical*. 2012 Feb 20;162(1):7-13.
- [39] Ricci PP, Rossi AS, Gregory OJ. Orthogonal sensors for the trace detection of explosives. *IEEE Sensors Letters*. 2019 Oct 2;3(10):1-4.
- [40] Martín-Palma RJ, Martínez-Duart JM. *Nanotechnol. Microelectron. Photonics*; Elsevier, Oxford, 2017; pp 243–263.
- [41] Hunt C. *Encyclopedia of Paleoclimatology and Ancient Environments*. Reference Reviews. 2009 Oct 23.
- [42] Sanjuán AM, Ruiz JA, García FC, García JM. Recent developments in sensing devices based on polymeric systems. *Reactive and Functional Polymers*. 2018 Dec 1;133:103-25.
- [43] Shukla SK, Kushwaha CS, Singh NB. Recent developments in conducting polymer based composites for sensing devices. *Materials Today: Proceedings*. 2017 Jan 1;4(4):5672-81.
- [44] Surya SG, Nagarkar SS, Ghosh SK, Sonar P, Rao VR. OFET based explosive sensors using diketopyrrolopyrrole and metal organic framework composite active channel material. *Sensors and Actuators B: Chemical*. 2016 Feb 1;223:114-22.
- [45] Loch AS, Stoltzfus DM, Burn PL, Shaw PE. High-Sensitivity Poly (Dendrimer)-Based Sensors for the Detection of Explosives and Taggant Vapors. *Macromolecules*. 2020 Feb 17;53(5):1652-64.

- [46] Blue R, Thomson N, Taylor SJ, Fletcher AJ, Skabara PJ, Uttamchandani D. Miniature nitro and peroxide vapor sensors using nanoporous thin films. *IEEE Sensors Journal*. 2016 Apr 27;16(24):8767-74.
- [47] Yuan W, Shi G. Graphene-based gas sensors. *Journal of Materials Chemistry A*. 2013;1(35):10078-91.
- [48] Novotný F, Urbanová V, Plutnar J, Pumera M. Preserving fine structure details and dramatically enhancing electron transfer rates in graphene 3D-printed electrodes via thermal annealing: toward nitroaromatic explosives sensing. *ACS applied materials & interfaces*. 2019 Sep 16;11(38):35371-5.
- [49] Pérez EM, Martín N. π - π interactions in carbon nanostructures. *Chemical Society Reviews*. 2015;44(18):6425-33.
- [50] Samaeifar F, Abdollahi H. Graphene oxide for high sensitivity detection of 2, 4-Dinitrotoluene by developing of a heat absorption monitoring sensor. *Sensors and Actuators B: Chemical*. 2019 Oct 15;297:126726.
- [51] Yew YT, Ambrosi A, Pumera M. Nitroaromatic explosives detection using electrochemically exfoliated graphene. *Scientific reports*. 2016 Sep 16;6(1):1-1.
- [52] Guo S, Wen D, Zhai Y, Dong S, Wang E. Platinum nanoparticle ensemble-on-graphene hybrid nanosheet: one-pot, rapid synthesis, and used as new electrode material for electrochemical sensing. *ACS nano*. 2010 Jul 27;4(7):3959-68.
- [53] Shi L, Hou AG, Chen LY, Wang ZF. Electrochemical sensor prepared from molecularly imprinted polymer for recognition of TNT. *Polymer Composites*. 2015 Jul;36(7):1280-5.
- [54] Avaz S, Roy RB, Mokkapati VR, Bozkurt A, Pandit S, Mijakovic I, Menciloglu YZ. Graphene based nanosensor for aqueous phase detection of nitroaromatics. *RSC advances*. 2017;7(41):25519-27.
- [55] Star A, Han TR, Gabriel JC, Bradley K, Grüner G. Interaction of aromatic compounds with carbon nanotubes: correlation to the Hammett parameter of the substituent and measured carbon nanotube FET response. *Nano letters*. 2003 Oct 8;3(10):1421-3.
- [56] Woods LM, Bădescu ȘC, Reinecke TL. Adsorption of simple benzene derivatives on carbon nanotubes. *Physical Review B*. 2007 Apr 17;75(15):155415.
- [57] Zhang Y, Xu M, Bunes BR, Wu N, Gross DE, Moore JS, Zang L. Oligomer-coated carbon nanotube chemiresistive sensors for selective detection of nitroaromatic explosives. *ACS Applied Materials & Interfaces*. 2015 Apr 15;7(14):7471-5.
- [58] Stefano JS, Lima AP, Nascentes CC, Krzyzaniak SR, Mello PA, Gonçalves JM, Richter EM, Nossol E, Munoz RA. Electrochemical detection of 2, 4, 6-trinitrotoluene on carbon nanotube modified electrode: Effect of acid functionalization. *Journal of Solid State Electrochemistry*. 2020 Jan;24(1):121-9.
- [59] Stefano JS, Lima AP, Nascentes CC, Krzyzaniak SR, Mello PA, Gonçalves JM, Richter EM, Nossol E, Munoz RA. Electrochemical detection of 2, 4, 6-trinitrotoluene on carbon nanotube modified electrode: Effect of acid functionalization. *Journal of Solid State Electrochemistry*. 2020 Jan;24(1):121-9.
- [60] Wang M, Fu Q, Zhang K, Wan Y, Wang L, Gao M, Xia Z, Gao D. A magnetic and carbon dot based molecularly imprinted composite for fluorometric detection of 2, 4, 6-trinitrophenol. *Microchimica Acta*. 2019 Feb;186(2):1-1.
- [61] Ju B, Wang Y, Zhang YM, Zhang T, Liu Z, Li M, Xiao-An Zhang S. Photostable and low-toxic yellow-green carbon dots for highly selective detection of explosive 2, 4, 6-trinitrophenol based on the dual electron transfer mechanism. *ACS applied materials & interfaces*. 2018 Mar 28;10(15):13040-7.
- [62] Pisanic Ii TR, Zhang Y, Wang TH. Quantum dots in diagnostics and detection: principles and paradigms. *Analyst*. 2014;139(12):2968-81.
- [63] Zhou W, Coleman JJ. Semiconductor quantum dots. *Current Opinion in Solid State and Materials Science*. 2016 Dec 1;20(6):352-60.
- [64] Alivisatos AP. Semiconductor clusters, nanocrystals, and quantum dots. *science*. 1996 Feb 16;271(5251):933-7.
- [65] Ghasemi F, Hormozi-Nezhad MR. Determination and identification of nitroaromatic explosives by a double-emitter sensor array. *Talanta*. 2019 Aug 15;201:230-6.
- [66] Abbasi F, Akbarinejad A, Alizadeh N. CdS QDs/N-methylpolypyrrole hybrids as fluorescent probe for ultrasensitive and selective detection of picric acid. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2019 Jun 5;216:230-5.

- [67] Nguyen A, Gonzalez CM, Sinelnikov R, Newman W, Sun S, Lockwood R, Veinot JG, Meldrum A. Detection of nitroaromatics in the solid, solution, and vapor phases using silicon quantum dot sensors. *Nanotechnology*. 2016 Feb 10;27(10):105501.
- [68] Cui Y, Jin Y, Chen X, Wu J. Two-dimensional electrochemiluminescence on porous silicon platform for explosive detection and discrimination. *ACS sensors*. 2018 Jul 31;3(8):1439-44.
- [69] Chou KF, Dennis AM. Förster resonance energy transfer between quantum dot donors and quantum dot acceptors. *Sensors*. 2015 Jun 5;15(6):13288-325
- [70] Wang S, Li N, Pan W, Tang B. Advances in functional fluorescent and luminescent probes for imaging intracellular small-molecule reactive species. *TrAC Trends in Analytical Chemistry*. 2012 Oct 1;39:3-7.
- [71] Khan ZM, Saifi S, Aslam Z, Khan SA, Zulfequar M. A facile one step hydrothermal synthesis of carbon quantum dots for label-free fluorescence sensing approach to detect picric acid in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry*. 2020 Feb 1;388:112201.
- [72] Ganiga M, Cyriac J. Detection of PETN and RDX using a FRET-based fluorescence sensor system. *Analytical Methods*. 2015;7(13):5412-8.
- [73] Gong W, Li H, Gong X, Zhang Z, Lu Z. Fabrication of amine functionalized CdSe@ SiO₂ nanoparticles as fluorescence nanosensor for highly selective and sensitive detection of picric acid. *Spectrochimica Acta Part A: Molecular And Biomolecular Spectroscopy*. 2020 Jun 5;233:118221.
- [74] Peveler WJ, Roldan A, Hollingsworth N, Porter MJ, Parkin IP. Multichannel detection and differentiation of explosives with a quantum dot array. *ACS nano*. 2016 Jan 26;10(1):1139-46.
- [75] Peveler WJ, Roldan A, Hollingsworth N, Porter MJ, Parkin IP. Multichannel detection and differentiation of explosives with a quantum dot array. *ACS nano*. 2016 Jan 26;10(1):1139-46.
- [76] Komikawa T, Tanaka M, Tamang A, Evans SD, Critchley K, Okochi M. Peptide-functionalized quantum dots for rapid label-free sensing of 2, 4, 6-trinitrotoluene. *Bioconjugate Chemistry*. 2020 Apr 13;31(5):1400-7.
- [77] Qian J, Hua M, Wang C, Wang K, Liu Q, Hao N, Wang K. Fabrication of l-cysteine-capped CdTe quantum dots based ratiometric fluorescence nanosensor for onsite visual determination of trace TNT explosive. *Analytica Chimica Acta*. 2016 Nov 23;946:80-7.
- [78] Hassanzadeh J, Khataee A, Oskoei YM, Fattahi H, Bagheri N. Selective chemiluminescence method for the determination of trinitrotoluene based on molecularly imprinted polymer-capped ZnO quantum dots. *New Journal of Chemistry*. 2017;41(19):10659-67.
- [79] Filanovsky B, Markovsky B, Bourenko T, Perkas N, Persky R, Gedanken A, Aurbach D. Carbon electrodes modified with TiO₂/metal nanoparticles and their application for the detection of trinitrotoluene. *Advanced Functional Materials*. 2007 Jun 18;17(9):1487-92.
- [80] Riskin M, Tel-Vered R, Bourenko T, Granot E, Willner I. Imprinting of molecular recognition sites through electropolymerization of functionalized Au nanoparticles: development of an electrochemical TNT sensor based on π -donor– acceptor interactions. *Journal of the American Chemical Society*. 2008 Jul 30;130(30):9726-33.
- [81] Jiang Y, Zhao H, Zhu N, Lin Y, Yu P, Mao L. A simple assay for direct colorimetric visualization of trinitrotoluene at picomolar levels using gold nanoparticles. *Angewandte Chemie*. 2008 Oct 27;120(45):8729-32.
- [82] López-López M, García-Ruiz C. Infrared and Raman spectroscopy techniques applied to identification of explosives. *TrAC Trends in Analytical Chemistry*. 2014 Feb 1;54:36-44.
- [83] Dasary SS, Singh AK, Senapati D, Yu H, Ray PC. Gold nanoparticle based label-free SERS probe for ultrasensitive and selective detection of trinitrotoluene. *Journal of the American Chemical Society*. 2009 Sep 30;131(38):13806-12.
- [84] Yang L, Ma L, Chen G, Liu J, Tian ZQ. Ultrasensitive SERS detection of TNT by imprinting molecular recognition using a new type of stable substrate. *Chemistry–A European Journal*. 2010 Nov 8;16(42):12683-93.
- [85] Guo S, Wen D, Zhai Y, Dong S, Wang E. Platinum nanoparticle ensemble-on-graphene hybrid nanosheet: one-pot, rapid synthesis, and used as new electrode material for electrochemical sensing. *ACS nano*. 2010 Jul 27;4(7):3959-68.
- [86] Guo CX, Lu ZS, Lei Y, Li CM. Ionic liquid–graphene composite for ultratrace explosive trinitrotoluene detection. *Electrochemistry Communications*. 2010 Sep 1;12(9):1237-40.

- [87] Guo CX, Lei Y, Li CM. Porphyrin functionalized graphene for sensitive electrochemical detection of ultratrace explosives. *Electroanalysis*. 2011 Apr;23(4):885-93.
- [88] Hrapovic S, Majid E, Liu Y, Male K, Luong JH. Metallic nanoparticle- carbon nanotube composites for electrochemical determination of explosive nitroaromatic compounds. *Analytical chemistry*. 2006 Aug 1;78(15):5504-12.
- [89] Wang Y, Yao HB, Wang XH, Yu SH. One-pot facile decoration of CdSe quantum dots on graphene nanosheets: novel graphene-CdSe nanocomposites with tunable fluorescent properties. *Journal of Materials Chemistry*. 2011;21(2):562-6.
- [90] Qi X, Pu KY, Zhou X, Li H, Liu B, Boey F, Huang W, Zhang H. Conjugated-polyelectrolyte-functionalized reduced graphene oxide with excellent solubility and stability in polar solvents. *Small*. 2010 Mar 8;6(5):663-9.