Colloidal Quantum Dots for Explosive Detection: Trends and Perspectives

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ABSTRACT: Sensitive, accurate, and reliable detection of explosives has become one of the major needs for international security and environmental protection. Colloidal quantum dots, because of their unique chemical, optical, and electrical properties, as well as easy synthesis route and functionalization, have demonstrated high potential to meet the requirements for the development of suitable sensors, boosting the research in the field of explosive detection. Here, we critically review the most relevant research works, highlighting three different mechanisms for explosive detection based on colloidal quantum dots, namely photoluminescence, electrochemical, and chemoresistive sensing. We provide a comprehensive overview and an extensive discussion and comparison in terms of the most relevant sensor parameters. We highlight advantages, limitations, and challenges of quantum dot-based explosive sensors and outline future research directions for the advancement of knowledge in this surging research field.

KEYWORDS: *Chemoresistive Sensors, Colloidal Quantum Dots, Electrochemical Sensors, Explosive Detection, Luminescent Sensors, Nanomaterials, Nanotechnologies, Nitroaromatic Compounds*
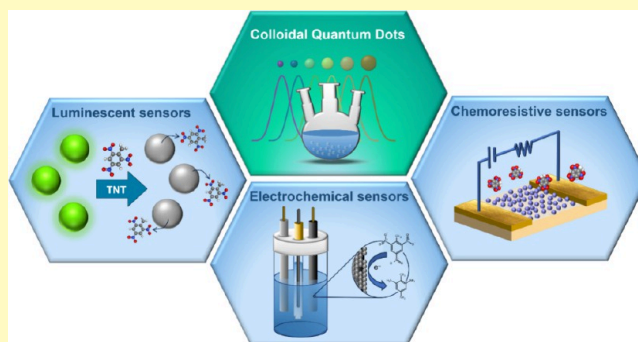
Explosive threats, including improvised explosive devices, have become one of the most important issues of international concern over defense and homeland security around the world,[1] with a continued and consistent pattern of harm also on civilians, accounting for 59% of total casualties.[2] In addition, the contamination of soil and water by chemicals used in military explosives poses significant risks to human health and ecologic systems since they can easily penetrate biological tissues, resulting in toxicity, mutagenicity, and carcinogenicity.[3,4] Such concerns have given rise to a huge demand for accurate and rapid detection of explosives in several scenarios, including terrorism countermeasures, custom and border control, transportation hub security, mine detection, and environmental or forensic examination of soil and water.

Chemical explosives encompass a large variety of compounds including nitroaromatics, acid salts, organic peroxides, nitrate esters, and nitramines.[5] Nitroaromatic compounds (NACs), such as trinitrotoluene (TNT) and its degradation product, dinitrotoluene (DNT), are the most used compounds in both military and homemade explosive devices, making them a common focus in explosive detection. Nevertheless, the increasing use of improvised explosive devices fostered research into the detection of other groups of explosive substances, such as peroxides and acid salts.[6] The room-temperature vapor pressures of explosive materials may vary over several orders of magnitude, ranging from the highly

volatile diacetone diperoxide and ethylene glycol dinitrate (10^{-4} atm) to the ultralow volatile cyclotetramethylene-tetranitramine (HMX, 10^{-17} atm) and triaminotrinitrobenzene (TATB, 10^{-18} atm), down to the nearly nonvolatile guanidine nitrate (10^{-23} atm), with most NACs spanning in the 10^{-6}–10^{-11} atm range. Extensive information on the vapor pressure of explosives can be found elsewhere.[7,8] Due to such low values, the trace detection of explosives or their precursors is a very challenging task that can be further burdened when explosive devices are wrapped or packaged to avoid detection (effective vapor pressure may be reduced by up to a factor of 1000).[9] To overcome these limitations, the detection of explosive traces has been pursued mainly in liquid and solid samples. Regardless of the sensing medium and analyte phase, sensitivity improvements have been obtained by exploiting the possibility of mechanically concentrating the analyte close to the sensing elements.
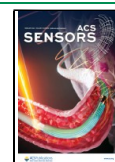
There are several recent reviews on techniques, methods, and instrumentation designed for the detection of bulk

explosives in containers, especially for luggage and vehicle screening applications as well as those designed to detect, identify, and quantify trace explosives.[10−14] Currently, many effective techniques exist for detecting trace explosives. The most common include ion mobility spectrometry (IMS), mass spectrometry (MS), gas chromatography (GC), and chemiluminescence (CL). In addition, many approaches with different levels of technological development have been investigated, such as optical, photoacoustic, Raman, and terahertz spectroscopy, and several sensor-based techniques.

Although many available systems allow for accurate measurements, they are typically bulky, expensive, and require trained technical staff and time-consuming procedures that often involve transportation of the sample to a certified laboratory. For these reasons, they are often deployed only at strategic locations where there is a controllable environment for detection, such as airports or government buildings or even confined to a laboratory environment. However, current needs require fast and accurate detection of explosives also in virtually uncontrollable locations, such as indoor and outdoor public places or transportation networks and infrastructures, with hardly trackable vehicular and pedestrian traffic. The mass deployment of miniaturized, sensitive, low-cost, and easy-to-operate sensors would address many of these issues, representing a breakthrough toward highly efficient explosive detection systems. Lots of explosive sensors have been proposed and demonstrated in the past two decades, resorting to several approaches, including chemical, electrochemical, biosensors, and optical sensors, with a clear trend to exploit the characteristics of nanomaterials.[11,15−17] Nanomaterials possess unique chemical and physical properties with respect to their bulk counterparts, providing new opportunities for the fabrication of gas sensors with improvements of sensitivity and selectivity, such as increased surface-to-volume ratio,[18] tunable photoluminescence,[19] easily adjustable depletion region[20] and interfacial potential,[21] targeted catalytic activity,[22] and surface-enhanced Raman scattering.[23] Among others, nanostructured semiconductors experiencing the quantum confinement regime, commonly referred to as quantum dots (QDs), are particularly interesting since the spatial confinement of both charge carriers may largely enhance the aforementioned effects. In particular, QDs prepared by colloidal synthetic methods (CQDs) emerged as a very promising platform in several applications, including sensors, thanks to their solution processability that, in principle, allows low-cost, low-temperature, and large-area fabrication. Moreover, surface chemistry modification reactions can be devised[24] to add further versatility and functionality to the CQDs and to ensure their compatibility with a large variety of substrates, including silicon, thus enabling their integration with electronics.

Here, we review for the first time the scientific literature specifically focused on the use of CQDs for the detection of explosive traces, thus providing a valuable complement to review papers on sensors based on CQDs for generic gas detection[19,25,26] and explosive sensors based on nanomaterials other than CQDs.[11,27−30] We first recall the key parameters used to evaluate the sensor performances, and then we provide a comprehensive overview of the most relevant research works for explosive detection highlighting three different mechanisms, namely photoluminescence, electrochemical, and chemoresistive sensing. We compare the reported parameters, highlighting the advantages and limitations of the three types

of explosive sensors. We thus offer a critical discussion of the present challenges and foresee future directions to enabling effective explosive trace detection with CQD sensors.

■ PERFORMANCE PARAMETERS FOR SENSING APPLICATIONS

Several parameters can be used to evaluate the performance of a sensor and to assess its suitability for practical use.[31] The most common ones, including sensor response, sensitivity, dynamic range, limit of detection, response and recovery times, reversibility, chemical recovery, selectivity, anti-interference, repeatability, reproducibility, and stability are briefly described in this section.

The *sensor response* can be represented in various forms depending on the nature of the sensor, and it is generally defined as the change of the sensor output signal due to the change in the analyte concentration. Different definitions have been adopted in literature, such as $\Delta X/X_0$, X/X_0, or simply ΔX (where X_0 and X are the output signals before and after exposure to the analyte, respectively, with $\Delta X = X - X_0$). The relationship between the *sensor response* and the concentration of the analyte that can be detected by the sensor is represented by the *calibration curve*, whose slope is the *sensitivity* of the sensor. The *dynamic range* refers to the analyte concentration range of values used in the *calibration curve*, while the *linear dynamic range* (LDR) is the analyte concentration range over which the *sensor response* is proportional to the analyte concentration (hence, the *sensitivity* is constant). The *limit of detection* (LOD) is the lowest analyte concentration that can be detected with a specified statistical uncertainty. According to the International Union of Pure and Applied Chemistry (IUPAC) definition, the LOD can be evaluated as the minimum analyte concentration that produces an output signal three times larger than the noise, as defined below:

$$LOD = 3\frac{RMS_{noise}}{slope} \tag{1}$$

where RMS_{noise} is the root−mean−square noise of the sensor, while slope refers to the *calibration curve*. The LOD can be determined by direct measurement of the noise and of the slope of the calibration curve, thus being univocally determined with laboratory instrumentation. When it comes to performance evaluation of fast, nonreusable fluorescent sensors, it is often useful to also determine the *naked-eye LOD*, which is defined as the minimum analyte concentration that can be detected by a human operator without using any specific measurement instrumentation or technique. It should be observed that this parameter is subject to the operator's sensitivity and that it should be determined with a statistical approach accounting for cognitive biases (i.e., double blind tests). The *response time* is the time taken by the sensor output signal to achieve 90% of its total change upon target analyte exposure, whereas the *recovery time* is the time taken by the sensor output signal to return to 10% of its total change after target analyte removal. The *recovery time* is related to the *reversibility*, namely the ability of the sensor output to return to its original value (baseline) once the analyte is removed. *Chemical recovery* is a concept typically applied to electrochemical sensors operating in aqueous media, and it aims at evaluating a possible analyte loss in an aqueous solution due to the matrix complexity. *Chemical recovery* measurements are performed by spiking known concentrations of the analyte

(C_A) to the real test solution (for example, tap water), applying the established electrochemical sensing protocol, and finally comparing the measured analyte concentration (C_S) subtracted by the contribution of the analyte already present in the unspiked test solution (C_U) with the expected one.[32] Typically, the percentage recovery (% R) is calculated as follows:

$$\% \, R = \frac{(C_S - C_U)}{C_A} \times 100 \qquad (2)$$

Selectivity is the ability of the sensor to respond only to the target analyte, while not showing any response to different chemical compounds. *Selectivity* can be estimated by analyzing and comparing the calibration curves of the analyte and a defined set of interfering compounds, separately or by analyzing real-world samples, where the analyte is mixed with known interfering compounds. *Anti-interference* is the ability of the sensor to detect the target analyte in the presence of other interfering components. It should be observed that, even if anti-interference gives a better understanding of the field performance of a sensor, it is seldom evaluated in the scientific literature, and only a selectivity analysis is often conducted. *Repeatability* and *reproducibility* refer to the similarity between the results of successive measurements of the same analyte and performed by the same (*repeatability*) or different (*reproducibility*) operators, apparatus, laboratories, and/or intervals of time analysis. *Stability* is the capability of the sensor to produce repeatable outputs after a certain storage period. For luminescent sensors, also *photostability* must be considered, defined as the capability of the emission intensity to remain stable during a long-time continuous excitation. All these parameters are fundamental to evaluate and compare the sensors reported in the literature.

LUMINESCENT SENSORS

In the last two decades, luminescent probes based on CQDs have become a popular tool for explosive detection due to their peculiar optical properties including broad absorption spectra, narrow and tunable emission spectra together with high photoluminescence quantum yields, long-term stability, and strong resistance to photobleaching.[33,34] Moreover, CQDs also show exceptional brightness and photostability if compared to organic dyes and luminescent proteins.[35,36] In most of the published works, the sensing mechanism is based on changes in the CQD luminescence and in particular on the decrease in the luminescence intensity (quenching) upon exposure to the target analytes (Figure 1).[37]

Sensing Mechanisms. Photoinduced luminescence (PL) occurs when a luminophore absorbs an electromagnetic

Figure 1. Schematic illustration of luminescence quenching of CQDs in response to the presence of the target analyte (TNT, in this case).
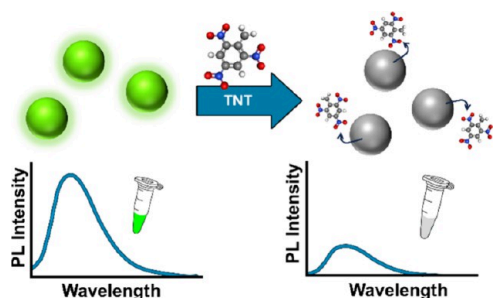
radiation reaching higher energy states, then returning back to the ground state via the emission of a photon, whose energy is not larger than that of the absorbed radiation.[38] A variety of processes can result in PL quenching, including Förster resonance energy transfer (FRET), photoinduced electron transfer (PET), and inner filter effect (IFE).[39,40]

In the FRET process, a donor species at the excited state transfers energy to a nearby acceptor species at the ground state through a nonradiative, resonant electromagnetic interaction, resulting in the quenching of the donor PL. Such a Coulombic energy transfer process between the excited donor and the acceptor occurs through space, provided that the corresponding radiative transitions have sufficiently high oscillator strength and that the corresponding dipoles have a favorable mutual orientation. The spectral overlap between donor emission and acceptor absorption can be used to evaluate the efficiency of the FRET process. This efficiency scales with an inverse sixth-power law of the donor-to-acceptor separation due to the dipole–dipole coupling mechanism, thus requiring a close distance in the donor–acceptor pair.[38,41,42] Sensors based on FRET, typically rely on luminophores whose absorption spectrum changes due to the interactions with the target analyte, thus modifying the overlap between the absorption spectrum and the emission spectrum of the luminescent CQDs and changing the rate of luminescence quenching.

PET is an energy exchange process that involves the transfer of an electron between a donor species at the excited state and a nearby acceptor at the ground state. When back electron transfer is negligible, PET quenches the donor PL. Thermodynamically, PET requires that the LUMO of the donor lies above the LUMO of the acceptor (the excited donor acts as a reductant) or that the HOMO of the donor lies below the HOMO of the acceptor (the excited donor acts as an oxidant). Kinetically, PET rate may compete with the rate of the donor PL. PET also requires orbital overlap between the donor and the acceptor and its efficiency displays an exponential dependence with distance.[43−45] Luminescent nanomaterials can be strongly quenched by nitroaromatics via PET, since these compounds act as electron acceptors due to the presence of benzene rings with electron-withdrawing nitro groups. For example, TNT can interact with electron-rich primary amines on the surface of CQDs to form the so-called Meisenheimer complexes, resulting in a PET process from the luminophore to the analyte, which further leads to PL quenching.[46]

IFE is a form of radiative energy transfer since the photons emitted by an excited luminophore are directly reabsorbed by a nearby species at the ground state. In this case, there is no direct interaction between the luminophore and the target analyte, while the absorber should be able to change its optical properties in the presence of the analyte. In particular, the absorber should exhibit a change in its optical absorption properties proportional to the concentration of the analyte, while the luminescent species should be unaffected by the analyte.

Functionalization of the CQDs. In general, the aforementioned PL quenching mechanisms require the chemical modification of the luminescent CQDs, which can be achieved by introducing specific binding sites for the target analyte on the surface of the CQDs. In the literature, different approaches have been proposed and some of them were also aimed at obtaining a selectivity toward specific analytes while

reducing the PL quenching in the presence of nonexplosive interfering molecules. To this end, the employment of antibodies provided outstanding results.[47] A notable example of this approach was provided by Goldman et al. with a pioneering sensor based on CQDs for TNT detection in aqueous solution, where the anti-TNT specific antibody fragments were attached to the surface of CdSe-ZnS core—shell CQDs via metal-affinity coordination.[48] The authors exploited the high binding specificity of the antibody for its target antigen, which enables the discrimination between closely related molecules differing by only a few molecular groups.[49] Specifically, the antibody sites were saturated with a dye-labeled TNT analogue, the black hole quencher-10 labeled with trinitrobenzene (TNB-BHQ10), that quenched the CQD PL via proximity-induced FRET (see Figure 2A). The addition
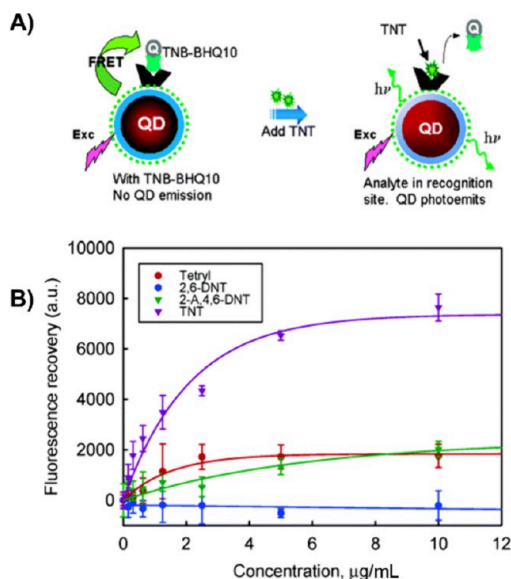
Figure 2. Hybrid CQD-antibody fragment PL sensor. (A) Schematic illustration of the sensing mechanism: in the presence of TNT, the FRET is eliminated and the CQD PL increased following the release of the dye-labeled TNT analogue (TNB-BHQ-10) from the conjugate. (B) Comparison of the CQD PL recovery with increasing concentration of TNT and TNT analogues added to the CQD conjugate preassembled with TNB-BHQ-10. Reprinted with permission from ref 48. Copyright 2005 American Chemical Society.

of soluble TNT displaced the labeled antigen, suppressing FRET and resulting in a concentration-dependent recovery of the CQD PL. Figure 2B illustrates the CQD probe that exhibited a much higher PL recovery toward TNT with respect to its analogues. This work paved the way for a new generation of sensors to be applied in the security domain. Unfortunately, the production of specific antibodies for sensing applications is particularly expensive, complex, and time-consuming, and the resulting sensors are characterized by a short shelf life. One feasible alternative consists in the employment of specifically developed peptides that can be synthesized with binding sites for both the CQDs and the target analyte.[50] Another possibility is to exploit the innate specificity of molecularly imprinted polymers (MIPs) for the analyte of interest. MIPs are biomimetic polymers that are produced containing the template or target molecule bound to a functional group of the host.[51] During the fabrication process, the template molecule is removed from the polymer host, leaving a target specific cavity

available for rebinding that is specific to both the shape and chemical functionality of the template. Stringer et al. designed an innovative luminescence sensor based on the postpolymerization pairing of amine-functionalized CdSe CQDs and MIPs.[52] The sensor was successfully applied to the detection of DNT and TNT in solution, obtaining 30.1 and 40.7 μM LOD, respectively. Similarly, MIPs were employed by many other authors, demonstrating outstanding sensitivities and the possibility to realize qualitative assays by naked-eye inspection of the color change of the luminescence.[53−56]

Doping is considered another effective approach to tailor and improve the properties of the CQDs, including their sensitivity for analyte detection. Among the most employed strategies, the Mn^{2+} doping of ZnS CQDs stands out, which ensured the use of CQDs based on nontoxic elements exhibiting bright PL in the visible spectral range; such Mn^{2+}:ZnS CQDs were employed for the detection of NACs, although a straightforward comparison with undoped ZnS CQDs was missing.[57,58] Doping is also widely employed in carbon dots (CDs), in which heteroatoms (e.g., nitrogen, boron, phosphorus) directly modify the electronic structure of the CDs.[59−61] N/P codoped CDs were synthesized by Li et al. by using adenosine derivatives as precursors to achieve efficient quenching upon exposure to TNP.[62] It was found that, compared to the sole N-doped CDs, the N/P codoped CDs exhibited higher PL quantum yield. The CDs prepared from adenosine monophosphate were able to linearly detect TNP in the range 0.1−30 μM with 30 nM LOD.

While doping is, typically, obtained during the CQD synthesis, postsynthetic chemical modification of the CQD characteristics has been proposed as a feasible route for sensitivity and selectivity enhancement. The chemical modification of the CQD surface by the introduction of ligands that mediate the CQD-explosive interactions has been thoroughly explored by many authors. The ligands of choice are, typically, short chain aliphatic molecules with at least two different functional moieties: a binding moiety that coordinates the CQD surface and a recognition moiety that interacts with the target explosive molecule.[63,64] In 2012, Freeman et al. investigated different amine capping layers (tyramine, dopamine, 5-hydroxydopamine, and 6-hydroxydopamine) as electron donating ligands to modify mercaptopropionic acid (MPA)-capped CdSe/ZnS CQDs.[65] They demonstrated that the increase of the electron donating character of the ligand layers led to an enhancement of the CQD PL quenching, thus enhancing the overall sensitivity of the PL probe through NACs or RDX in solution. Nguyen et al. also reported on Si CQDs with different surface modifications (monomer dodecyl-, oligomer dodecyl-, and dodecyl(hexyl)-amine) obtaining a nM LOD for DNT in solution.[66] Other commonly employed ligands for explosive detection purposes include creatinine,[67] methionine,[68] and cysteine.[69]

Sensing in Liquid and Solid Phase. The detection environment plays a crucial role in the determination of LOD and of the sensing performance in general. Most of the luminescence-based sensors discussed in the literature operate either in liquid or in the solid phase. Operation in liquid is the easiest and more straightforward approach since CQDs can be easily suspended in solution, and detection is obtained by the direct addition of a small amount of the target analyte to the CQD solution. Unfortunately, this approach poses issues in quantifying the analyte concentration since an accurate measurement of the PL intensity is required. To address this

issue, Fan et al. proposed the employment of a high-resolution smartphone camera coupled with a green-emitting CQD platform to perform a quantitative analysis of TNP concentration in solution with LOD = 27 nM.[70]

Detection in the liquid phase can be made even easier by immobilizing the CQDs on a solid substrate or porous scaffolds and dipping them in a solution where the explosive target may be present.[71,72] To this extent, Han et al. designed a portable platform for TNP detection by immobilizing polyethylenimine (PEI)-capped CdSe/Cd$_x$Zn$_{1-x}$S CQDs onto polyamine-6 (PA6) electrospun membrane, as illustrated in Figure 3A.[73] The PL quenching resulted from the reaction
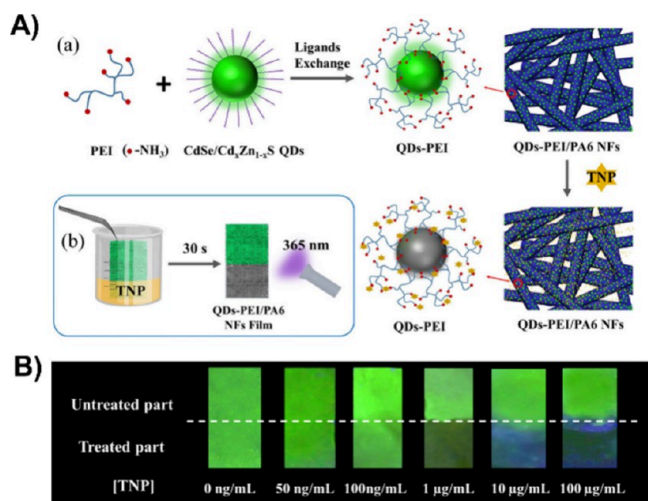
Figure 3. Polyethylenimine-capped CQD luminescent sensor. (A) (a) Schematic of the fabrication process of the CQDs-PEI/PA6 nanofibers and PL quenching of CQDs-PEI by TNP; (b) visual detection of TNP. (B) Digital images of membranes after being dipped in TNP solutions with different concentrations. Reprinted with permission from ref 73. Copyright 2020 Elsevier.

between amino groups of PEI, nitro groups and phenol hydroxyl groups of TNP. In addition, the high hydrophilicity and porosity of the electrospun film promoted a strong absorption of TNP thanks to hydrogen bonds between the amide moieties of the PA6 matrix and nitro groups of TNP. The brightness reduction of the composite film could be perceived by the naked eye under the 365 nm UV light with a visible detection limit of 0.44 μM TNP and with a 30 s response time (see Figure 3B).

Furthermore, the PL intensity of the film showed excellent stability over at least 30 days due to the protection with PA6, while the PL of the CQD dispersion declined rapidly with time and was quenched almost completely after storage in 25 °C for 10 days due to CQD aggregation, as their surface was oxidized.

Another popular substrate for CQD deposition consists of simple filter paper that, after being soaked in a CQD solution, can act as a portable and dippable luminescent probe.[66,74] With this approach, Tian et al. designed an on-site visual detector for TNT explosive residues in groundwater, using the immobilized blue-luminescent amine-capped CDs in a cellulose paper sensor.[46]

Similar approaches were also employed for the realization of luminescent probes operating by direct contact with solid samples, as demonstrated by the pioneering work by Zhang et al. where a dual emission from CdTe CQD ratiometric probe was deposited on paper and employed with outstanding

sensitivity toward solid TNT traces.[75] Zhu et al. demonstrated a sensor based on filter paper soaked in a solution of MoS$_2$ CQDs.[76] As depicted in Figure 4A−C, MoS$_2$ CQDs were
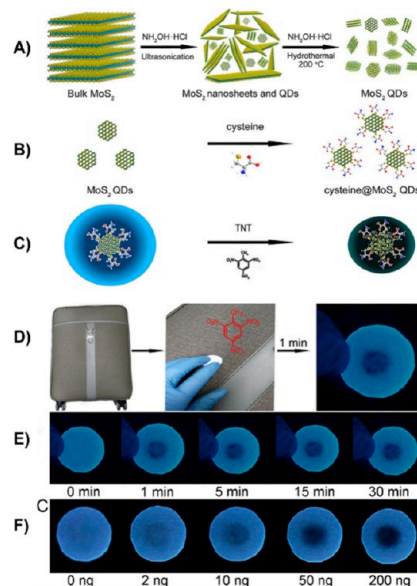

Figure 4. Monodisperse three-layered MoS$_2$ CQD luminescent sensor. (A) Schematic showing the fabrication process of the pristine MoS$_2$ CQDs, (B) modification of the MoS$_2$ CQDs with cysteine, and (C) the resultant TNT sensing. (D) Process for visual detection of TNT residues on luggage surfaces using the cysteine@MoS$_2$ CQDs decorated filter paper. PL quenching caused by (E) 100 ng TNT after different time intervals and by (F) different TNT concentrations. Reprinted with permission from ref 76. Copyright 2018 American Chemical Society.

fabricated through an ultrasonic-hydrothermal method using hydroxylamine hydrochloride as stripping agents and were further modified with cysteine to better interact with TNT molecules. Interestingly, the authors attribute the high sensitivity of the proposed sensor to the planarity of the MoS$_2$ CQDs that contributes to enhance the interaction with flat aromatic TNT molecules due to $\pi-\pi$ interactions and decreased steric effects. The PL probe was successfully applied for assaying TNT traces deposited on luggage cases, obtaining a detection limit of 2 ng. Figure 4D−F show the test paper-based assay in action as the quenching spots become darker with increasing TNT concentration.

Gas-Phase Detection. Detection in the liquid and solid phase is facilitated by the direct contact between the CQDs and the sample under analysis. The same does not apply in the case of gas-phase detection, where the analyzed volume is typically large, and the number of explosive molecules is extremely small due to the low vapor pressure of the analytes. For this reason, few examples of devices operating in air are discussed in the literature. Wu et al. reported on a multisensory array of ZnS CQDs embedded in a fibrous scaffold and capped with different surface ligands. In the presence of the analyte, supramolecular interactions, such as host−guest and electrostatic interactions, caused CQD PL quenching.[77] The resulting PL fingerprints allowed for the discriminative detection of TNT, DNT, TNP, and NB vapors. In this case, the gas-phase operation was obtained through the very high equivalent surface granted by the nanofibrous membranes employed as scaffolds for the CQDs. In this work, however, the sensors

were characterized only in saturated vapor atmosphere and the LOD was not evaluated.

Recently, our group reported an optical sensor exploiting the solid-state PL of ethylenediamine (EDA) treated PbS CQDs cast on a silicon substrate for NACs vapor detection.[78] The evaluation of the PL quenching was obtained with low-cost and low-power electronics (a blue LED pump and a NIR photodetector) integrated with the PL probe in a compact fixture. The system could work in a standalone mode without the need for specific instrumentations or human operators. Starting from this promising result, we designed a novel architecture for gas sensing applications based on the integration of a solid-state CQD PL probe with a CQD photodetector on the same silicon substrate.[79] The main element of the architecture was a silicon substrate with both surfaces coated with PbS CQD films. The upper CQD layer, suitably functionalized, acted as a PL probe, pumped by a pulsed blue LED. The change in PL intensity associated with the interaction between the PbS CQDs and NB vapor was measured by the PbS CQD photodetector fabricated on the opposite surface of the silicon substrate (Figure 5). This
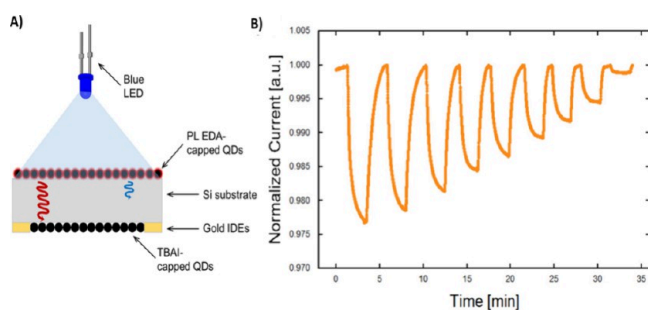
Figure 5. CQD luminescent probe combined with a CQD photodetector. (A) Schematic of the optical arrangement; the upper CQD layer of a silicon substrate is functionalized with EDA thus acting as a PL probe pumped by a blue LED. On the opposite side of the substrate, CQDs functionalization with TBAI acts as the photodetector. (B) Normalized current curves to different NB concentrations (131–1180 ppb) as a function of time. Reprinted with permission from ref 79. Copyright 2022 IOP Publishing Ltd.

approach enabled explosive detection in the vapor phase and extremely low NB concentrations (down to 1 μM), with a LOD estimated to be as low as 16 nM. Also, the sensor presented long-term stability over a measurement period of 70 days, and it exhibited a stable response for various humidity conditions.

Multi Criteria Sensing. Aside from devices functionalized with MIPs or antibodies, most of the sensors relying on luminescent CQDs share some selectivity issues due to nonspecific interactions that can interfere with the PL intensity; in the path toward selectivity enhancement, several authors proposed the employment of multicriteria sensing systems, where sensors with slightly different responses are integrated in an array[80] and pattern recognition algorithms are exploited to identify the fingerprint of explosive molecules. For instance, Peveler and co-workers reported about a multichannel array consisting of modified core−shell CdSe/ZnS CQDs.[81] The multicolor CQDs were functionalized via a simple ligand exchange procedure with different surface receptors, either macrocyclic (i.e., calixarene and cyclodextrin) or with −OH and −OMe terminated compounds (Figure 6).

These receptors underwent nonspecific supramolecular interactions with the explosives in the vapor phase, such as host−guest binding, electrostatic interaction and $\pi-\pi$ stacking, thus inducing variable PL quenching of the CQDs. Pattern recognition of the PL quenching data provided clear identification for five different explosives (DNT, TNT, tetryl, RDX, and PETN) residues in wastewater, with an accuracy higher than 80% for discrimination.

With a similar approach, Wu et al. reported a multichannel array consisting of nanofibrous membranes loaded with ZnS CQDs and its application for the discriminative detection of explosives.[77] The sensing platform exploited the differential response introduced by different surface ligands, including lysine, cysteine, trifluoroacetyl lysine, and cysteine hydrochloride to determine the fingerprints of different NACs obtaining discriminative detection of TNT, DNT, TNP, and NB vapors.

The peculiarity of multicriteria sensing consists in the enhancement of the overall selectivity by the exploitation of several, low-selectivity sensors combined with pattern recognition techniques. The choice of specific ligands and sensitizing agents, however, can improve the overall device performance and simplify the pattern recognition task. In this context, molecular recognition probes can also become part of multicriteria sensors. Xu and Lu designed a TNT luminescence probe by coupling MIP-coated CQDs with ratiometric PL techniques and mesoporous silica materials.[53] In this work, the molecular imprinting technique assured the selectivity but not the sensitivity that was obtained by mesoporous silica and ratiometric luminescent technique. Specifically, two differently sized CdTe CQDs emitting red (λ_{em} 640 nm) and green (λ_{em} 540 nm) PL were hybridized by embedding the red-emitting ones in silica nanoparticles as the core and embedding the green ones in the mesoporous imprinted silica shell. During the process, cetyltrimethylammonium bromide (CTAB) was employed as the template for mesoporous silica and TNT imprinted silica shell was prepared on the surface of the red CQDs/SiO$_2$ by the surface imprinting method using TNP as dummy template (see Figure 7). While the PL of the green CQDs could be selectively quenched by rebound TNT, the PL of the red CQDs was kept constant with the protection of the silica shell. Hence, the PL color changed from yellow-green to red-orange, enabling visual detection of TNT with excellent sensitivity (50−600 nM LDR; 15 nM LOD) and selectivity.

Multicriteria sensing can be realized also by gathering information with different measurement techniques from the same sensing material. For example, Gao et al. employed Au nanoparticle-CQD hybrids as sensing material in a trimode platform capable of on-site discrimination and detection of TNT by colorimetric, luminescence, and surface-enhanced Raman scattering (SERS) analysis.[82] The scheme is reported in Figure 8A. Electrostatic interactions were used to self-assemble mercaptopropionic acid-capped CdTe CQDs on the surface of cysteamine-modified Au nanoparticles, resulting in PL quenching due to energy transfer. The addition of TNT induced the formation of the strong cysteamine-TNT complex (Meisenheimer complex), leading to the release of the CQDs, with the resulting enhancement of colorimetric (Figure 8B) and PL (Figure 8C) signals of the hybrid system. In addition, SERS capability to provide fingerprint signatures of analytes and amplify the normally weak Raman intensities of TNT was exploited.[83] In particular, the superior affinity of TNT toward cysteamine triggered self-aggregation of Au nanoparticles and
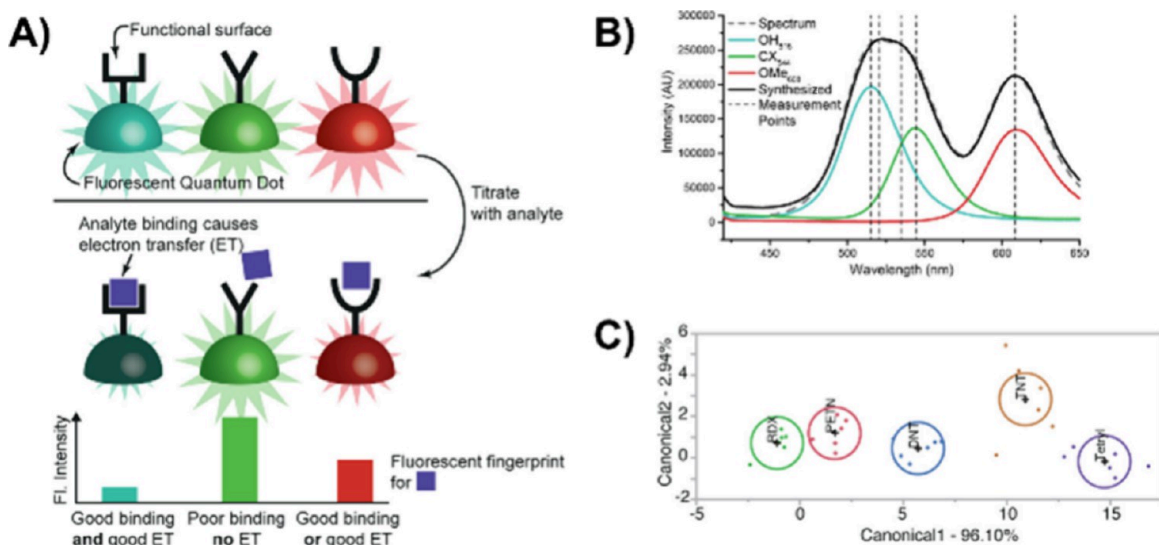
Figure 6. Multichannel array based on modified CQDs. (A) Scheme of the array design. CQDs of three colors were functionalized with different ligands leading to a luminescent fingerprint for the explosive analytes. (B) Overall PL spectrum of the mixture of three CQDs and the relative contributions of each. The dashed lines represent the five wavelengths used to discriminate the explosives. (C) Canonical plot for the determination of five explosives (RDX, PETN, DNT, TNT, Tetryl). Reprinted with permission from ref 81. Copyright 2016 American Chemical Society.
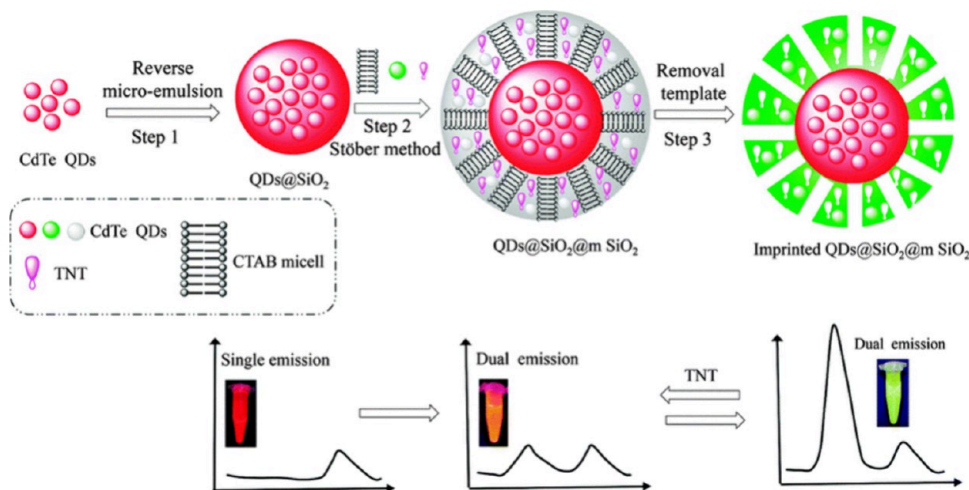
Figure 7. MIP@CQDs luminescent sensor. Schematic illustration of the synthesis of mesoporous structured MIP@CQD ratiometric probe and the sensing mechanism of TNT. Reprinted with permission from ref 53. Copyright 2015 Royal Society of Chemistry.

the consequent enhancement of the SERS signal, thus allowing the discrimination of TNT from its analogues (NB, TNP, RDX, 4-NT, 4-NP, 1,3-DNB, 1,4-DNB, 2,4-DNT, 2,4-DNP, and 2,6-DNT, as shown in Figure 8D) and its quantitative determination from various matrices including soil, clothing, fruit, and liquor.

Another successful example of multicriteria sensing is represented by the work of Milburn et al., where a CQD-based ratiometric sensor was coupled with a colorimetric, gel-encapsulated enzymatic sensor to qualitatively detect and differentiate unknown nitroaromatic compounds.[84] The ratiometric sensor was obtained by combining the PL response of Si CQDs with the persistent PL of luminescent proteins, whereas acetylcholinesterase was chosen as the enzyme in the colorimetric assay since it was preferentially inhibited by nerve agents. The PL sensor detected TNT, DNT, and NP with micromolar LOD and the colorimetric sensor provided an accurate differentiation of hazardous nitroaromatic explosives from chemically similar nerve agents within 5−10 min.

Trends and Perspectives. In summary, CQDs have spread as PL probes for sensing applications, including explosive detection, thanks to their unique physical and chemical properties, resulting in a large body of literature. Several researchers are focusing on the development of sensors with lower detection limits, enhanced sensitivity, and selectivity as well as low-cost and ease of use. Table 1 shows a performance comparison between a selection of the PL sensors discussed in this review. The complete table can be found in the Supporting Information (Table S1). It can be observed that the best detection limits for TNP and TNT in the solution phase are in the nano to femtomolar range, respectively, which is more than suitable for trace detection applications. Selective determination of NACs in the presence of primary interferents has been achieved by developing multichannel arrays, multimodal sensors, and by coupling CQDs with molecular probes with high specificity for the target analyte. It is also evident that it is not possible to identify a specific sensing mechanism among FRET, PET, and IFE that
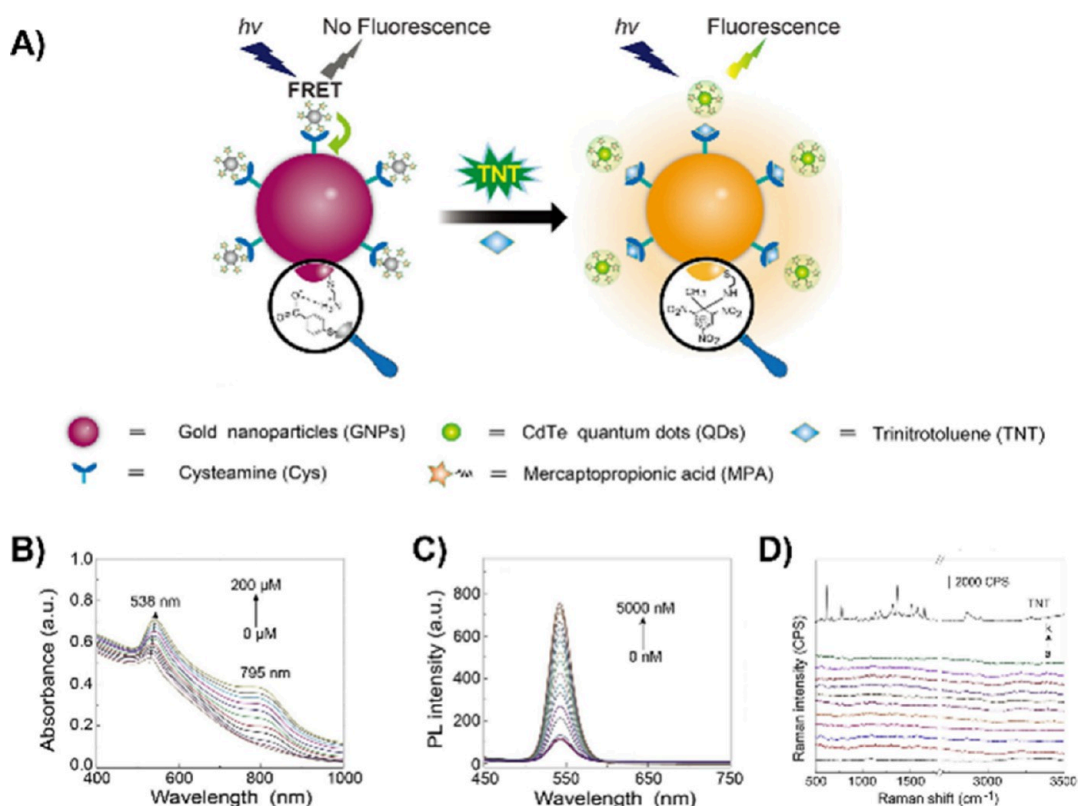
Figure 8. Trimode colorimetric, luminescent, and SERS sensing platform based on Au nanoparticles/CQD core−satellite assemblies for TNT detection. (A) Schematic illustration of trimode sensing platform. (B) Absorption and (C) PL spectra of GNPs-CQDs after addition of various TNT concentrations (5 μL, 0−200 μM). (D) SERS spectrum of the dispersion of GNPs-CQDs after exposed to coexisting compounds (2,4-DNP, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,4- DNB, 4-NP, 4-NT, TNP, RDX, and NB) at 1 μM and TNT at 1 nM. Reprinted and adapted with permission from ref 82. Copyright 2021 Elsevier.

outperforms the others, and similar characteristics are obtained by sensors exploiting all the different PL quenching processes. In terms of sensor design, however, some differences can be observed: it can be argued that both in FRET- and PET-based sensors, donor and acceptor must be in close contact in order to grant efficient quenching of the PL. The same does not apply to IFE, where donor and acceptor interact via a photon emission and absorption mechanism, thus allowing for a larger separation between the two. For this reason, it is arguable that FRET- and PET-based devices can be harder to design and optimize with respect to IFE-based sensors. On the other hand, most of the devices discussed in this review rely on a PET mechanism since it can be easily exploited thanks to the formation of Meisenheimer complexes between electron-poor benzenic rings (typical of nitroaromatic explosives) and electron-rich species that are easily attached to CQDs. It is also worth mentioning a sensing mechanism other than PL quenching, where the interactions between the target analyte and the probe lead to an increase of the CQD PL intensity through the removal of the quenching effect (OFF-ON switching).[85] Initially, CQDs forming a stable hybrid assembly with an energy acceptor (quencher) show little, if any, PL due to a PET process. During exposure to the analyte, this disassembles the CQD/acceptor adducts, thus prompting the release of the CQDs and restoring their PL. The OFF-ON mechanism has been successfully applied to the detection of explosives.[86,87] Such an approach is extremely promising for sensitivity enhancement and reduction of the LOD, principally due to enhanced signal-to-noise ratio since in the OFF-status

the noise is dramatically reduced, thus providing a stable and reliable reference prior to analyte detection. However, this method is particularly sensitive to interferences since the competitive binding could involve a variety of analyte-independent actors. A similar promising alternative could be the chemiluminescence sensing, which does not require a light excitation source also implying an intrinsically dark background.[88,89] Despite chemiluminescence has been used for explosive detection[90,91] and CQDs have been proved as effective chemiluminophores,[92−94] there are few examples to date of explosive detection based on CQDs as chemiluminescence enhancers.[54,95]

It should be noted that many luminescent sensors reported so far are based on CQDs comprising toxic metal ions, especially Cd and Pb. Even though such materials proved outstanding performance in terms of sensitivity, their applicability is limited by their intrinsic toxicity that could lead to undesired environmental or health impacts.[96] In recent years, two main strategies emerged to face this problem:[96] (1) the encapsulation of the original CQDs with a biocompatible protective shell (e.g., polymers, phospholipids, silica shells) to prevent direct contact with the surrounding environment, (2) the design of CQDs starting from nontoxic and eco-friendly materials, such as silicon- and carbon-based QDs.

The first route was followed by several authors aiming at the reduction of toxicity-related issues without losing the advantages offered by CQDs. In the work of Gong and co-workers, CdSe QDs were embedded in SiO_2 nanoparticles and modified with amino groups on the surface to form core−shell

Table 1. Analytical Performance of Selected CQD-Based Luminescent Sensors for Explosive Detection

Material	Analyte	Media[a]	Substrate	Technique	LDR	LOD	Field validation	Ref
Amine-capped CDs	TNT	L	Filter paper	PET	0–1 μM	0.213 μM	Groundwater	46
antibody-capped CdSe–ZnS CQDs	TNT	L, S		FRET	1–33.3 nM	-	-	48
MIP capped CdSe CQDs	TNT, DNT	L		PET	-	40.7 μM TNT; 30.1 μM DNT	-	52
MIP/CdTe CQD composites	TNT	L		PET	50–600 nM	15 nM	Tap water, soil	53
AM/β-cysteamine/ZnS:Mn²⁺ CQD nanocomposites/	TNT, TNP	L		PET	0.22–34.9 μM TNP; 0.04–0.44 μM and 0.44–2.2 μM TNT	3.4 nM TNP; 2.2 nM TNT	Lake water	57
N/P-CDs	TNP	L		IFE and PET	0.1–30 μM	30 nM	Sea water, river water, tap water	62
dopamine-capped CdSe/ZnS CQDs	NACs, RDX	L		PET		5 nM RDX; 10 nM TNT	-	65
Dodecyl and amine-terminated Si CQDs	NB, 2,4-DNT	L, S, V	Filter paper, fiber-optic sensor	FRET and PET		DNT, NB ~ nM (liquid)	-	66
CDs	TNP	L		IFE	0.1–15.8 μM	27 nM	Spiked water	70
PEI-capped CdSe/CdxZn₁₋ₓS CQDs	TNP	L	PA6 Electrospun membrane	PET		0.44 μM	-	73
Dual–emission CdTe CQDs	TNT	S	Filter paper	FRET	0–0.1 mM	5–50 ng/mm²	Rubber, paper, fabric	75
Three-Layered amine capped MoS₂ CQDs	TNT	L, S	Test paper	PET	2–800 nM	1 nM solution, 2 ng substrate assay	Tap/pond water, luggage case	76
Mn²⁺ doped ZnS CQDs	TNT, DNT, TNP, NB	V	PU nanofibrous membranes	PET			-	77
Amine-capped PbS CQDs	NB	V	Silicon	PET	1–9.6 μM	16 nM	-	79
CdSe/ZnS CQDs	DNT, TNT, tetryl, RDX, PETN	L	Filter paper	PET	11–85 μM	11 μM TNT; 3.5 μM Tetryl	Tap water	81
Cysteamine-Au nanoparticle/MPA-CdTe CQD core–satellite assemblies	TNT	L		FRET	10 fM–200 μM	3.2 fM	Soil, clothing, fruit, liquor	82
FP/Si CQD hybrids	TNT, 2,4-DNT, 4-NP	L	Filter paper	PET		1.9 μM TNT; 3.7 μM DNT; 10.6 μM NP	-	84
3-Aminopropyltriethoxysilane-cappedCdSe CQD@SiO₂ nanoparticles	TNP	L		PET	0.1–100 μM	0.05 μM	-	97
Amine-capped Si CQDs	TNT	L		FRET	5–500 nM	1 nM	Spiked tap water	100

[a]L = Liquid; S = Solid; V = Vapor.

nanoparticles that could selectively detect TNP with a detection limit of 50 nM.[97] Indeed, silica with high surface absorption and good biocompatibility is ideally suitable for the formation of recognition sites on the surface of CdSe CQDs and limits its toxicity by reducing the exposure of free Cd^{2+} ions. The combination of CQDs with organic materials allows the realization of core−shell nanocomposites with specific properties and/or superior sensing performance.[98,99] For example, Bai et al. developed an efficient one-pot strategy for the preparation of hydrophilic CQD nanocomposites via light-induced in situ polymerization of hydrophobic $ZnS:Mn^{2+}$ CQD capped with allyl mercaptan used as building blocks.[57] With this strategy, a hydrophilic nanocomposite was fabricated without complicated synthetic and purification procedures and, most importantly, the CQD PL was preserved. The CQD nanocomposites were further functionalized with β-cysteamine to introduce amino groups onto the surface, thus ensuring the selective binding toward TNT and TNP and a successful detection in real water samples.

The second route for toxicity reduction is based on the complete absence of toxic elements. For instance, amine-capped Si CQDs have been explored as a potentially nontoxic PL probe for the detection of TNT in aqueous solutions in the innovative work of Ban and co-workers.[100] The device showed promising results, indicating a linear relationship in the 5−500 nM range with nanomolar LOD. In this context it also worth mentioning CDs, that have become an increasingly popular alternative in the past decade due to the low toxicity, ease of synthesis, abundant and inexpensive precursors, chemical inertness, and water solubility.[40,101] Several different examples of PL sensing devices based on CDs are available in the literature for operation on both liquid and solid samples.[102−104]

Concerning the applicability, it should be noted that, to date, most of the CQD PL probes are rarely tested with real samples (e.g., wastewater, contaminated soil) which show considerable analytical complexity, but instead are used in the laboratory environment and operated by trained personnel. To enable on-site detection in real environments, it is necessary to develop portable lab-on-a-chip devices, which take advantage of microchip systems with drive and readout electronics circuits and that can be easily operated in a standalone mode without the need for specific instrumentation. Some progress has been made through the fabrication of portable probes by immobilizing CQDs on solid supports, including polymeric matrixes, xerogels, filter papers, and silicon wafers. However, a greater effort must be devoted in this direction. Also, very few data are available for explosive detection in the vapor phase.

As a final consideration, although a big deal of concern has rightly been expressed over homemade and improvised explosives (e.g., triacetone peroxide, TATP; ammonium nitrate and fuel oil, ANFO; cyclotrimethylene trinitramine, RDX; etc.), very few examples of CQD-based sensors targeting these substances are available in the literature.[65,81,105,106] These works rely on the same sensing mechanisms described for the nitroaromatic compounds and below we provide some remarkable and very recent examples. In 2021, Tawfik et al. demonstrated the possibility to detect TATP in solution with polythiophene-capped CdTe CQDs, achieving a competitively low detection limit of 0.055 mg L^{-1} in water;[107] the proposed device relied on an OFF-ON mechanism where the CQD PL was first quenched upon exposure to Hg^{2+} ions via electron transfer, and then the PL recovery was induced by the addition

of TATP to the solution. Ennis et al. published a proof-of-concept study on the realization of a field-applicable sensor by electrospinning CdSe CQDs into polymer fibers and measuring the PL quenching upon exposure toward different kinds of explosive vapors including TATP and RDX, even if with very low efficiency with respect to nitroaromatic compounds.[108] Although promising, these results need to be confirmed in validation studies. Due to the strategic importance of nonmilitary explosives in the context of homeland security applications, greater efforts must drive the scientific community on developing the most efficient and accurate technology with the least human intervention, always considering these compounds are extremely sensitive to mechanical shock and unsafe to handle, thus making laboratory test enormously challenging.
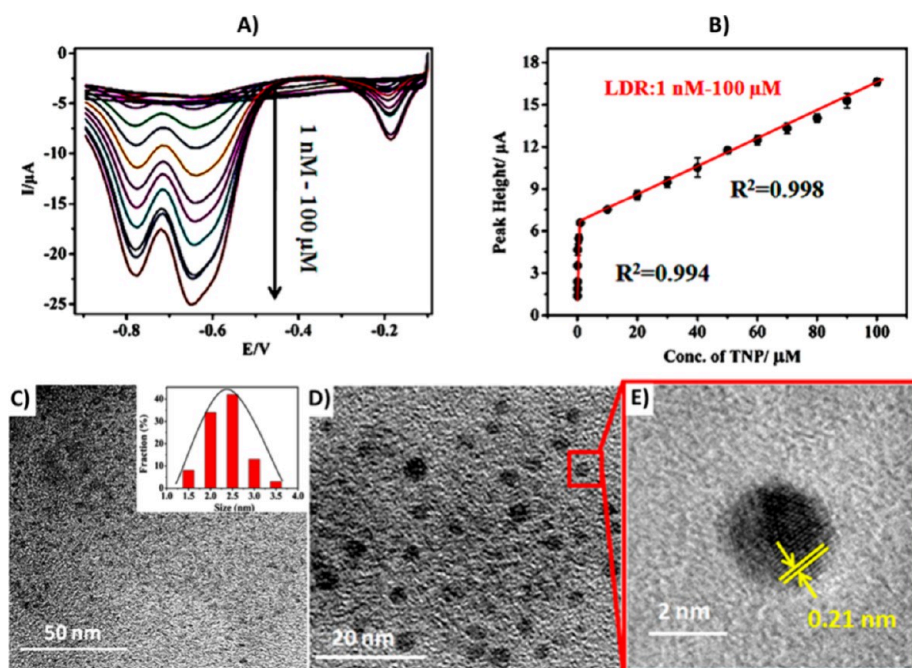
ELECTROCHEMICAL SENSORS

In this section, we review and discuss the research on CQD-based electrochemical sensors for explosive detection. Good sensitivity, selectivity toward one or more analytes, fast response, repeatability, and accuracy have made electrochemical sensing one of the election techniques for small-molecule detection and, in recent years, it has been gathering growing interest in the field of explosive detection.[109,110] In general, electrochemical sensors exploit a redox reaction involving the target analyte at the interface between a conducting solution (electrolyte) and the surface of the working electrode (WE) used as the transduction element. The electron exchange due to the ongoing chemical reactions is responsible for the variation of an electrical signal (current, potential, or capacitance) proportional to the analyte concentration (Figure 9). In the classical three-electrode
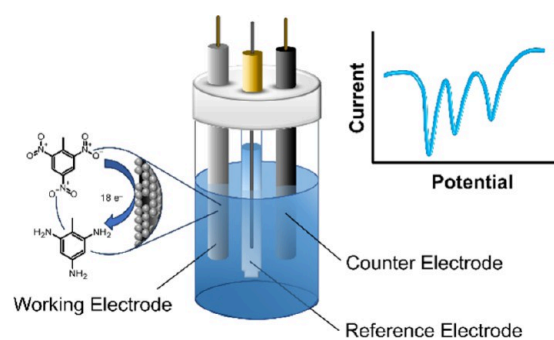
Figure 9. Schematic representation of the working principle of a typical electrochemical sensor using a three-electrode system. The analyte redox reactions take place on the CQD-modified WE, generating a measurable change in an electrical signal.

configuration adopted in most cases, the solvated charge carriers flow between the WE and the counter electrode (CE), balancing the current observed at the WE; the potential of the WE is measured and controlled with respect to a reference electrode (RE) having constant potential and low current density.

Voltammetry and amperometry are the most employed electrochemical techniques for sensing purposes, in which an electric current is measured as a function of the applied potential and related to the change in the oxidation state of the electroactive species. The suitable modification of the WE surface with nanomaterials having excellent conductivity and

Figure 10. Polyaniline-derived N-doped GQDs electrochemical sensor. (A) The DPV response of the N-GQD/GCE with increasing concentration of TNP from 1 nM to 100 μM; (B) The corresponding linear relation between the peak height and the concentration of TNP; (C, D) HR-TEM images of the synthesized N-GQDs with their size distribution (inset of figure c); (E) HR-TEM image of a single N-GQD. Reprinted with permission from ref 118. Copyright 2019 American Chemical Society.

high adsorption capacity can significantly improve the sensor response signals.[111]

CQDs possess high electron density and, due to their intrinsically high surface-to-volume ratio, provide enhanced electroactive surface area and high electron-transfer efficiency, thus remarkably amplifying the electrochemical signals. Despite the successful application in different fields, such as biomedical and pharmaceutical assay,[112] there are no reports in the the literature, to the best of our knowledge, about electrochemical sensors for explosive detection working with CQDs. This may be related to the tendency of chalcogenide and halide semiconductors to undergo corrosion in aqueous media under an electrical bias. On the other hand, there are numerous papers describing electrochemical sensors from carbon-based nanoparticles, which many authors refer to as quantum materials, such as CDs and graphene quantum dots (GQDs). Even if the quantum-confinement effect in CDs and GQDs is still debated,[113] we explicitly discuss carbon-based nanomaterial sensing devices as they are actively explored for explosive detection applications due to their high chemical stability and absence of toxic metals.[114]

Due to the favorable properties described above, electrochemical sensors can benefit from the presence of CQDs in two ways: (i) directly deposited on the electrode surface, CQDs act simultaneously as preconcentrating elements and charge transfer enhancers, and (ii) they are also quite effective as immobilizing agents, fostering the density of functionalization sites and the bonding stability of further sensing elements. In the following paragraphs, we discuss these two roles of CQD separately, distinguishing them as CQD-based and CQD-assisted electrodes, respectively.

CQD-Based Electrodes. In 2015, Zhang and co-workers first employed N-rich amine-passivated CDs to build a dual-mode luminescent/electrochemical platform for TNT quantification.[115] Both methods achieved a LOD down to the

nanomolar level, with the electrochemical assay showing a wider LDR (5 nM−30 μM), high specificity for TNT, satisfactory stability, and good applicability to real sample determination. Interestingly, CDs immobilization produced a reduction current for TNT four-times higher than the bare glassy carbon electrode (GCE) due not only to the high intrinsic activity and large surface area of CDs, but also to TNT accumulation on the electrode surface as a consequence of the strong TNT-amine interactions. Likewise, John et al. took advantage of the acid−base pairing between TNT and the electron donor −OH groups naturally formed on water-soluble CDs from an inexpensive green source.[116] The CD-based electrochemical sensor showed a 0.35 nM LOD with remarkable reusability over a long period and stability after one month of storage, outperforming the corresponding luminescent one.

The ability to adsorb the analyte on the electrode and catalyze its redox reactions is a key point for enhancing electrode sensitivity. From this point of view, GQDs are promising materials for nitroaromatic detections, being able to establish strong $\pi-\pi$ interactions between the two-dimensional planar structure of graphene and the aromatic rings of NACs. Graphene can also facilitate electron transfer during electrochemical reaction processes thanks to its high electronic conductivity, which can be further increased by heteroatom doping and size control. Cai et al. proposed N-doping to enhance the electrochemical activity of a GQD-modified GCE for TNT analysis.[117] N-doping decreases the HOMO−LUMO energy gap of the GQDs, resulting in enhanced conductivity and electron transfer ability. The sensor exhibited a linear response to TNT concentration from 4.4 nM to 1.8 μM with a detection limit of 0.88 nM. As a further improvement, Ramachandran et al. proposed a simple bottom-up synthetic route to produce optimized N-GQDs employing a polyaniline (PANI) precursor as an in situ N-containing aromatic carbon
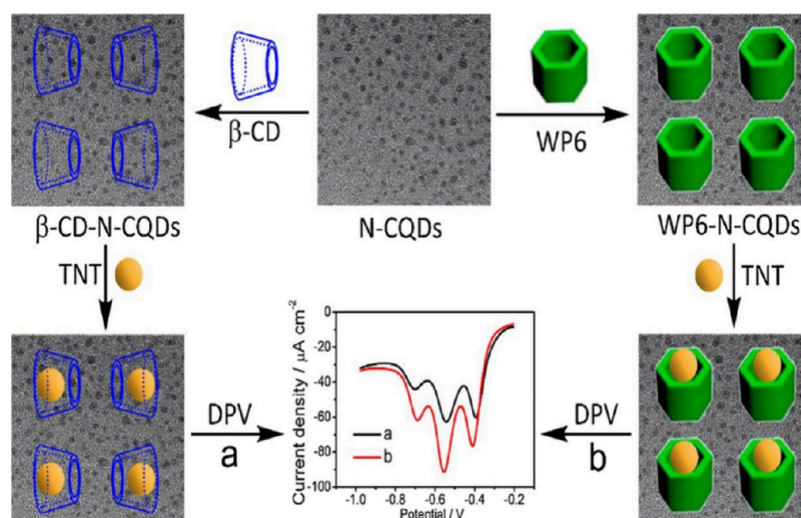
Figure 11. Water-soluble pillar[6]arene functionalized nitrogen-doped CDs electrochemical sensor. Schematic of β-CD-N-CDs and WP6-N-CDs nanocomposites used for electrochemical sensing and recognition of TNT. Reprinted with permission from ref 119. Copyright 2018 Elsevier.

source (Figure 10).[118] The integration of N rings into the aromatic structure of graphene allowed for differentiation between NACs with very similar chemical structures due to their peculiar peak profiles exhibited in the differential pulsed voltammetry (DPV). Two separate linear dynamic ranges (0.001−1 μM and 1−100 μM) and a detection limit of 1 nM were obtained. Notably, the platform was highly stable, keeping 80.2% of its initial sensitivity after seven months, and showed high reliability with good accuracy and precision for TNP sensing in tap and groundwater.

CQD-Assisted Electrodes. A promising strategy to boost the sensor's performance in terms of both sensitivity and selectivity is the combination of the CQDs with molecular recognition elements to form hybrids with increased stability, sensitivity, and binding specificity. Ran et al. realized a TNT sensor integrating N-CDs and macrocycles that can form stable and selective host−guest inclusion complexes or nano-structured supramolecular assemblies for organic analytes (Figure 11).[119]

Both β-cyclodextrin and water-soluble pillar[6]arenes (WP6) proved effective in enhancing TNT detection with respect to N-CDs GCE electrode. WP6, which formed the more stable complex with TNT, also achieved better performance, confirming the prominent role of suitable surface modification for the accumulation of large amounts of TNT molecules on the electrode surface toward enhancing electrode sensitivity. The WP6-optimized device achieved a 0.95 nM LOD, with the presence of analogues not impacting TNT detection, and satisfying performance were also obtained with tap and lake water.

The highest sensitivity has been obtained by resorting to aptamers (Aps) together with GQDs for the functionalization of the WE. Aps are artificial oligonucleotides that could be simply and reproducibly prepared via chemical synthesis. Moreover, Aps are low-cost, small-sized, and can be easily labeled and modified with a variety of molecules, linkers, and other functional groups.[120] Shahdost-Fard et al. employed thiol-functionalized GQDs to bind Ag nanoparticles, which in turn firmly immobilized NH_2-Aps onto the surface of a GCE for specific TNT reduction.[121] The efficiency of the obtained aptasensor relied on an amplification strategy: thiol-GQDs allowed a high density of the Ag nanoparticles on the modified

GCE surface due to the typical high surface-to-volume ratio; the increased amount of Ag nanoparticles, in turn, loaded more Ap molecules as a receptor element of TNT. When the interaction with the TNT molecule occurred, the formation of the Ap/TNT complex caused the folding of the aptamer structure, leading to the decrease in the DPV oxidation signal of rutin, employed as a redox probe. This strategy allowed a 0.001 pM−0.300 pM LDR and an ultralow LOD of 0.33 fM TNT, representing the best detection limit for QD-based electrochemical sensors ever reported (see Table 2). Furthermore, the selective recognition between the Ap and TNT enabled the excellent selectivity of the aptasensor over possible interfering compounds (Figure 12).

According to the general miniaturization trend, electro-chemistry has experienced a growing effort toward developing simple and low-cost electrode platforms for replacing more extensive instrumentation and materials. Screen-printed electrodes (SPEs) can be considered a well-established method for fabricating portable, miniaturized, and disposable electro-chemical sensors, meeting the needs for in situ, ready-to-use solutions. In a typical SPE configuration (shown in Figure 13A), the electrochemical cell is printed on a solid flat substrate (such as ceramic, plastic, or paper) by depositing a combination of layers of different materials (carbon, gold, silver, platinum, etc.) with high versatility of the design.[122,123] As well as the traditional WE, the surface of SPEs can be easily modified with different nanomaterials to allow selectivity toward specific analytes.

Very recently, Bressi and co-workers employed CDs drop cast on a commercial SPE for the detection of NB in water with good results, obtaining a linear response range of 0.1−2000 μM for NB, a 13 nM LOD as well as excellent selectivity toward NB in the presence of other 12 interferents (Figure 13B).[124]

Trends and Perspectives. Nanomaterial-modified electro-des are proving their potential in the development of electrochemical sensors for explosive detection due to their electrocatalytic effects and raise of sensitivity. Carbon-based nanomaterials have been used both as direct electrode modifiers because of their ability to increase the electron transfer efficiency and analyte concentration at the electrode surface and as effective immobilizers for specific molecular

Table 2. Analytical Performance of CQD-Based Electrochemical Sensors for Explosive Detection

| Material	Analyte	Technique	LDR	LOD	Selectivity	Long-term Stability	Repeatability (same WE)	Reproducibility (different WE)	Validating Sample	Ref
N-CDs/GCE	TNT	DPV, CA	5 nM–30 μM	1 nM	NB, 2-NT, 4-NT, 2,4-DNT, 2,6-DNT	96% after 1 week	-	-	Tap water	115
GQDs/GCE	TNT	LSV, CA	4.4 nM–1.8 μM	0.88 nM	2,4-DNT, 2-NT; benzidine, phenol, hydrazine; Cu^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}, NO_3^-; Triton X-100, sodium dodecyl sulfate	~92% after 1 month	~0.5% RSD by five successive measurements	Acceptable using five electrodes	Tap, ground and lake water	117
N-GQDs/GCE	TNP	DPV, CA	0.001–1 μM; 1–100 μM	1 nM	2,4-DNP, 2-NP, 2,4-DNT; Hg^{2+}, Ag^+, Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Sn^{4+}, Cu^{2+}, Cr^{6+}; Phenol, NB, NM	80.2% after 7 months	-	1.14% RSD using five electrodes	Tap and groundwater	118
WP6-N-CQDs/GCE	TNT	DPV, CA	0.001–1.0 μM; 1–20 μM	0.95 nM	NB, 4-NT, 2-NT, 2,6-DNT, 2,4-DNT	88.2% after 10 days	-	4.2% RSD using six electrodes	Tap and, lake water	119
Ap/Ag nanoparticles/ thiol-GQDs/GCE	TNT	DPV, CV	0.001 pM–0.300 pM; 5 μM–45 μM	0.33 fM	RDX, 4-Nitroaniline, 1-Bromo-4-nitrobenzene, p-Toluidine and DNT	90% after 14 days	2% RSD by six successive measurements	4% RSD using five electrodes	River water, soil	121
CDs/SPE	NB	DPV, CV, LSV	0.1–2000 μM	13 nM	Phenyl pyruvic acid, toluene, aniline, Cd, Pb and Ni, nitrates, K, Cl, NH4Br, TNP, p-NT	1.22% RSD after 30 days	1.02% RSD by five successive measurements	-	Wastewater	124

recognition elements, relying on their high surface area, good interfacial properties, and high surface activity. The reported devices provided a more than satisfactory nanomolar detection limit for TNT and TNP. A notable exception is represented by the work of Shahdost-Fard et al., where an unprecedented femtomolar LOD was obtained, possibly stemming from the high specificity of aptamer molecules as recognition probes for TNT on the electrode surface.

Comparison data regarding the sensing material, target analyte, electrochemical techniques employed, LDR, LOD, selectivity, stability, repeatability, reproducibility, and real samples tested are listed in Table 2. The reported electrochemical sensors demonstrated satisfactory chemical recoveries (Table 3), suggesting good stability and reproducibility in real water and soil samples.

It is worth noting that no reference to nanomaterial-based electrochemical sensors operating in the vapor phase exists in the literature, either in general or applied to explosives detection. However, electrochemical gas sensors are well-established in industrial gas safety,[125] and some applications for homeland security can also be found.[126,127] CQDs, for their part, are well suited to the requirement of the ideal sensing material, which should possess a high specific surface area, highly reactive surface sites for a specific gas molecule adsorption, and significant charge transfer ability.

The main challenge in realizing a fast-response electrochemical gas sensor is to ensure accessibility to the working electrode, which is in contact with an internal liquid electrolyte solution containing the reference and counter electrodes. A gas-permeable membrane envelops the electrochemical cell to prevent interferences from other substances; the diffusion of the gas through the membrane and, above all, through the liquid electrolyte is the rate-limiting step. Improvements were obtained by replacing the common liquid electrolytes, such as phosphate buffer (PBS) and potassium chloride, with low-volatility materials with wide electrochemical windows and intrinsic conductivity, such as room-temperature ionic liquids (RTILs).[128] Even better performances can be achieved by employing solid-state electrochemical sensors based on solid polymer electrolyte membranes such as Nafion or inorganic solid electrolytes, such as Yttria stabilized zirconia (YSZ).[129] Hydrogels immobilizing a liquid electrolyte might also be a viable route.[130] Of particular interest, in this context, is the possibility of forming stable colloidal systems with robust transport pathways and large surface areas by aggregating them in a controlled fashion, leading to a macroscale gel.[131] The macroscale objects thus formed fully retain the size-dependent properties of the initial building blocks, while the three-dimensionally connected pore network ensures electronic/ionic communication and high accessibility to the ambient, being metal chalcogenide CQD gels a notable example.[132] Recently, Geng et al.[133,134] proposed an electrochemical gelation method allowing direct gel formation on electrode substrates. This new strategy could offer the key to drastically reduce the time for gas diffusion, thus possibly enabling the realization of devices with fast response time (Figure 14).

Finally, the development of planar electrode devices such as the previously mentioned SPEs, thin-film electrodes, and interdigitated electrodes could facilitate the fabrication of miniaturized devices, thus promoting the transition from traditional lab-based techniques to cheaper and quicker tests for environmental monitoring.[135]
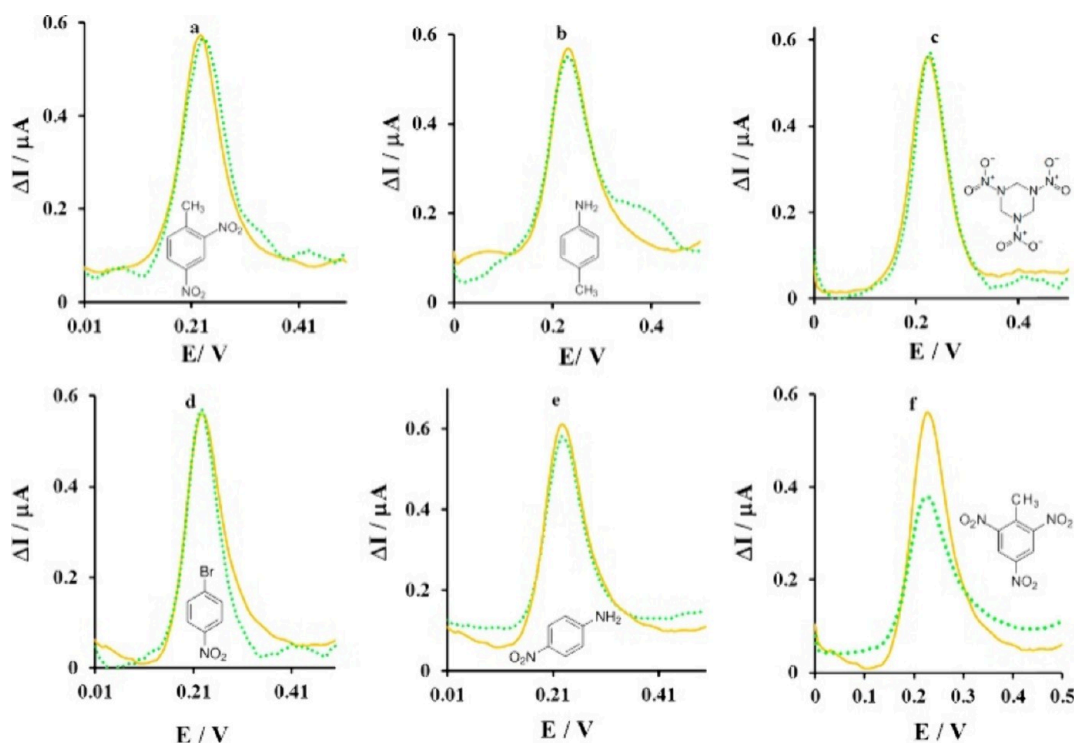
Figure 12. Aptasensor based on an AgNPs/thiol-GQD nanocomposite for TNT detection. The DPV results after incubation with 1 fM TNT (f) and (a) 2,4-Dinitrotoluene, (b) p-Toluidine, (c) RDX, (d) 1-Bromo-4-nitrobenzene, and (e) 4-Nitroaniline with 10^3-fold higher concentration than of the TNT. Reprinted with permission from ref 121. Copyright 2017 Elsevier.
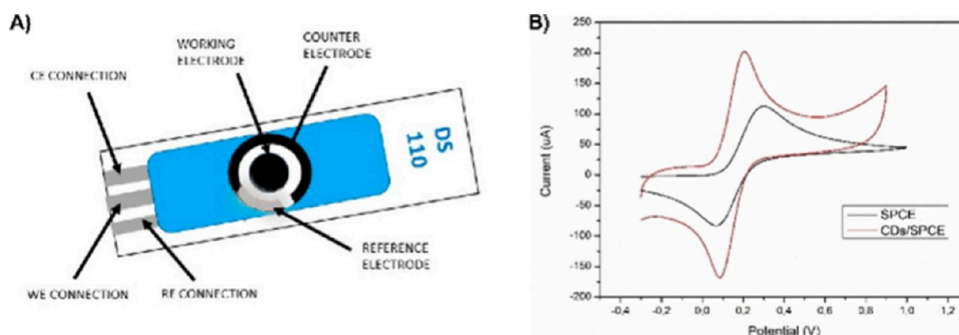
Figure 13. (A) Schematic representation of a screen-printed electrode module used for electrochemical analysis. Orange peel waste-derived CD voltammetric sensor. Reprinted with permission from ref 122. Copyright 2020 The Authors. Published by MDPI. (B) CV of SPE and CDs/SPE in the presence of 10 mM $K_3[Fe(CN)_6]$ at a scan rate of 50 mVs. Reprinted with permission from ref 124. Copyright 2023 The Authors. Published by Wiley-VCH GmbH.

Table 3. Chemical Recovery Test Results of NACs in Real Environmental Samples

Samples	Target	Added amounts	Measured amounts	Recovery (%)	RSD (%)	Ref
Tap water	TNT	50 nM	-	98.3–103.1	-	115
Tap, ground and lake water	TNT	8.8 nM	8.72 nM	99	0.25	117
			8.94 nM	101.5	1.26	
			8.72 nM	99	0.84	
Ground and tap water	TNP	2 μM	1.98 μM	99	-	118
			2.02 μM	101		
Tap and lake water	TNT	0.8 μM	0.74 μM	92.5	8.1	119
			0.75 μM	93.8	6.7	
River water, Soil	TNT	10 fM	9.80 fM	98	-	121
		50 fM	5.08 fM	101.60		
Wastewater	NB	-	-	98	-	124

■ CHEMORESISTIVE SENSORS

Electrochemical and luminescence sensors grant high sensitivity and selectivity toward the target analytes, but, at the same time, they still pose some usability issues. More specifically, electrochemical devices need precise control of the electrode potentials, thus requiring a fixed potential reference electrode and high-precision readout circuits.[136] On the other hand, luminescence transducers need to be coupled with specific photodetectors and the whole system should be sealed in a package that is permeable to the target analyte and yet able to grant the dark conditions needed by the photodetector to avoid external interferences. Moreover, in both cases, even if operation in air has been demonstrated, only a few working examples have been discussed in the literature, while most of the research focused on explosive detection in water and/or solid samples.
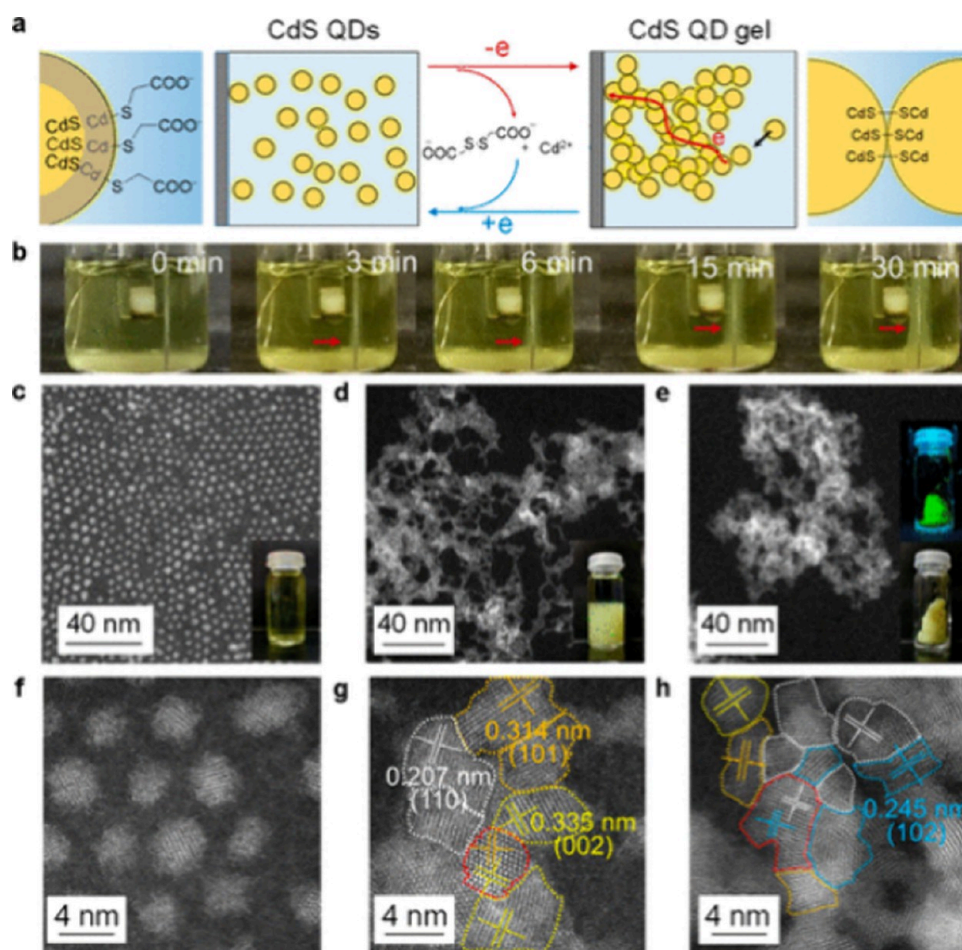
Figure 14. Electrogelation of CdS CQDs. (a) Schematic of the reversible electrogelation mechanism for CdS CQDs. (b) CdS gel growth on a Pt wire electrode as a function of electrogelation time at an electrode potential of 1.2 V vs Ag/AgCl/sat. KCl electrode. (c−e) Low-magnification STEM and TEM images of CdS CQDs, wet gel, and aerogel, respectively. (f−h) High-resolution STEM images of CdS CQDs, wet gel, and aerogel, respectively. Reprinted with permission from ref 134. Copyright 2020 American Chemical Society.

Chemoresitive devices are good candidates to overcome such limitations; first, chemoresistors are direct sensing devices (like the electrochemical sensors) and not indirect transducers (like luminescent devices), thus they are able to directly generate an electric signal in response to the target analyte. Moreover, unlike electrochemical devices, the sensitivity of the sensor performance to the applied potential is limited, and no reference electrode is required. For these reasons, several research works are available in the literature regarding gas sensing through chemoresistive sensors based on CQDs, from air quality and environmental monitoring to human health applications.[25,26,137] According to the Scopus database, the number of papers dealing with chemoresistive gas sensors published each year increased by more than 10 times over the past decade, demonstrating a growing interest in such technology. All this knowledge is expected to be transferred also to the realization of CQD gas sensors for explosive detection in the coming years.

Chemoresistive sensors were first introduced more than 50 years ago, and they have been based, for a long time, on metal oxide (MO_X) films.[138] Their operation is based on the conductivity variation of the MO_X film when exposed to reducing agents that can alter the potential barrier between neighboring grains thus changing the overall film's resistance. In order to obtain high sensitivity, the chemical reactivity of the film has to be enhanced by heating the device at high temperatures, resulting in high power dissipation and difficult integration. The use of CQDs recently boosted the development of chemoresistors since the small dimensions produced a significant increase in sensitivity at room temperature.[138] In addition, the simplicity of surface functionalization allowed for the enhancement of the selectivity toward specific analytes. Figure 15 shows a schematic representation of a CQD-based chemoresistor.

Despite all these advantages and the high number of scientific papers dealing with chemoresistors operating in
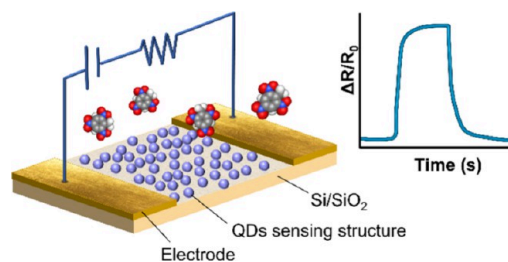
Figure 15. Schematic of a chemoresistive structure with golden (Au) electrodes using CQDs as sensing material and a typical response curve of the gas sensor.

air,[139−141] only few examples exist that employ CQDs for the realization of chemoresistive sensors for explosive detection. The first example of chemoresistive explosive detector was proposed in 2016 by Pal et al.[142] and relied on a CD/ polypyrrole (Ppy) nanocomposite demonstrating a 0.14 μM LOD toward TNP in water solution. Interestingly, the device also showed some sensitivity toward DNP and NP whereas the response to NB was negligible. In this case, the CDs were employed to enhance the conductivity of the Ppy and the as-synthesized composite was directly employed for the sensor fabrication, without further functionalization. The first example of CQD-based chemoresistive explosive sensor operating in air was provided by Wu et al., who employed unfunctionalized Mn-doped ZnS CQDs.[143] The LOD of the proposed device toward DNT was outstanding (13.7 pM) but, due to the lack of specific functionalization, the device selectivity was poor. To overcome this issue and enhance the selectivity, the authors employed an array of several sensors with different amount of Mn doping (results in Figure 16). The sensitivity of the devices
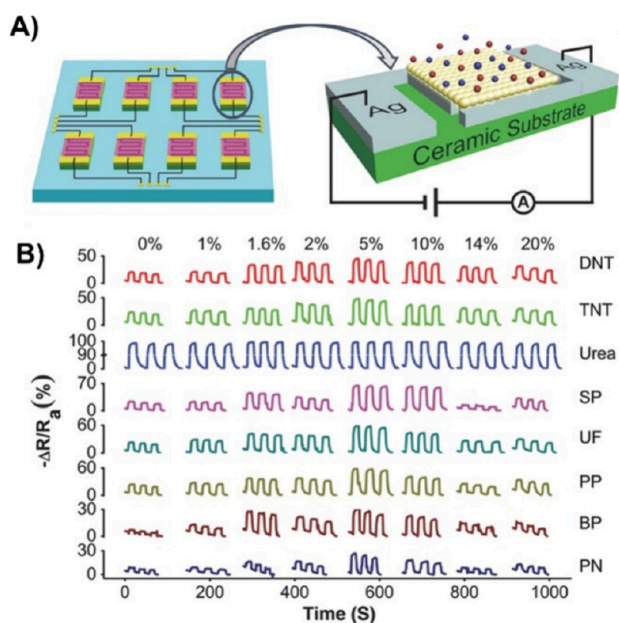
Figure 16. Mn²⁺-doped ZnS CQD chemoresistive sensor. (A) Schematic diagram of a single chemoresistive gas sensor and of the whole array. (B) Response curves of the array to different analyte vapors at room temperature. Reprinted with permission from ref 143. Copyright 2016 John Wiley and Sons, Inc.

toward different analytes showed a strong dependence on the Mn concentration and simple pattern recognition algorithms could be employed to discriminate between several different explosives and precursors.

A diverse approach for selectivity enhancement consists in the functionalization of the CQD surface with specific ligands that can form electronically active complexes with specific analytes, thus altering the overall conductivity of the CQD film. Our group recently demonstrated the efficiency of this approach, realizing a chemoresistor based on PbS CQDs for the detection of NACs (see Figure 17).[144] The CQDs were functionalized with EDA to allow the formation of a Meisenheimer complex between the −NH₂ functional group and the electron-poor aromatic ring of the target NACs. The proposed device showed a LOD for NB of 16 nM in air, and we also demonstrated good selectivity toward aromatic and
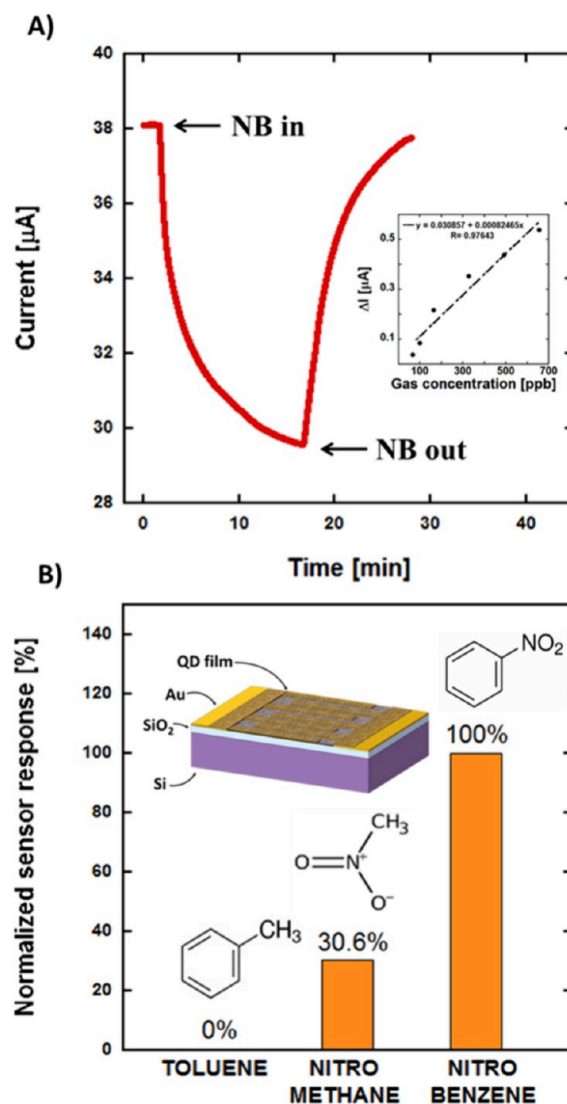
Figure 17. PbS CQD chemoresistive sensor. (A) Real-time current change obtained with 1.87 ppm of NB. The inset shows the linear fit in the 65−655 ppb range. (B) Sensor response of the sensor to toluene, NM, and NB at the same concentration of 5 ppm, normalized with respect to the sensor response value for NB. The inset shows the schematic of the device. Reprinted and adapted with permission from ref 144. Copyright 2022 The Authors. Published by American Chemical Society.

aliphatic interferents (i.e., toluene, nitromethane). Table 4 summarizes the sensing parameters of the mentioned devices.

Even if a small number of papers focused on chemoresistive explosive detectors operating in air, the performance of the few devices available in literature are outstanding, both in terms of sensitivity and selectivity. The ease of fabrication, low-cost, and effectiveness of such devices make them a promising alternative for the realization of high-sensitivity explosive detection systems that can be easily deployed in many different scenarios, integrating them in wider sensor networks with the typical approach of IoT systems. To reach this goal, however, some issues should still be solved, improving the lifetime of the sensors, and reducing their sensitivity toward environmental conditions (e.g., temperature and relative humidity).

Table 4. Analytical Performance of CQD-Based Chemoresistive Sensors for Explosive Detection

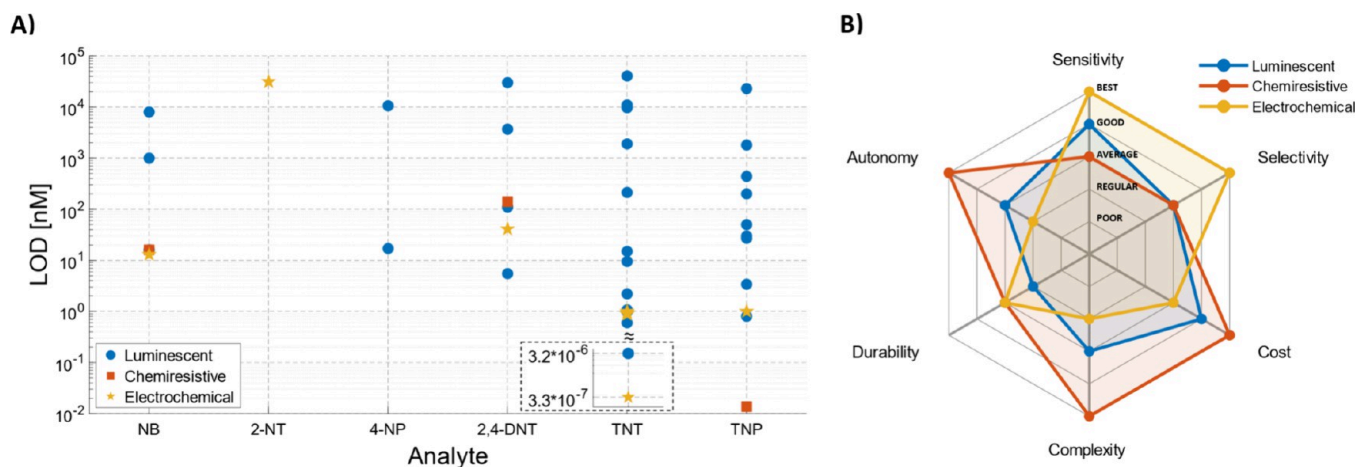| Material	Substrate	Analyte	Media	LDR	LOD	Selectivity	Ref
CdS/Ppy nanocomposite	Glass	TNP	Liquid, soil	1 μM–1 mM	1.4×10^{-7} M	2,4-DNP, 4-NP, PH, QN, 4-MBA	142
Mn^{2+}-ZnS QDs	Ag IDEs on Ceramic	DNT	Vapor	0.45–2.4 nM	13.7 pM	Urea, UF, SP, PP, BP, PN, TNT	143
Amine-capped PbS CQDs	Au IDEs on Silicon	NB	Vapor	0.5–130 μM	16 nM	Toluene, NM	144

Figure 18. (A) Limit of detection of the previously summarized sensors toward different nitroaromatics. (B) Spider plot comparison of the characteristics of the candidate CQD technologies for explosive detection.

CONCLUSIONS AND OUTLOOK

The landscape of sensing devices based on CQDs and specifically designed for the detection of explosives is quite vast and, mainly due to the importance of the problem of fast and reliable detection in sensitive contexts, many different approaches have been proposed in the literature. Three main sensing technologies have arisen, namely luminescent, electrochemical, and chemoresistive sensing. Each approach showed different peculiarities, strengths, and weaknesses and, at present, it is difficult to identify a winning technology that can fulfill the requirements in terms of sensitivity, selectivity, durability, ease of use, and autonomy from human operators in all the different application scenarios. Figure 18A provides a comparison of each technology in terms of sensitivity toward different explosives, while Figure 18B represents a visual comparison of the main techno-economic characteristics of the candidate technologies.

Luminescence-based sensing has demonstrated good sensitivity and selectivity, thanks to the possibility of exploiting different reaction mechanisms between the sensing material and the target analyte. The ease of fabrication of the sensors is a valuable strength of this approach, together with the variety of possible CQD surface functionalization. Overall, luminescence-based sensors proved slightly less performant when compared to electrochemical devices, while they also rely on additional hardware (i.e., light sources, photodetectors) to be operated and to quantitatively determine the amount of analyte in the samples. On the other hand, the possibility of realizing qualitative detection systems on low-cost substrates (e.g., paper) and the ability to operate such sensors by physical contact on solid samples, make luminescence-based devices best suited for random testing in sensitive environments such as airports and government buildings. Finally, human operators do not need specific training to efficiently run qualitative tests. On the negative side, only a few examples of luminescence-based sensors operating in the air have been discussed in the literature, thus suggesting a difficulty of implementation of durable, sensitive, and selective devices.

Electrochemical devices showed the best performance in terms of sensitivity and selectivity and opened a wide range of possibilities for in situ monitoring and multielement detection. However, the limited operating temperature range affecting their stability, the short shelf life, together with the need for trained operator control hamper their deployment on a vast scale. Unexpensive, miniaturized, and tailorable SPEs represent a great alternative to traditional laboratory standard techniques reducing analytical operations and simplifying the required readout systems; nevertheless, important shortcomings still need to be fixed, such as the great variability in performance from batch to batch linked to the material used and the quality of the printing technique selected (in turn affecting electrodes cost). Finally, most electrochemical devices are still operating in the liquid phase, thus hindering their employment in air monitoring systems.

Chemoresistive sensors have been barely discussed in the literature, and only few examples exist, operating either in water or in air. Even so, the performance shown by such devices, in terms of both sensitivity and selectivity, is already comparable with state-of-the-art luminescence-based devices, thus suggesting that further optimizations are still feasible. The possibility to integrate the sensors with simple, off-the-shelf readout electronics is one of the biggest strengths of chemoresistive devices, making them good candidates for the realization of distributed sensing systems and environmental monitoring.

The strengths and weaknesses of the different sensors and devices discussed in this review still do not allow for the identification of a best-suited sensing approach for every field of application where explosive detection is needed. In the near future, we expect further development for all the different kinds of devices, but we can envisage some specialization strategies for each class of sensors. More specifically, luminescence-based systems should be the solution of choice for fast, qualitative

analysis in critical environments such as airports. In this sense, further efforts are needed to reduce the limit of detection and to enhance the selectivity of the sensors. Also, given the disposability of the sensors, toxic metal-free approaches should be preferred. On the other hand, electrochemical devices appear as the best option for applications where high sensitivity and selectivity are needed and where specialized personnel and instrumentation are available. SPEs are promising for the reduction of the time needed for sample analysis, but, at the same time, specific strategies for improving the reusability of the electrodes should be adopted. Finally, thanks to the possibility of being operated in air and due to the simple readout electronics, chemoresistive devices appear best-suited for the realization of long-lasting, low-power, distributed sensing systems, allowing for long-term environmental monitoring and security systems. Efforts are still needed to enhance the sensitivity and selectivity of chemoresistive sensors, but the approaches already developed in the context of electrochemical and luminescent sensors could be easily transferred and implemented (e.g., MIPs, antibodies, etc.).

Even if several different sensors and devices have been proposed in the literature, only few of them focus on non-nitroaromatic and improvised explosives; given the uttermost importance of fast and reliable detection of such substances for homeland security applications, we believe that the scientific community should increase its efforts toward the realization of dedicated sensors. At the same time, it should also be observed that such substances are often extremely hazardous due to high instability at room temperature. For this reason, experiments should be subject to thorough safety assessment and should involve police forces and specialized equipment.

Finally, the reliability of sensors for field applications goes through their fine characterization with respect to environmental conditions, with the goal of developing a robust sensor whose performance is not affected by parameters such as temperature and humidity. This clearly has an impact on the long-term stability and on the overall cost of the proposed sensor. To this extent, an evaluation of the anti-interference properties of a sensor is extremely important, but authors rarely mention this topic, and few data are available regardless of the type of sensor. Therefore, a major effort needs to be devoted in this direction, as well. Similarly, even if a vast literature is available about disposable and easy-to-use luminescent sensors (e.g., luminescent solutions and paper-based sensors) the naked-eye LOD is seldom evaluated, thus not allowing for a clear comprehension of the effectiveness of the proposed sensors in real-life applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssensors.3c02097.

> Complete table reporting the performance of the CQD-based luminescent sensors for explosive detection (PDF)

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Author Contributions

The authors equally contributed to the paper. All authors have read and agreed to the submitted version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

AN, aniline; BA, benzoic acid; BD, benzaldehyde; BP, Black Powder; CA, chronoamperometry; CB, chlorobenzene; CDs, carbon dots; CN, chloronitrobenzene; CQDs, colloidal quantum dots; CV, cyclic voltammetry; DMDNB, 2,3-dimetil-2,3-dinitrobutano; DHB, dihydroxybenzene; DNB, dinitrobenzene; DNBA, dinitrobenzoic acid; DNP, dinitrophenol; DNT, dinitrotoluene; DPV, differential pulse voltammetry; EDA, ethylenediamine; EDTA, ethylenediaminetetraacetic acid; EIS, electrochemical impedance spectroscopy; FP, fluorescent protein; FRET, Förster resonance energy transfer; GCE, glassy carbon electrode; GQDs, graphene quantum dots; IDEs, interdigitated electrodes; IFE, inner filter effect; LDR, linear dynamic range; LOD, limit of detection; LSV, linear pulse voltammetry; MA, methylamine; MB, methylbenzene; MBA, methoxybenzoic acid; MIPs, molecularly imprinted polymers; NA, nitrobenzoic acid; NA*, nitrobenzyl alcohol; NACs, nitroaromatic compounds; NANA, nitroaromatic nerve agents; NAT, nitroacetophenone; NB, nitrobenzene; NBM, nitrobenzenemethanol; NM, nitromethane; NN, nitroaniline; NP, nitrophenol; NPH, nitrophenylhydrazine; NR, nanorod; NT, nitrotoluene; PET, photoinduced electron transfer; PETN, pentaerythritol tetranitrate; PH, phenol; PN, Potassium Nitrate; PL, photoluminescence; PP, potassium permanganate; QDs, quantum dots; QN, 1,4- benzoquinone; RDX, cyclotrimethylenetrinitramine; RSD, relative standard deviation; SERS, surface-enhanced Raman scattering; SP, Sulfur Powder; SPE, screen printed electrode; Tetryl, 2,4,6-trinitrophenyl-*N*-methylnitramine; TNT, 2,4,6-trinitrotoluene; TNP, 2,4,6-trinitrophenol; UF, Urea Fertilizer

■ VOCABULARY

Chemoresistive sensors, a class of chemical sensors whose electrical resistance changes in response to the direct chemical interaction between the sensing material and the analyte; Colloidal quantum dots, solvent dispersible nanoscopic crystals of inorganic semiconductor materials, whose size is smaller than the exciton Bohr radius thus showing quantum confinement effects; Electrochemical sensors, a class of sensors that exploits a redox reaction involving the analyte at the interface

between the electrolyte and the surface of the working electrode as the transducer element; Explosive, a material that can be initiated to undergo very rapid and self-propagating decomposition resulting in the formation of more stable material, liberation of heat or the development of sudden pressure effect; Luminescent sensors, a class of optical sensors that relies on any phenomenon of luminescence change (intensity, wavelength, anisotropy, or lifetime) to detect the analyte; Photoluminescence, the phenomenon that occurs when a luminophore absorbs an electromagnetic radiation reaching an excited state then returning back to the ground state via the emission of a photon whose energy is lower than that of the absorbed radiation

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