

Optical gas sensor based on the combination of a QD photoluminescent probe and a QD photodetector

Abstract

We report on a sensor architecture for detection of hazardous gases. The proposed device is based on the integration of a solid-state quantum dot (QD) photoluminescent probe with a QD photodetector on the same substrate. The effectiveness of the approach is demonstrated by developing a compact optical sensor for trace detection of explosives in air. The proposed architecture is very simple and consists of a silicon substrate with both surfaces coated with QD films. The upper layer acts as photoluminescent probe, pumped by a blue LED. The change of photoluminescence intensity associated to the interaction between the QDs and the target analyte is measured by the QD photodetector fabricated on the opposite side of the substrate. The sensor is mounted into a small chamber provided with the LED and the front-end electronics. The device is characterized by using nitrobenzene as representative nitroaromatic compound. Extremely low concentrations (down to 0.1 ppm) can be detected by the proposed device, with a theoretical detection limit estimated to be as low as 2 ppb. Results are repeatable and no ageing effect is observed over a 70-day period. The proposed architecture may provide a promising solution for explosive detection in air as well as other sensing applications, thanks to its sensitivity, simple fabrication process, practical usability, and cost effectiveness.

KEYWORDS: quantum dots, nitroaromatic explosives, solid-state photoluminescent probe, gas sensor.

1. Introduction

Three-dimensionally quantum confined semiconductor nanomaterials have emerged as a versatile material system with remarkable optical and electrical properties [1]. In particular, the bandgap of the quantum dots (QDs) is size dependent, resulting in absorption and emission spectra that can be easily tuned during QD synthesis [2], thus enabling the selection of the spectral range of interest according to the targeted application. As a consequence, QDs have been incorporated as active elements in a wide variety of devices, especially in optoelectronics [3]. Indeed, PbS QD absorption edge can easily be tuned from 900 nm to 1.8 μm and photodetectors based on this material have been well-optimized in terms of QD size control, low dispersion and reproducibility [4]. Finally, due to their high luminescence efficiency, emission wavelength tunability, operation stability and solution processability, QDs have long been researched for light-emission diodes [5].

Although initially targeted at optoelectronic applications, semiconductor QDs are attracting growing interest from the sensor research community in a continuing search for inexpensive, sensitive and selective sensors [6]–[8]. This can be attributed to other peculiar characteristics of the QDs, such as high electron-transfer efficiency, feasibility for surface modification and functionalization, ease of synthesis and fabrication [9]. Moreover, the very large surface-to-volume ratio of the QDs provides a high surface reactivity even at room temperature [10]. The QD luminescence capabilities have been exploited for the fabrication of several different sensors, thanks to the strong correlation between the QD surface chemistry and the photoluminescence (PL) efficiency. Moreover, surface functionalization is a key element for the fabrication of highly selective sensors. It is envisaged in particular that QDs can be successfully employed as fluorescent probes for the detection of explosive compounds such as nitroaromatic compounds (NACs) [11]. This approach has been typically

employed in the liquid phase, where both the QDs and the target analyte were dispersed in the same solution, achieving outstanding detection limits ($\sim$ nM) [12]–[16]. However, the high sensitivity achieved does not compensate for a notable inherent limitation, i.e., the fact that detection occurs in an aqueous medium, whereas vapor detection is not allowed. Furthermore, this QD-based approach relies on cumbersome and expensive instrumentation to quantify the change in PL intensity. As a result, this strategy is not applicable for the instant on-site identification of NACs, for which vapor detection is more appropriate.

Recently, a QD PL probe in the solid-state form was demonstrated, employing it as a sensor for vapor explosive detection based on the measurement of the solid-state PL variation produced by PbS QDs cast on a silicon substrate [17]. In that case, the PL signal was acquired with a commercial IR photodetector and the signal was evaluated with a lock-in amplifier. Herein, we propose an even more compact system for NACs detection in air, by coupling the QD PL element with a QD photodetector fabricated on the opposite side of the same silicon substrate.

2. Material and methods

2.1 PRINCIPLE OF OPERATION

Figure 1(a) shows the system architecture whose main element is a $10 \times 10 \times 0.7 \text{ mm}^3$ silicon substrate with both surfaces coated with a PbS QD film. The upper QD layer, suitably functionalized with ethylenediamine (EDA), acts as a PL probe, pumped by a blue LED. The change of PL intensity associated to the interaction between the QDs and the target analyte is measured by a QD photodetector treated with tetrabutylammonium iodide (TBAI) - and fabricated on the opposite side of the substrate. The silicon substrate cuts off the blue pump, while it is transparent to the NIR light emitted by the upper QD layer ($\lambda_{\text{PL}} = 1400 \text{ nm}$). The emitted photons can reach the QD photodetector that, in turn, generates a photocurrent proportional to the PL intensity. The sensor is mounted into a small custom-made chamber provided with the LED and the front-end electronics. The spectra in **Figure 1(b)** allow for a better understanding of the proposed device architecture and its operating principle. The yellow curve showing the spectral response of the PbS QD photodetector, exhibits an excitonic absorption peak at 1320 nm and a significant photoresponse up to 1600 nm.

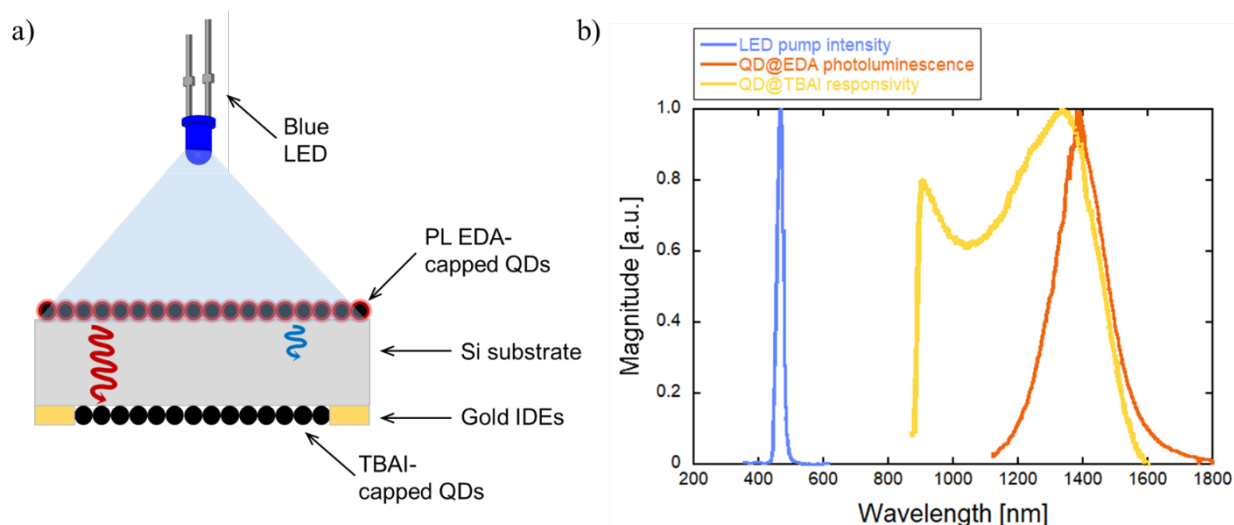


Figure 1. a) Schematic of the optical arrangement; b) Solid-state QD PL spectrum (orange), QD photodetector spectral response (yellow) and LED pump emission spectrum (blue). All curves are normalized to their maximum.

Below 1000 nm the response is abruptly cut off by the silicon substrate which acts as an optical filter. The photodetector spectral response exhibits a satisfactory overlap with the solid-state PL spectrum from the QDs of the upper layer (in orange). The LED light peaked at $\lambda = 465$ nm, whose emission spectrum is shown in **Figure 1(b)** (in blue), is clearly blocked by the silicon substrate and does not affect the photocurrent signal. The sensing mechanism for NACs detection and its selectivity is already well-demonstrated in literature and it depends on the functionalization of the QD surface with an amine ligand [18]. Briefly, the charge transfer between the electron-rich amine ligands and the electron-poor benzene ring of the NACs, with the consequent formation of an unstable Meisenheimer complex, quenches the PL, thus allowing for selective NAC detection.

2.2 EXPERIMENTAL DETAILS

Colloidal PbS QDs have been synthesized in a three-neck flask connected to a standard Schlenk line set up under oxygen- and water-free conditions, as reported elsewhere [19] (details provided in the SI). The QD dispersion was deposited on both sides of a silicon substrate by drop casting (top layer) and spin coating (bottom layer). The top layer was functionalized with EDA, while the bottom layer was treated with tetrabutylammonium iodide (TBAI). The bottom Si layer was equipped with prepatterned gold interdigitated electrodes (IDEs) for photocurrent measurement. Further details about device fabrication are reported in SI.

Figure 2 shows the two deposited films analyzed with a scanning electron microscope (SEM). It can be observed in **(a)** how the spin coated QDs (photodetector side) form a dense and homogeneous film thus completely covering the IDEs and providing a very uniform surface morphology. In **(b)** the QD film that would contact the target gas appears to be continuous but rough with several cracks on the film surface as is typical for drop-casting.

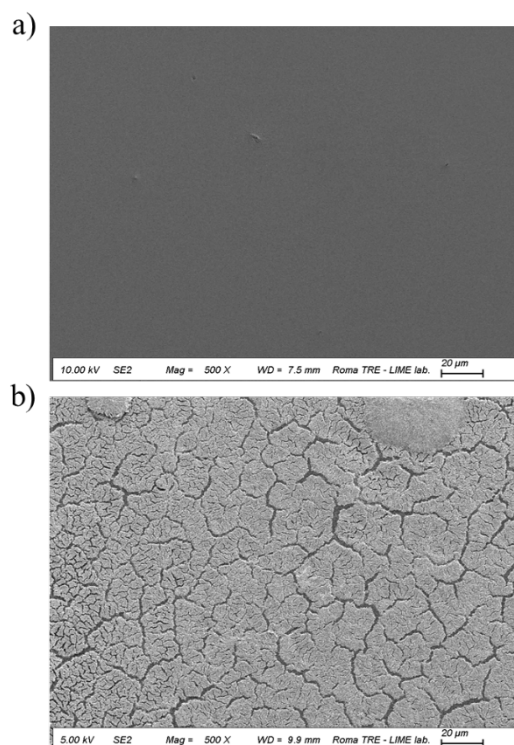


Figure 2. SEM micrographs of the QD films in the a) spin-coated layer (photodetector) and b) drop-casted layer (luminescent probe).

The device performance was assessed by employing nitrobenzene (NB) as a safe representative NAC. The sensing mechanism for di- and tri-nitro substituted toluene analogues passes for the formation of a Meisenheimer complex as well, but the enhanced electron-withdrawing effect exerted by the presence of multiple nitro groups is expected to greatly facilitate complex formation resulting in a sharper system response and a lower detection limit. Details of the experimental set up and its schematic have been reported in the SI. Briefly, the device was kept in a custom-made 3D-printed measurement chamber. A constant flow of ambient air was mixed with the target gas source to obtain different concentrations ranging from 131 ppb to 1.18 ppm at room temperature (20 °C) and 30% relative humidity, using mass flow controllers. The total gas flow rate was fixed at 1000 ml/min. The device was exposed to the target gas sample for 2 min at each gas concentration and the air flow was restored for 2 min. The blue LED illuminating the QD sensing layer was driven with a constant current of 10 mA. A DC voltage of 1 V was applied to the QD photodetector through a Keithley multimeter (Keithley Instrument, USA) and the current was monitored during target gas exposure and release. The gas-sensing performance was evaluated in terms of sensitivity, repeatability, and selectivity. The sensor response (S) reported in this work is defined as:

$$S = \frac{I_a - I_g}{I_a} \times 100 \quad (1)$$

where I_g and I_a represent the sensor current in the tested gas and ambient air, respectively. In addition, the response and recovery time were defined as the times required for the sensor current to reach 90% of the final value upon gas exposure and air recovery, respectively.

3. Results and discussion

Figure 3 shows the real-time current change of the proposed device toward 1 ppm NB at 20°C. Initially, the current generated by the TBAI -treated QD photodetector is relatively stable at about 438.0 μ A in air. After the supply of NB gas into the measurement chamber and the resulting PL quenching of the EDA -treated QD film, the current decreases and rapidly reaches a minimum of 428.6 μ A in 2 minutes. After 2 minutes, the NB gas is stopped and fresh air is supplied to the measurement chamber. The sensor current gradually returns to its original position, indicating the full baseline recovery. The current change is about 9.4 μ A, with response and recovery times of 66 s and 83 s, respectively. The sensor noise was calculated using the standard deviation in the sensor current in the baseline before NB exposure. Here 800 data points (corresponding to a 260 s timespan) are shown, and the calculated noise current was 6.62 nA, as shown in the inset in **Fig. 3**.

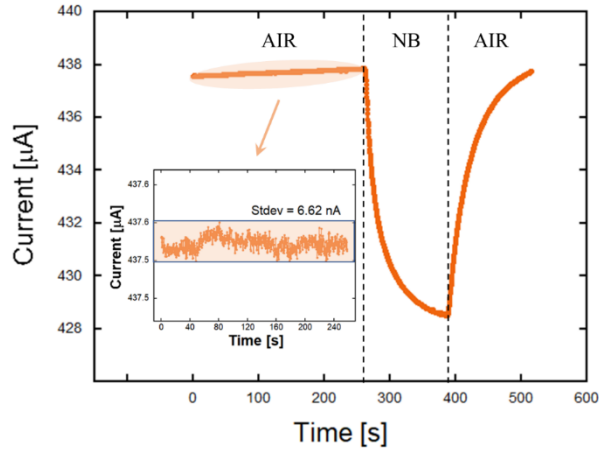


Figure 3. Real-time current change to 1 ppm NB gas. The inset shows the noise current of the baseline.

The effect of increasing the concentration of NB vapors was investigated in the 131 ppb – 1.18 ppm range, at room temperature (**Figure 4(a)**).

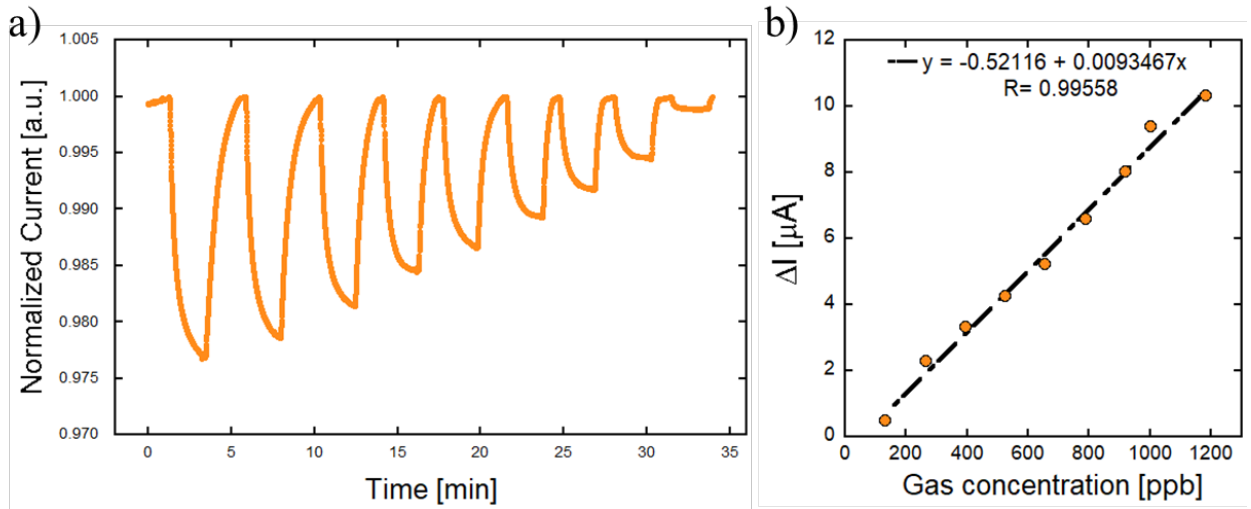


Figure 4. (a) Normalized current curves to different NB concentrations as a function of time. (b) Linear fitting of the device $\Delta I = (I_a - I_g)$ to different NB concentrations in the 131–1180 ppb range.

The sensor response S calculated according to **Eq. 1** was found to be proportional to NB concentration. In addition, the device exhibited a reversible behavior as it recovered to its original baseline current after the removal of NB vapors, regardless the NB concentration. The current variations ΔI , response and recovery times measured for different NB concentrations are shown in **Table I**.

Concentration [ppb]	ΔI [μA]	Response time [s]	Recovery time [s]
131	0.49	53.4	57.7
262	2.29	56.4	24.9
393	3.34	56.2	33.5
524	4.26	62.7	36.4
655	5.24	68.62	63.5
786	6.6	52.3	52.7

916	8	60.3	59.6
1000	9.4	66	83.3
1180	10	69	121.3

Table I. Measured current variations, response and recovery times at different NB concentrations.

A moderate increase of the response and recovery times with increasing gas concentration was observed.

For the higher NB concentration tested (1.18 ppm), we obtained a response and a recovery time of 69 s and 121 s, respectively. The current variations obtained from the data in **Figure 4(a)** were plotted as a function of NB gas concentration in **Figure 4(b)** and a linear fit was performed. The corresponding sensitivity is about 9.3 nA/ppb in the whole range. The lowest detectable NB concentration of 131 ppb is associated to limitations of our experimental set up. However, a theoretical detection limit of the sensor can be estimated as the minimum NB concentration for which a variation of the sensor current is three times higher than the noise, according to the following equation [20]:

$$DL = 3 \times \frac{RMS}{slope} \quad (2)$$

where, *RMS* is the root mean square noise, evaluated using the standard deviation over 500 data points acquired in a 160 s time span in the baseline of a current vs time curve, and *slope* is the slope of the linear fit in **Figure 4(b)**. A remarkable detection limit of 2.3 ppb has been obtained.

The repeatability of the measurements was investigated by exposing the sensor to 1 ppm of NB for multiple adsorption-desorption cycles. The dynamic curves are shown in **Figure 5**. The sensor exhibited a good repeatability after 10 testing cycles, as a nearly constant current variation with no significant changes was observed, with an average sensor response of $2.13 \pm 0.05\%$.

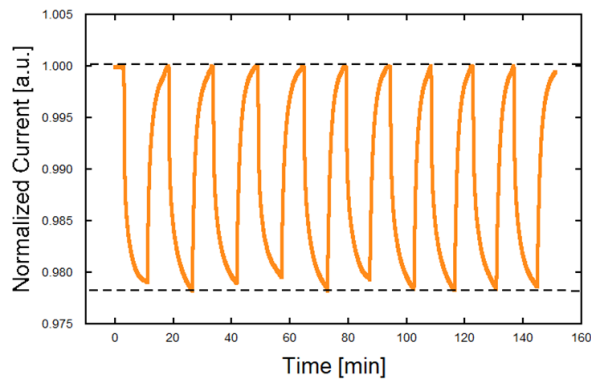


Figure 5. Repetitive cycles of current variation towards 1 ppm NB.

Long-term stability is an important feature to assess the reliability of gas sensors. Hence, we performed measurements of the sensor response towards 1 ppm NB over a period of 70 days (see SI). The response remained basically stable with a mean value $\pm$ standard deviation of $2.08 \pm 0.09\%$, which confirms an excellent long-term stability of the sensor during the complete measurement tenure.

The stability of the device performance with the relative humidity (RH) is another important characteristic of gas sensing devices in practical application. Therefore, the effect of relative humidity on NB sensing performance of the device was measured under different relative humidity conditions up to 40% RH, a practical range of values for indoor applications. The humidification was obtained by the saturation method with a glass bubbler; ambient air, left to flow through a bubble of water for collecting the saturated water vapors, is mixed to ambient air in fixed ratio just to get the desired level

of humidity as measured by a commercial sensor. **Figure 6** displays the change of the sensor current under a relative humidity in the 10–40% range for a fixed 524 ppb NB concentration. The initial sensor baseline decreases as the relative humidity increases but the relative current variation (response to gas inlet) is not significantly affected, as shown in the inset. It can be noted that the sensor always recovers to its initial current.

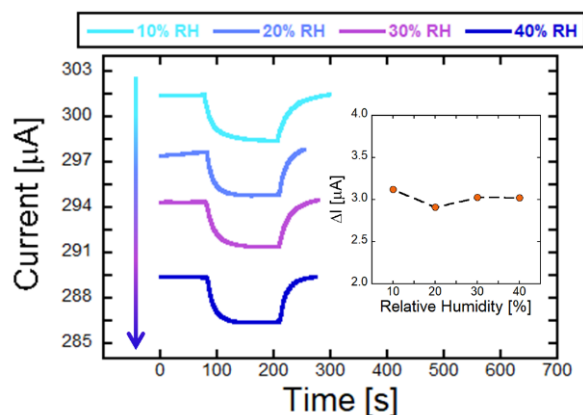


Figure 6. Response curves to 524 ppb NB at different relative humidity at 20 °C.

In order to study the device selectivity to NB, the device was exposed to a fixed 1 ppm of different interfering gases (toluene, nitromethane, xylene and aniline) at room temperature. For this purpose, compounds with different substituents in the aromatic ring have been selected. Nitromethane, which has a strong electron-withdrawing group but is not aromatic, was also tested. The corresponding sensor responses (current variation) are shown in **Figure 7**. The sensor was highly selective towards NB vapors, exhibiting no response to toluene, nitromethane and xylene. In fact, the formation of the Meisenheimer complex, which is responsible for the response of the sensor to the NB, requires the presence of both an aromatic ring and one or more substituents capable of delocalizing the negative charge of the adduct. No other significant aspecific interactions are established between the PbS QDs and the considered gases. It should be noted that the sensor was slightly responsive to aniline, with a current variation of opposite sign with respect to NB. The results demonstrate that the response of the proposed system is quite selective for NB.

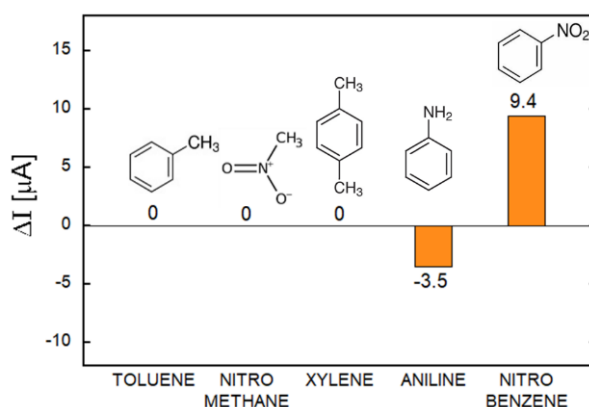


Figure 7. Selectivity of the device to NB and other interference gases at the same concentration of 1 ppm.

Finally, **Table II** shows a comparison between our work and recently published devices for nitroaromatic explosive detection. For each of these, the sensing material, substrate (if present), medium, target analyte, theoretical detection limit, lowest detectable concentration and sensing method were reported. Fluorescent-based sensors, including metal-organic frameworks (MOFs), QDs

and polymer -based sensors, chemiresistive sensors and electrochemical sensors are the three categories considered. Fluorescent-based methods for explosive detection have been extensively investigated in recent years since they accomplish most of the criteria required in field for an effective sensing, such as sensitivity and selectivity [21]. However, these materials often require complicated and long-term synthetic routes and suffer from the limited application to the aqueous medium. To achieve the on-site detection of explosives, most of the fluorescent-based works reported in the table developed a paper sensor based on the common filter paper impregnated with the fluorescent sensing material. Chemiresistors, that change their conductivity in response to a chemical interaction, are perhaps the simplest possible element to build a sensor [22]. They offer clear advantages in terms of ease of fabrication, integration with silicon technology and suitability for vapor detection. However, their response is significantly affected by temperature and humidity. Electrochemical systems for on-site detection of explosives can be high-sensitive, selective, with the advantages of minimal space and power requirements and low-cost instrumentation [23]. However, electrochemical sensors require mobile electrolyte and electrodes can be easily fouled. Conducting polymer coatings can help in this regard at the cost of introducing more complexity to the sensor. Compared to these reports, the proposed approach provides the advantages of compactness, simplicity in the fabrication process, low-cost and a detection limit that is better than or comparable to that of the state-of-the-art values. A further significant observation is that, thanks to the silicon substrate, the device can be easily integrated into a portable and highly efficient detector.

Sensing material (Sensor type)	Substrate	Medium	Target	DL	Lowest detectable concentration	Method	Ref
Fluorescent 8-hydroxyquinoline zinc encapsulated into the pores of Zeolitic imidazole framework-8 (MOFs sensor)	Suspended in ethanolic solution	Liquid	TNT	Colorimetric : 1.2 μ M; Fluorescent: 212 nM	100 ppb	Visible color changes; Fluorescence quenching	[24]
Titanium metal-organic framework nanorods (ZSTU-1) (MOFs sensor)	ZSTU-1 nanorods in ethanol solution	Liquid	PA NB DNT PNP	12.3 μ M (2.8 ppm)	PA 12.1 ppm; NB 61.2 ppm; 2,4-DNT 44.4 ppm; 2,6-DNT 70.1 ppm; PNP 6.9 ppm	Luminescence quenching	[25]
Blue emissive carbon dots in combination with yellow and red emissive CdTe QDs (QD ratiometric sensor array)	Micro centrifuge tube	Aqueous solution	TNT, TNP, DNT	-	5.0 μ mol L ⁻¹	Fluorescence quenching	[26]
Lysine, cysteine, trifluoroacetyl lysine and cysteine modified nanofibrous membrane loaded with Mn ²⁺ -doped ZnS QDs	Nanofibrous Membranes	Vapor	TNT, DNT, PA, NB	-	TNT 4 ppb; DNT 180 ppb; PA 0.0077 ppb; NB 3×10^5 ppb	Fluorescence quenching	[27]

(QD multichannel fluorescent sensor array)							
Fluorescent nanoporous polymers, HPP-2 (Fluorescent polymer sensor)	Filter paper	Solution, solid and vapor	NT, DNT, TNT, NP, DNP, PA	NT 57.3 ppb; DNT 43.39; TNT 4.62; NP 63.02; DNP 40.84; PA 4.43	NT, DNT, NP and DNP 10^{-4} mol/L; TNT and PA 10^{-5} mol/L	Fluorescence quenching	[28]
Alanine based dansyl tagged copolymer P(MMA-co-Dansyl-Ala-HEMA) (DCP) (Fluorescent polymer sensor)	Thin film on a microbiological slide; DCP in THF solution	Solution, vapor	TNT TNP DNT	TNT 9.1 μ M (2.07 ppm); TNP 3.7 μ M (0.85 ppm); DNT 10.1 μ M (1.84 ppm)	TNT 29 μ M; TNP 14 μ M; DNT 36 μ M	Fluorescence quenching	[29]
Organic molecule (fluorescent probe) TPMCN	Filter paper	Vapor	NB	0.16 ppm	10 ppm	Fluorescence quenching	[30]
Flower-like polyaniline (Chemiresistive sensor)	Filter paper	Vapor	TNT, PA, DNT	TNT 0.094 ppb; PA 0.029 ppb; DNT 15.04 ppb	TNT 1.82 ppb; PA 0.19 ppb; DNT 80 ppb	Electric current variation	[31]
Polyvinyl Alcohol/Polypyrrole/ Molecularly Imprinted Polymer Nanocomposite (Chemiresistive sensor)	Copper IDEs on silicon wafer	Vapor	DNT	400 ppb	-	Change in resistance	[32]
Boron-doped diamond/graphene nanowall electrodes (Electrochemical sensor)	-	Aqueous solution	TNT	73 ppb	240 ppb (1.07×10^{-6} M)	Reduction peak currents (differential pulse voltammetry)	[33]
Gold Nanoparticles/Poly(Carbazole-Aniline) Film-Modified Glassy Carbon sensor electrodes (Electrochemical sensor)	-	Aqueous solution	TNT DNT	TNT 25 μ g L ⁻¹ ; DNT 30 μ g L ⁻¹	TNT 83 μ g L ⁻¹ ; DNT 100 μ g L ⁻¹	Reduction peak currents (square wave voltammetry)	[34]
PbS QDs (Combination of a QD photoluminescent probe and a QD photodetector)	Gold IDEs on silicon wafer	Vapor	NB	2 ppb	131 ppb	Fluorescence quenching + Current variation	This work

Table II. Examples of recent literature articles on sensors for the detection of nitroaromatic explosives.

4. Conclusions

We reported on a simple, sensitive, compact and portable optical sensor for the detection of NB in air, based on an innovative device architecture employing modified PbS QDs with a dual function. The sensor is based on a silicon substrate with both surfaces coated with QD films. On one side, the functionalization of QD film using EDA provided the sensitivity for NB detection. Indeed, NB molecules interact with the modified QD film causing a PL quenching that is detected by means of the QD photodetector fabricated on the other side of the silicon substrate. The proposed device was responsive towards a wide range of NB concentrations (131 ppb – 1.18 ppm) with a calculated detection limit down to a few ppb. Also, the device was found to be selective towards NB gas, with excellent repeatability in response to multiple cycles of the same NB concentration. The sensor presented long-term stability over a measurement period of 70 days and it exhibited a stable response for various humidity conditions. These results suggest that the proposed architecture is very promising for practical applications in the field of gas sensors.

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References

- [1] M. F. Frasco and N. Chaniotakis, “Semiconductor quantum dots in chemical sensors and biosensors,” *Sensors*, vol. 9, no. 9, pp. 7266–7286, 2009, doi: 10.3390/s90907266.
- [2] J. Y. Kim, O. Voznyy, D. Zhitomirsky, and E. H. Sargent, “25th anniversary article: Colloidal quantum dot materials and devices: A quarter-century of advances,” *Adv. Mater.*, vol. 25, no. 36, pp. 4986–5010, 2013, doi: 10.1002/adma.201301947.
- [3] A. P. Litvin, I. V. Martynenko, F. Purcell-Milton, A. V. Baranov, A. V. Fedorov, and Y. K. Gun’Ko, “Colloidal quantum dots for optoelectronics,” *J. Mater. Chem. A*, vol. 5, no. 26, pp. 13252–13275, 2017, doi: 10.1039/c7ta02076g.
- [4] A. De Iacovo, C. Venettacci, L. Colace, L. Scopa, and S. Foglia, “High Responsivity Fire Detectors Based on PbS Colloidal Quantum Dot Photoconductors,” *IEEE Photonics Technol. Lett.*, vol. 29, no. 9, pp. 703–706, 2017, doi: 10.1109/LPT.2017.2680741.
- [5] X. Gong *et al.*, “Highly efficient quantum dot near-infrared light-emitting diodes,” *Nat. Photonics*, vol. 10, no. 4, pp. 253–257, 2016, doi: 10.1038/nphoton.2016.11.
- [6] V. Galstyan, “‘Quantum dots: Perspectives in next-generation chemical gas sensors’ – A review,” *Anal. Chim. Acta*, vol. 1152, p. 238192, 2021, doi: 10.1016/j.aca.2020.12.067.
- [7] M. Ganesan and P. Nagaraaj, “Quantum dots as nanosensors for detection of toxics: A literature review,” *Anal. Methods*, vol. 12, no. 35, pp. 4254–4275, 2020, doi: 10.1039/d0ay01293a.
- [8] F. Mitri, A. De Iacovo, M. De Luca, A. Pecora, and L. Colace, “Lead sulphide colloidal quantum dots for room temperature NO₂ gas sensors,” *Sci. Rep.*, vol. 10, no. 1, pp. 1–9, 2020, doi: 10.1038/s41598-020-69478-x.
- [9] C. H. R. J. D. Schiffman, and R. G. Balakrishna, “Quantum dots as fluorescent probes: Synthesis, surface chemistry, energy transfer mechanisms, and applications,” *Sensors Actuators, B Chem.*, vol. 258, pp. 1191–1214, 2018, doi: 10.1016/j.snb.2017.11.189.
- [10] C. Giansante, “Library Design of Ligands at the Surface of Colloidal Nanocrystals,” *Acc. Chem. Res.*, vol. 53, no. 8, pp. 1458–1467, 2020, doi: 10.1021/acs.accounts.0c00204.
- [11] X. Sun, Y. Wang, and Y. Lei, “Fluorescence based explosive detection: From mechanisms to sensory materials,” *Chem. Soc. Rev.*, vol. 44, no. 22, pp. 8019–8061, 2015, doi: 10.1039/c5cs00496a.

- [12] T. Komikawa, M. Tanaka, A. Tamang, S. D. Evans, K. Critchley, and M. Okochi, "Peptide-Functionalized Quantum Dots for Rapid Label-Free Sensing of 2,4,6-Trinitrotoluene," *Bioconjug. Chem.*, vol. 31, no. 5, pp. 1400–1407, 2020, doi: 10.1021/acs.bioconjchem.0c00117.
- [13] Z. M. S. H. Khan, S. Saifi, Shumaila, Z. Aslam, S. A. Khan, and M. Zulfeqar, "A facile one step hydrothermal synthesis of carbon quantum dots for label-free fluorescence sensing approach to detect picric acid in aqueous solution," *J. Photochem. Photobiol. A Chem.*, vol. 388, p. 112201, 2020, doi: 10.1016/j.jphotochem.2019.112201.
- [14] S. Kadian and G. Manik, "A highly sensitive and selective detection of picric acid using fluorescent sulfur-doped graphene quantum dots," *Luminescence*, vol. 35, no. 5, pp. 763–772, 2020, doi: 10.1002/bio.3782.
- [15] P. Sharma and M. S. Mehata, "Colloidal MoS₂ quantum dots based optical sensor for detection of 2,4,6-TNP explosive in an aqueous medium," *Opt. Mater. (Amst.)*, vol. 100, no. October 2019, p. 109646, 2020, doi: 10.1016/j.optmat.2019.109646.
- [16] W. Gong, H. Li, X. Gong, Z. Zhang, and Z. Lu, "Fabrication of amine functionalized CdSe@SiO₂ nanoparticles as fluorescence nanosensor for highly selective and sensitive detection of picric acid," *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, vol. 233, p. 118221, 2020, doi: 10.1016/j.saa.2020.118221.
- [17] F. Mitri *et al.*, "A compact optical sensor for explosive detection based on NIR luminescent quantum dots," *Appl. Phys. Lett.*, vol. 119, no. 4, 2021, doi: 10.1063/5.0060400.
- [18] S. Xu *et al.*, "Dummy molecularly imprinted polymers-capped CdTe quantum dots for the fluorescent sensing of 2,4,6-trinitrotoluene," *ACS Appl. Mater. Interfaces*, vol. 5, no. 16, pp. 8146–8154, 2013, doi: 10.1021/am4022076.
- [19] C. Giansante, "Surface Chemistry Control of Colloidal Quantum Dot Band Gap," *J. Phys. Chem. C*, vol. 122, no. 31, pp. 18110–18116, 2018, doi: 10.1021/acs.jpcc.8b05124.
- [20] H. Liu *et al.*, "Enhancement of hydrogen sulfide gas sensing of PbS colloidal quantum dots by remote doping through ligand exchange," *Sensors Actuators, B Chem.*, vol. 212, no. 3, pp. 434–439, 2015, doi: 10.1016/j.snb.2015.02.047.
- [21] L. M. Martelo, L. F. Marques, H. D. Burrows, and M. N. Berberan-Santos, "Explosives Detection: From Sensing to Response," pp. 293–320, 2019, doi: 10.1007/4243_2019_9.
- [22] T. M. Swager, "Sensor Technologies Empowered by Materials and Molecular Innovations," *Angew. Chemie - Int. Ed.*, vol. 57, no. 16, pp. 4248–4257, 2018, doi: 10.1002/anie.201711611.
- [23] H. A. Yu, D. A. DeTata, S. W. Lewis, and D. S. Silvester, "Recent developments in the electrochemical detection of explosives: Towards field-deployable devices for forensic science," *TrAC - Trends Anal. Chem.*, vol. 97, pp. 374–384, 2017, doi: 10.1016/j.trac.2017.10.007.
- [24] O. Abuzalat, D. Wong, S. S. Park, and S. Kim, "Highly selective and sensitive fluorescent zeolitic imidazole frameworks sensor for nitroaromatic explosive detection," *Nanoscale*, vol. 12, no. 25, pp. 13523–13530, 2020, doi: 10.1039/d0nr01653e.
- [25] F. Zhong, C. Li, Y. Xie, H. Xu, and J. Gao, "Titanium metal-organic framework nanorods for highly sensitive nitroaromatic explosives detection and nanomolar sensing of Fe³⁺," *J. Solid State Chem.*, vol. 278, no. July, p. 120892, 2019, doi: 10.1016/j.jssc.2019.07.053.
- [26] F. Ghasemi and M. R. Hormozi-Nezhad, "Determination and identification of nitroaromatic explosives by a double-emitter sensor array," *Talanta*, vol. 201, no. April, pp. 230–236, 2019, doi: 10.1016/j.talanta.2019.04.012.
- [27] Z. Wu *et al.*, "Multichannel discriminative detection of explosive vapors with an array of nanofibrous membranes loaded with quantum dots," *Sensors (Switzerland)*, vol. 17, no. 11, 2017, doi: 10.3390/s17112676.
- [28] R. Sun, X. Huo, H. Lu, S. Feng, D. Wang, and H. Liu, "Recyclable fluorescent paper sensor for visual detection of nitroaromatic explosives," *Sensors Actuators, B Chem.*, vol. 265, pp. 476–487, 2018, doi: 10.1016/j.snb.2018.03.072.
- [29] V. Kumar, B. Maiti, M. K. Chini, P. De, and S. Satapathi, "Multimodal Fluorescent Polymer Sensor for Highly Sensitive Detection of Nitroaromatics," *Sci. Rep.*, vol. 9, no. 1, pp. 1–10, 2019, doi: 10.1038/s41598-019-43836-w.

- [30] Z. Cheng *et al.*, “A new strategy for selective fluorescence detection of benzaldehyde and nitrobenzene,” *Microchem. J.*, vol. 172, no. PB, p. 106896, 2022, doi: 10.1016/j.microc.2021.106896.
- [31] W. Zhang *et al.*, “Flexible chemiresistive sensor of polyaniline coated filter paper prepared by spraying for fast and non-contact detection of nitroaromatic explosives,” *Sensors Actuators, B Chem.*, vol. 304, p. 127233, 2020, doi: 10.1016/j.snb.2019.127233.
- [32] M. F. Koudehi and S. M. Pourmortazavi, “Polyvinyl Alcohol/Polypyrrole/Molecularly Imprinted Polymer Nanocomposite as Highly Selective Chemiresistor Sensor for 2,4-DNT Vapor Recognition,” *Electroanalysis*, vol. 30, no. 10, pp. 2302–2310, 2018, doi: 10.1002/elan.201700751.
- [33] A. Dettlaff *et al.*, “Electrochemical determination of nitroaromatic explosives at boron-doped diamond/graphene nanowall electrodes: 2,4,6-trinitrotoluene and 2,4,6-trinitroanisole in liquid effluents,” *J. Hazard. Mater.*, vol. 387, no. November 2019, p. 121672, 2020, doi: 10.1016/j.jhazmat.2019.121672.
- [34] Ş. Sağlam, A. Üzer, E. Erçağ, and R. Apak, “Electrochemical Determination of TNT, DNT, RDX, and HMX with Gold Nanoparticles/Poly(Carbazole-Aniline) Film-Modified Glassy Carbon Sensor Electrodes Imprinted for Molecular Recognition of Nitroaromatics and Nitramines,” *Anal. Chem.*, vol. 90, no. 12, pp. 7364–7370, 2018, doi: 10.1021/acs.analchem.8b00715.