

# Solid-state Photoluminescent Quantum Dots for Explosive Detection

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**Abstract:** Quantum dots are an emerging class of photoluminescent nanomaterials with peculiar properties arising from their nanometric size that allows the occurrence of strong quantum confinement effect. In recent years, these zero-dimensional semiconductor nanoparticles have been attracting increasing attention as luminescent probe for optical sensing applications. However, to date, almost all quantum dots- based sensors reported in literature exploit fluorescence from solutions whereas the development of solid-state photoluminescent quantum dots still remains a challenge. In this paper, we demonstrate the feasibility of exploiting the solid-state photoluminescence of PbS quantum dots deposited on a silicon substrate for vapor explosive detection, a worrying priority for homeland security and counter-terrorism applications.

## 1 INTRODUCTION

Explosive-based terrorism is an ongoing challenge to governments and societies worldwide due to the relative ease by which these weapons can be constructed and deployed (“Trace Chem. Sens. Explos.,” 2006). Organizations such as JIDO (US Department of Defense Joint Improvised-Threat Defeat Organization), AOAV (Action on Armed Violence), and CPOST (Chicago Project on Security & Threats) all collect detailed and updated statistics regarding their use and devastating effects (Hotchkiss, 2018). The alarming data that emerged, together with the increasing government regulations for enhanced security screening, is driving the global explosive trace detection market growth.

Common trace detection systems rely on spectroscopic approaches and allow for sensitive, selective, and fast detection. Such high performance,

however, comes at the cost of expensive and cumbersome equipment that can often be operated only by trained personnel. Moreover, the detection occurs through the analysis of specifically prepared specimen, while large environments cannot be efficiently monitored. Recently, fluorescent gas sensors have been proposed for the realization of nitroaromatic compounds (NAC) detectors that can overcome such limitations (Ma et al., 2015). Among them, sensors based on quantum dots (QD) have been realized exploiting their peculiar optical and electronic properties. These are semiconductor nanoparticles suspended in the solution phase. QD were first developed and studied as a promising material for photodetectors since they are easy to synthesize and their optical properties can be easily tuned via chemical approaches (Venettacci et al., 2019). As all nanocrystals, they are particularly suitable for gas sensing applications thanks to their large surface-to-volume ratio that allows outstanding

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reactivity even at room temperature (Galstyan, 2021; Mitri et al., 2020). Recently, we exploited the peculiar characteristics of PbS QD to demonstrate a chemiresistive device for NAC detection (Mitri et al., 2021). Due to their nanometric size, QD show strong quantum confinement effect thus exhibiting interesting optical properties such as intense, narrow and size-tunable luminescence. In addition, the QD's surface can be sensitized with a chemical approach, allowing selective reaction with specific analyte molecules. Several authors already demonstrated that amine treated-QD can be effectively employed as luminescent probes for the selective detection of NAC, but the proposed devices cannot detect these compounds in the vapor phase and still need to be operated with specific lab equipment (Akhgari et al., 2015). To date, almost all reported QD-based devices have involved fluorescence from solutions (Xu et al., 2020).

Herein, we demonstrate the proof-of-concept on employing the solid-state photoluminescence (PL) quenching of PbS QD deposited on a silicon substrate, as a fluorescent sensing platform for direct detection of nitrobenzene vapor (NB, as a representative NAC). We also demonstrate that the evaluation of the PL quenching can be easily obtained with low-cost and low-power electronics mounted in a compact optical chamber. The proposed device operates in air, at room temperature, and can detect NB with a concentration as low as 445 ppb.

## 2 DEVICE FABRICATION

### 2.1 QD Synthesis

PbS QD were synthesized in a three-neck flask connected to a standard Schlenk line under oxygen- and water-free conditions. PbO (450 mg), oleic acid (9.0 g), and 1-octadecene (3.0 g) were mixed at 80°C. The mixture was then heated at 100°C until it became completely transparent. The temperature was raised to 110°C and 210 $\mu$ L of bis(trimethyl)sulfide diluted in 2mL of 1-octadecene were rapidly injected in the solution. Heating was immediately stopped, and the solution cooled down to room temperature. The resulting QD were precipitated, purified, and dispersed in toluene with a 0.5 mM concentration. The size of the QD (4.7 nm) was determined through optical absorption measurements.

### 2.2 QD Deposition

Thermally oxidized silicon wafers were cut to a typical size of 10 $\times$ 10mm and were cleaned in a NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub> (1:1) solution. After being cleaned, the substrates were rinsed with deionized water and dried with dry air before they were used. Devices were fabricated with a layer-by-layer spin-coating deposition process. Specifically, a drop of the QD solution was deposited onto the substrate and spun at 3000 rpm for 30 s. Then, a drop of ethylenediamine (EDA) solution in acetonitrile (10% vol.) was deposited on the substrate and left reacting for 30 s, before spinning at 3000 rpm for 30 s. Finally, the substrate was washed with pure ethanol. The previous steps were repeated for 10 times. Figure 1 schematically shows the fabrication process.

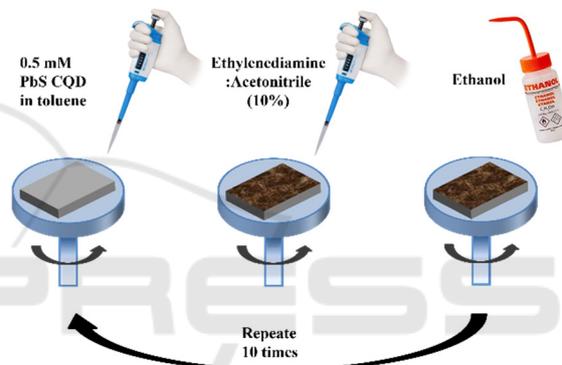


Figure 1: Schematic representation of the device fabrication process.

The resulting QD film was 200 nm thick. The deposited film was analysed with a scanning electron microscope (SEM). Figure 2 shows a representative SEM micrograph. The film appears uniform in thickness, with several cracks and voids. Such morphology may increase the total surface of the QD film, thus allowing for a more efficient interaction with the NB gas. We characterized the as-deposited film in terms of PL spectrum. The PL was measured exciting the film with a 532 nm laser source and analysing its emission spectrum by means of an IR spectrometer (Horiba iHR320) equipped with an extended InGaAs detector and a 600 lines/mm grating. Several PL spectra were acquired varying the temperature of the film between -10/+50°C and the laser power between 0.2/3mW. The resulting spectra did not show significant variations in terms of central wavelength, while the PL intensity was proportional to the pump power over the whole measurement range. Figure 3 shows a typical PL spectrum of the QD as deposited on the silicon substrate.

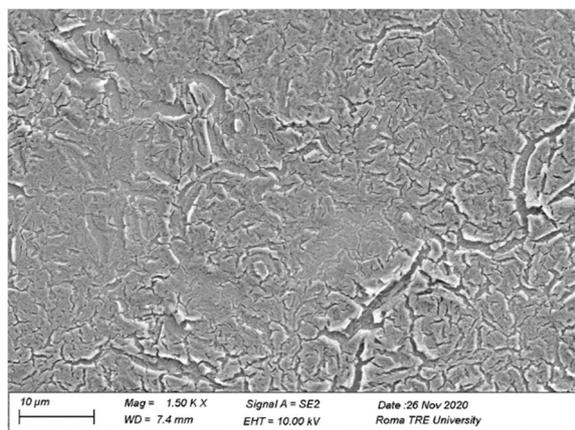


Figure 2: SEM micrograph of the QD film onto the silicon substrate.

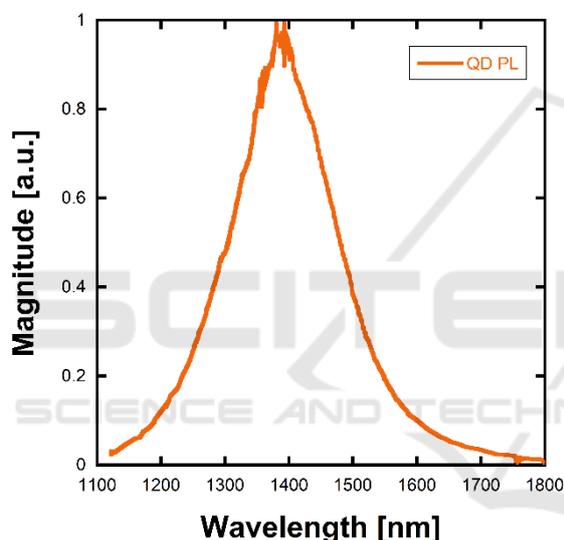


Figure 3: Solid-state QD PL spectrum.

### 3 SET-UP AND MEASUREMENT CHAMBER

The device response to NB gas was characterized with a custom measurement set-up. The device was kept in a closed 3D-printed measurement chamber, with in-let and out-let connectors. Ambient air was fluxed through the container. A closed glass container was filled with a small amount of NB and left settling for 1 hour to allow NB gas to reach the equilibrium vapor concentration. A couple of manual valves allowed the ambient air to be fluxed through the NB-filled container before entering the measurement chamber at a fixed flowrate of 800 mL/min. NB

concentration was varied by heating the glass container with a water bath. The 10 mL-volume measurement chamber contained the QD-coated silicon substrate, a germanium photodiode (PD) and a blue LED. The device was illuminated through the blue LED modulated by means of a 520 Hz, 0.5 Vrms sine oscillator whose mean value could be modulated through a dc offset. The Ge PD was placed directly below the device in order to detect the QD's fluorescence intensity by generating a proportional photocurrent then converted to voltage through a 10 kV/A transimpedance amplifier (Thorlabs, AMP120). Figure 4(a) shows the device's operating scheme. The corresponding output was demodulated by a lock-in amplifier and data were transferred to a personal computer. As shown in Figure 4(b), the blue LED (emission peak at  $\lambda=465$  nm) emits within the silicon substrate's low-transmittivity band whereas QD's PL (NIR PL peak at  $\lambda=1400$  nm) falls within the high-transmittivity band and the Ge photodetector spectral response. In this way, since the Ge PD is completely covered by the silicon substrate, just the NIR radiation reaches the PD that, in turn, generates a photocurrent proportional to the PL intensity. Temperature and relative humidity (RH) were monitored during the measurements and kept constant at 20°C, 30% RH through room-level air conditioning.

### 4 DEVICE CHARACTERIZATION

Figure 5 shows a typical signal measured during a complete 1.9 ppm NB gas release and purge cycle. The device showed complete baseline recovery after NB gas was purged from the measurement chamber. The maximum sensor response was obtained after 10 minutes since gas release. The amplitude of the photovoltage (PV) varied by 9.7% after 10 minutes since gas release. The phase angle showed the same behaviour of the amplitude with a decrease during NB exposure.

The measurements were repeated for different NB concentrations ranging from 445 ppb to 15.9 ppm. Figure 6 shows the corresponding real-time normalized PV amplitude change upon these increasing concentrations. A nonlinear behaviour is clearly observed, as the sensor response reaches a saturation plateau for NB concentrations higher than 5 ppm.

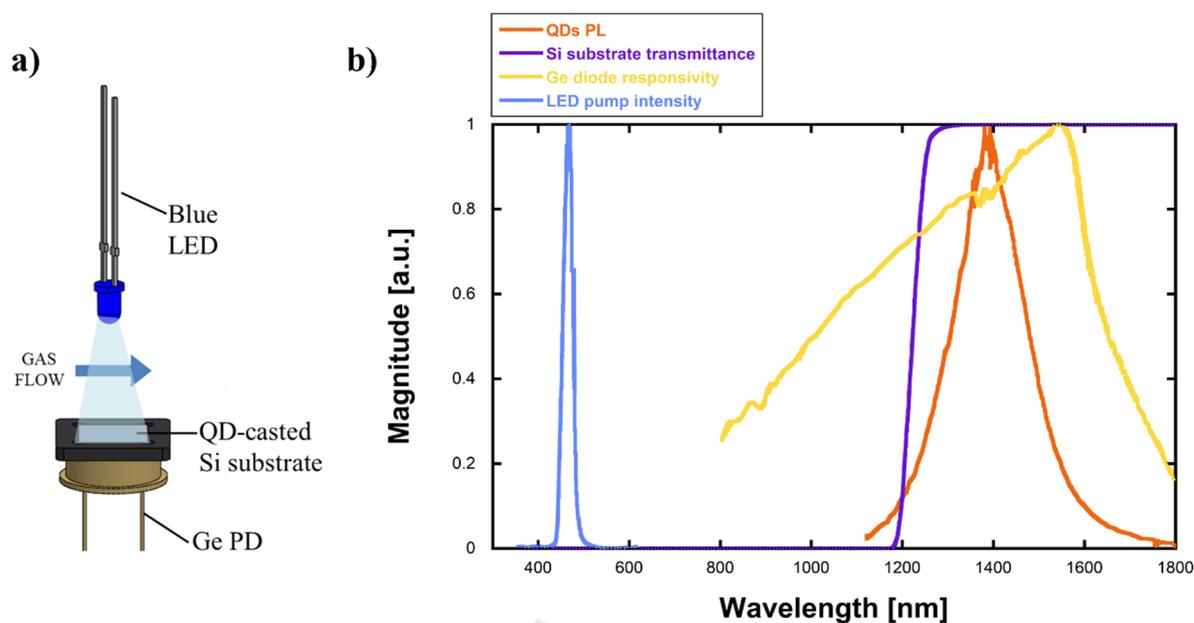


Figure 4: a) Schematic of the optical arrangement; b) QD-film PL spectrum, Si substrate's transmission, Ge diode's responsivity, and LED pump emission spectrum. All curves are normalized to their maximum.

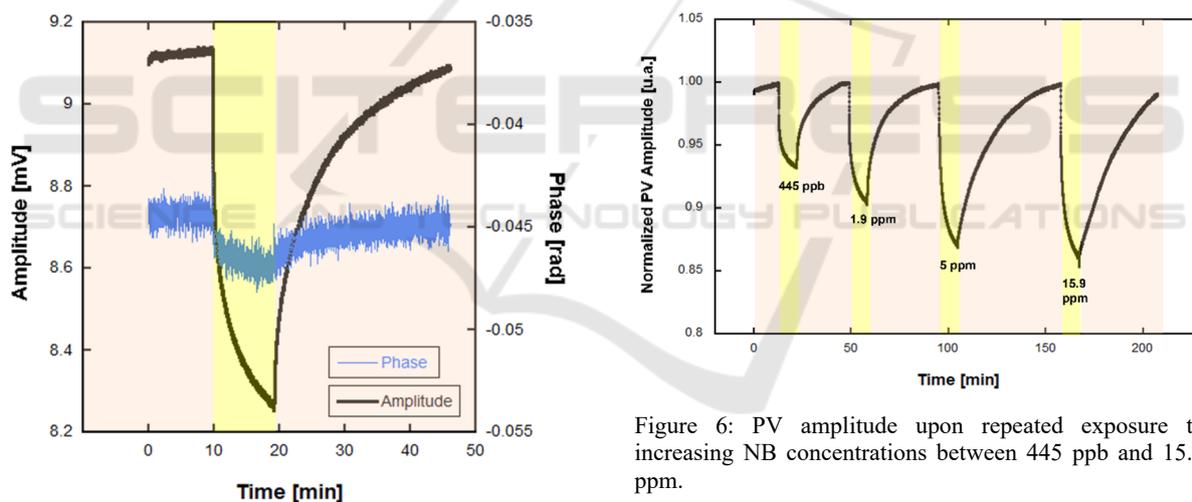


Figure 5: Amplitude and phase angle of the photovoltage upon sensor exposure to 1.9ppm of NB.

To investigate whether the system sensitivity may depend on PL emission intensity, a study varying the mean intensity of LED was performed, as reported in Figure 7. The PL quenching showed a weak dependence on the LED pump intensity. An optimal value of  $5.14 \text{ mW/cm}^2$  was identified. Environmental conditions (temperature and RH) were kept stable during all the measurements; however, given the aforementioned stability of the PL signal over a wide temperature range, we expect that the device can be effectively operated in environments, as well.

Figure 6: PV amplitude upon repeated exposure to increasing NB concentrations between 445 ppb and 15.9 ppm.

Concerning the sensing mechanism, amine-treated QD have been already employed for sensing NAC, assuming an electronic interaction between the negatively charged amino-groups and the electron-poor benzenic ring of the NB molecule, leading to the formation of Meisenheimer complexes, as shown in Figure 8 (Tian et al., 2017). Thus, the amine to NB charge-transfer, with the resonating negative charge stabilized by the withdrawing nitro group ( $-\text{NO}_2$ ), could be responsible for the significant QD PL quenching observed in the presence of the target gas.

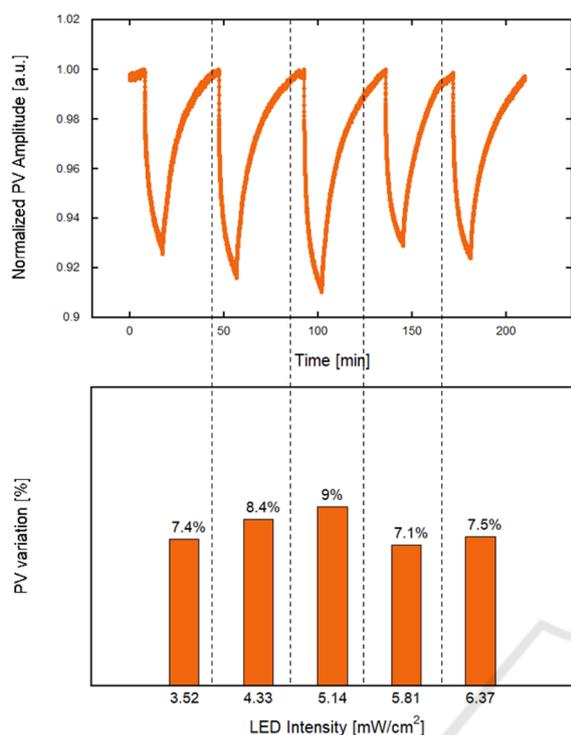


Figure 7: PV amplitude towards NB (1.9 ppm) varying LED intensity.

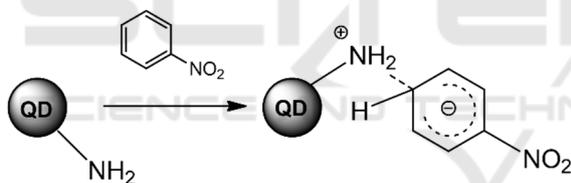


Figure 8: Schematic of the Meisenheimer-like amine-NB complex.

## 5 CONCLUSIONS

In this paper we demonstrated the feasibility of exploiting solid-state PL PbS QD as luminescent device for explosive vapor detection. The device showed good sensitivity and could detect NB vapor at room temperature in ambient air. The lowest measured NB concentration was 445 ppb, corresponding to a sensor response  $S = 4.4\%$  after 60 seconds exposure ( $S = 6.8\%$  after 10 minutes). The integration of QD luminescent probes into an appropriate solid support, a silicon chip, is an important step towards further device optimization into a portable, miniaturized, and low-cost device for the detection of explosives in strategic and sensitive environments.

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