



Abstract Cheap, Tunable and Versatile Nanoparticles for Explosive Detection: Quantum Dots [†]

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Abstract: In recent years, fluorescent probes based on quantum dots have become a popular tool for explosive detection. However, despite their high sensitivity, these probes still require lab-based instrumentation and procedures that are difficult to be converted into a small, low-power system. Furthermore, they are hardly applied to the detection of vapor-phase explosives, being limited to water samples. Herein, we propose two alternative ways of employing quantum dots as a sensing material to build simple devices for vapor explosive detection. First, we report on a compact optical system where a solid-state QD photoluminescent probe is successfully integrated with a QD photodetector on the same silicon chip. Therefore, a high-performance chemiresistive sensor whose electrical resistance changes proportionally to the target gas concentration is proposed.

Keywords: quantum dots; explosive detection; photoluminescent probe; chemiresistive sensor

1. Introduction

The application of QDs has spread to include photoluminescent (PL) probes for sensing applications, including explosive detection, thanks to their unique physical and chemical properties, resulting in a large body of literature on the field. Nevertheless, most QD PL probes are used in the laboratory environment and are operated by trained personnel. To enable on-site detection in real environments, it is necessary to develop portable lab-on-chip devices that can be easily operated in a standalone mode without the need for specific instrumentation. Some progress has been made by immobilizing QDs on solid supports, including polymeric matrixes, xerogels, and filter papers. Nevertheless, very few data are available for explosive detection in the vapor phase. Recently, our group developed an optical sensor that exploits the solid-state PL of EDA-treated PbS QDs cast on a silicon substrate for nitroaromatic compound (NAC) vapor detection [1]. The deposition of the QDs on a silicon substrate assures the compatibility of the sensing chip with complementary metal-oxide-semiconductor (CMOS) technologies for integrated multiplexing and signal processing. We also demonstrated that the evaluation of the PL quenching could be easily obtained with low-cost and low-power electronics integrated with the probe. Starting from this promising result, we now report on an optical system based on the integration of a solid-state QD PL probe with a QD photodetector on the same silicon chip [2]. We also propose a QD chemiresistive sensor for vapor explosive detection [3].

2. Materials and Methods

A dispersion of colloidal PbS QDs (4.7 nm diameter) in toluene was employed for device fabrication. The deposition substrate consisted of a Si/SiO2 chip with pre-patterned gold interdigitated electrodes. The devices were fabricated with layer-by-layer deposition techniques (spin-coating, drop-casting) combined with an in situ solid-state ligand exchange process to properly functionalize the QD surfaces. In the case of the optical



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). system, the QDs were also deposited on the back face of the substrate, where they were employed as a PL probe operating in air. Device performance was assessed by employing nitrobenzene (NB) as a representative NAC.

3. Discussion

3.1. Optical System

The device architecture basically consists of a silicon substrate with both surfaces provided with a QD film, as shown in Figure 1a. The upper QD layer, suitably functionalized with EDA, acts as a PL probe, pumped by a pulsed blue LED. During target gas exposure, NB molecules bind to the surface of the modified QD film through a donor–acceptor interaction causing PL quenching that is simply detected by means of the QD photodetector fabricated on the other side of the silicon substrate. Extremely low NB concentrations (down to 0.1 ppm) are detected, with a theoretical detection limit estimated to be as low as 2 ppb. The device is found to be highly selective towards NB gas and it exhibits a stable response for various humidity conditions. The results are repeatable and no ageing effect is observed over a 70-day period.



Figure 1. (a) Scheme of the optical system architecture; (b) linear fitting of the optical system (blue dots) and chemiresistive sensor (red dots). $\Delta I = (Ia - Ig)$ for different NB concentrations.

3.2. Chemiresistive Sensor

This work demonstrates that the change in conductivity of an EDA-capped PbS QD sensor can be effectively used for NB detection in air. The sensor exhibits very large sensitivity in terms of both the lowest measured (65 ppb) and lowest estimated (2 ppb) NB concentrations. Figure 1b provides a plot of the sensor response vs. NB concentration of the two sensors for different concentrations.

4. Patents

The QD chemiresistive sensor was granted a patent titled "Dispositivo per la rilevazione di esplosivi" (N. 10202000026729, filed in November 2020).

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