Available Online: 18 July 2025 DOI: 10.54254/2977-3903/2025.25322

An overview of PbS semiconductor quantum dot-based sensors

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Abstract. With the extensive application of sensor technology in industrial, medical, environmental monitoring and other fields, traditional sensors are difficult to meet the requirements in terms of sensitivity, response speed and other aspects due to material limitations. Therefore, the development of new sensor technology has become an urgent task. Quantum Dots (QDs), as Zero-Dimensional (0D) nano-semiconductor materials, demonstrate significant potential in sensing applications due to their unique properties, including the quantum confinement effect. Among them, PbS Semiconductor Quantum Dots (PbS QDs) exhibit particularly outstanding performance. This paper focuses on PbS QD-based sensors. Based on their characteristics, such as quantum confinement and high specific surface area, it systematically elaborates on preparation methods and performance advantages. Combining application cases across multiple domains, it analyzes the principles and progress of PbS QDs in biosensors, photoelectric sensors, and others. Although PbS quantum dots offer numerous advantages in sensors, they suffer from drawbacks such as poor environmental stability and lattice mismatch in heterojunctions. Future research can address these issues through strategies like core-shell structure design and hybridization with two-dimensional materials. It reveals technical challenges, forecasts industrialization directions, and highlights their potential to break through traditional bottlenecks and enhance detection performance.

Keywords: semiconductor quantum dots, Sensors, PbS quantum dots, Nanomaterials

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1. Introduction

With the rapid advancement of science and technology, sensor technology has also developed rapidly. The use of sensors has permeated almost every field of modern society, including industry, consumer electronics, healthcare, and environmental monitoring. Traditional sensors, constrained by material issues, struggle to meet the increasingly complex demands in terms of sensitivity, response speed, size, and integration. Developing new sensor technologies is urgent.

Quantum dots, as a type of zero-dimensional nano-semiconductor material, have found widespread application in the field of sensors due to their unique optical and electrical properties. The size-dependent quantum confinement effect allows effective tuning of the QD bandgap structure, enabling responses to optical and electrical signals. PbS semiconductor quantum dots, as an excellent QD material, are increasingly favored due to their superior performance.

This article mainly focuses on the applications, technological progress, challenges, and future development directions of PbS semiconductor quantum dots in areas such as biosensors, photoelectric sensors, gas sensors, and image sensors.

2. Characteristics of PbS semiconductor quantum dots

As an important zero-dimensional nanomaterial, PbS semiconductor quantum dots exhibit unique and excellent physicochemical properties, making them highly promising for sensor applications.

Their core characteristics stem from their nanoscale dimensions and material nature. Firstly, PbS QDs exhibit a significant quantum confinement effect. When the particle size decreases to approach their exciton Bohr radius (approximately 18 nm), carrier motion is spatially confined, causing their energy level structure to transition from a continuous band to discrete energy levels. The most intuitive manifestation of this effect is the tunability of their optical properties, such as a distinct blue shift in their spectrum. This means that by precisely controlling the QD size, their absorption and emission spectral ranges can be flexibly tuned, particularly offering advantages in the Near-Infrared (NIR) region. Secondly, PbS QDs possess an extremely high specific surface area. The large surface area means more surface atoms are exposed; these atoms have lower binding energies and higher reactivity. This not only lowers the material's melting point but, more importantly, greatly enhances its interaction efficiency with the surrounding environment or target analytes, laying the foundation for high-sensitivity sensing. Thirdly, PbS

QDs demonstrate excellent Photoluminescence (PL). They achieve efficient PL even under extremely low light intensity, especially in the NIR spectral region, which is crucial for improving the detection sensitivity and overall energy utilization efficiency of optoelectronic devices. Finally, although PbS QDs themselves are relatively sensitive to environmental factors (like light, oxygen, and moisture), their surface is highly modifiable. Through appropriate surface ligand engineering and modification strategies, their environmental stability can be significantly enhanced, resisting photo-oxidation and hydrolysis/oxidation. Simultaneously, specific functionalities (such as biocompatibility, and selective recognition capability) can be imparted, and their dispersibility improved. Tunable optoelectronic properties, high surface reactivity, efficient NIR luminescence, and a functionalizable surface, these characteristics collectively constitute the core competitiveness of PbS QDs in constructing high-performance, multi-type sensors.

3. Preparation of PbS quantum dot materials

Researchers have been exploring simple synthetic processes for preparing PbS QDs, among which the more mature methods mainly include organic phase synthesis, cation exchange method, pyrolysis method, etc. The corresponding synthetic definitions and characteristics are shown in Table 1.

Table 1. Overview of synthesis methods for PbS quantum dot materials

Method	Synthesis definition/characteristics
Organic synthesis method	Preparation of PbS QDs in an organic solvent system using organic ligands by controlling precursor thermal decomposition and reaction growth, enabling precise size and optical property control.
Cation Exchange	Transformation into PbS QDs by exchanging specific cations in solution with cations in a nanostructure template (containing Pb or S), allowing flexible control over composition and structure.
Pyrolysis	Generation of PbS QDs by thermal decomposition of precursor compounds containing Pb and S elements at a specific temperature.

3.1. Organic phase synthesis

PbS QDs are prepared in an organic solvent system using organic ligands by controlling the thermal decomposition and reaction growth of precursors, enabling precise control over size and optical properties.

At room temperature and pressure, lead halide (PbX_2) and N,N'-Diphenylthiourea (DPTU) are dissolved in DMF to form a precursor solution, which is then injected into toluene containing oleylamine (OLA). OLA serves a dual function: firstly, as a weak base, it deprotonates the PbX_2 [DPTU] complex, releasing active sulfur monomers and gradually forming PbS; secondly, as a dynamic ligand, it controls the nucleation and growth kinetics of the QDs. By adjusting the amount of OLA and the type of lead halide ($PbCl_2$ /Pb Br_2 /Pb I_2), the QD bandgap can be precisely tuned within the range of 750-1050nm. The resulting QDs, after Oleic Acid (OA) ligand exchange, achieve a Photoluminescence Quantum Yield (PLQY) of up to 45% due to the synergistic effect of in-situ halide passivation and OA steric protection. This method can be scaled up to gram quantities (up to 1.92g per batch) with high batch consistency and has been successfully applied in high-performance NIR light-emitting diodes (9.2 mW @ 160 mA) [1].

3.2. Cation exchange method

Using a nanostructure template containing Pb or S, specific cations in solution exchange with cations in the template, transforming it into PbS QDs, allowing flexible control over composition and structure.

First, ZnS nanorods are synthesized as precursors. Subsequently, $PbCl_2$ is dissolved in oleylamine to form a lead precursor solution, which is injected into the ZnS nanorod solution at 80-190℃. During the reaction, the dissolution of ZnS nanorods releases sulfur precursors, creating a high supersaturation environment that triggers the size focusing effect of PbS QDs, resulting in QDs with excellent monodispersity (size distribution as low as 2.9%) and tunable bandgap (0.65-1 eV). This method simultaneously achieves in-situ chloride ion passivation, endowing the QDs with high stability and a "clean" surface. Single-batch yields can reach 102 grams, suitable for infrared solar cell applications [2].

3.3. Pyrolysis method

At a specific temperature, precursor compounds containing Pb and S elements are thermally decomposed, causing them to decompose and react, generating PbS QDs.

First, Oleic Acid (OA) and 1-Octadecene (ODE) are introduced into a Pb Br_2 lead precursor solution. By adjusting the ODE content (0.5-9.5 ml), the QD size is controlled (3.6-5.4 nm), and the Oleylamine (OLA) amount (7.5-20 ml) is optimized to improve monodispersity. A combination of 5.5 ml ODE and 10 ml OLA yields the best monodispersity (absorption peak FWHM of 164 nm). The reaction is terminated by quenching in an ice-water bath. The resulting PbS QDs are passivated via in-situ replacement of surface hydroxyl (OH) groups by PbBr2, significantly reducing defects and extending the photoluminescence lifetime (30.1 ns). This method simplifies traditional processes and has been successfully applied in solar cell devices (efficiency 4.3%), providing efficient and stable QD materials for the photovoltaic field [3].

4. Applications of PbS quantum dots in sensors

4.1. Biosensors

PbS QDs have shown significant achievements in biosensor applications. Sensors utilizing PbS QDs generally feature high sensitivity and a wide detection range, giving biosensors enormous potential in the biomedical field. PbS QDs leverage their quantum tunneling effect and quantum confinement effect, exhibiting great potential in biosensors when conjugated to different biomolecules. Furthermore, PbS QDs can be used in conjunction with various detection techniques to obtain multidimensional information about biomolecules.

Utilizing the photoluminescence effect of PbS QDs, a fiber-optic sensor probe for biomedicine was fabricated, as shown in Figure 1 (a). PbS QDs efficiently absorb 980 nm laser light, converting it into heat, causing the temperature to rise inside a Fabry-Perot (F-P) cavity made of photoresist doped with PbS QDs. The temperature change causes UV-curable adhesive to expand and the optical path length to change, leading to a shift in the interference spectrum. Monitoring the spectral shift allows detection of microfluidic flow velocity. With only a 3℃ rise, a sensitivity of 7.7 pm/(mm/s) is achieved within a flow velocity range of 3.82 mm/s ~ 16.72 mm/s. Such sensors have broad application prospects in areas like blood microcirculation measurement and targeted drug delivery in biomedicine [4].

Zhao et al. established an electrochemical biosensor based on PbS colloidal quantum dots and the unnatural SARS-CoV-2 spike mini-protein receptor LCB using an electrical labeling method [5]. This achieved highly sensitive detection of the SARS-CoV-2 spike mini-protein receptor and related coronavirus biomarkers with a wide detection range (10 pg/ml ~ 1μg/ml). The detection limits were 3.31 pg/ml (4.607 fM under a three-electrode system) and 9.58 fg/ml (0.013 fM for the HEMT device), showing good advantages in biomarker monitoring, laboratory analysis, and in-situ detection.

4.2. Photoelectric sensors

Research shows that introducing photonic structures can significantly improve device light absorption and emission performance. Chen et al. summarized the use of different types of photonic structures, such as diffraction gratings, resonant cavities, plasmonics, and photonic crystals, and discussed in-depth the mechanisms of these structures in device applications [6]: Using diffraction gratings for light scattering and waveguide mode coupling increased the light absorption efficiency of the QD active layer by 3.4 times (experimentally verified in PbS QD solar cells achieving 86% NIR absorption); Utilizing the standing wave field formed by a grating cavity with multiple reflecting surfaces enables multi-beam interference to better optimize the light field distribution, improving the detector's External Quantum Efficiency (EQE), reaching 27% (under 1330 nm excitation); Using Localized Surface Plasmon Resonance (LSPR) from metal nanoparticles to enhance the spontaneous emission rate of QDs (using CdSe QDs as an example), combined with the band engineering of photonic crystals to form high-gain oscillation output. Synergizing photonic structures with QDs can surpass the limits of light-matter interaction in traditional devices, aiding in the design and fabrication of novel high-performance optoelectronic devices (such as monolithic integrated spectrometers, flexible lasers). For example, as shown in Figure 1 (b), quantum dot-based photonic integrated circuits exhibit more superior performance.

Constructing heterojunctions based on PbS QDs combined with relevant processing techniques significantly enhances device performance. Deng et al. developed a flexible photodetector based on an ultra-thin PbS QD (50 nm) active layer. A p-n heterojunction (n-ZnO/p-PbS) was constructed [7]. After variable-gradient ligand exchange (TBAI/EDT gradient treatment), a rectification ratio of 1700 was obtained, reducing the dark current to 4.84 $\mu A/cm^2$. Similarly, under the Fabry-Perot cavity effect, a carrier extraction rate of 97% was achieved under 1330 nm NIR light, and the response time was shortened to 20 ns due to the capacitive effect. Considering mechanical stability, a PET substrate was used. Periodic grating structures were fabricated using nanoimprint lithography. After ten thousand bending cycles (R = 7 mm), the device photocurrent retention rate remained over 95%, far exceeding the fatigue limit of traditional thin-film devices.

4.3. Gas sensors

Using PbS QD materials as the core, constructing heterojunction structures or introducing polymer doping can further optimize carrier transport. Combining this with UV light excitation or room-temperature chemical adsorption mechanisms enables highly sensitive detection of harmful gases (down to parts-per-billion levels). The synergistic effect of both approaches can further enhance gas sensor performance. Wang T., et al. reported a UV-light-enhanced ZnO/PbS composite sensor [8]. Figure 1 (c) shows the synthesis process of PbS QDs modiffed ZnO. Porous ZnO was prepared via ZIF-L pyrolysis. UV light excitation induces the generation of photogenerated electron-hole pairs in PbS, which are rapidly transferred across the heterojunction interface to the ZnO surface, promoting oxygen adsorption and the generation of Reactive Oxygen Species (ROS). These ROS undergo oxidation reactions with TEA molecules (triethylamine), causing a significant decrease in resistance. Experiments showed that ZnO/PbS-0.2 exhibited a response value (Ra/Rg) as high as 13600 to 100 ppm TEA under 365 nm illumination, five times that of pure ZnO, with a detection limit as low as 198 ppb, far exceeding international emission standards (1 ppm).

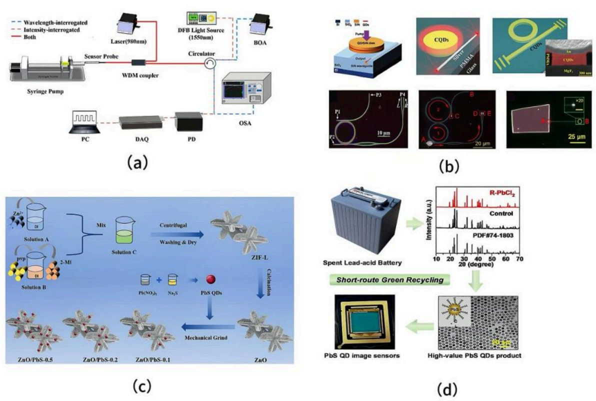

Figure 1. Applications of PbS quantum dots in sensors. (a) Biosensor; (b) Photoelectric sensor; (c) Gas sensor; (d) Image sensor [4,6,8,10]

Kwon et al. developed a poly (3-hexylthiophene) (P3HT)-doped PbS QD thin-film sensor. P3HT and PbS QDs were co-blended simultaneously using a solution process to improve film stability and carrier mobility. The sensor maintained good performance even at 30% relative humidity, facilitating gas detection in harsh environments [9]. Moreover, utilizing photogenerated carrier regulation and room-temperature interface engineering broke the traditional trade-off between sensitivity and power consumption in room-temperature gas sensors.

4.4. Image sensors

Image sensors are used in fields like intelligent vision, industrial inspection, and biomedicine. PbS QD image sensors, with their tunable NIR response, solution-process compatibility, and flexibility, present a valuable alternative to silicon-based devices. PbS QDs (size 5 nm) were extracted chemically from waste lead-acid battery plates, modified with thiol ligands, and coated onto a silicon substrate to form a photosensitive layer. The general preparation process is shown in Figure 1 (d). A responsivity of 0.8 A/W was achieved in the NIR band (1000-1300 nm), enabling precise detection of abnormal heat spots on circuit boards (resolution≤1mm). Simultaneously, this method recovered heavy metals from waste lead-acid batteries. The PbS QDs could be formed into films via solution processing directly on silicon substrates, compatible with mature CMOS processes, reducing solution costs by approximately half, making it an economical and effective industrial thermal imaging solution [10].

Addressing the limitation that traditional silicon-based devices have a narrower spectral range in the visible compared to the infrared, Zhang et al. prepared a stacked coating of PbS QDs (3-6 nm) with gradually varying sizes. Leveraging the quantum confinement effect broadened the spectral response to the full spectrum (450-1550 nm wavelength range). This coating was integrated onto a microlens array to create a spectrally resolving device. The device achieved an EQE of 22% at a 1300 nm wavelength, aiding in accurately distinguishing vegetation water content. Its cost is only one-third that of InGaAs sensors, greatly improving the cost-effectiveness of wide-spectrum imaging [11].

Currently, flexible image sensors are a major hotspot for advancing technology. Focusing on the needs of wearable and curved imaging, Shultz et al. deposited colloidal PbS QDs onto a polyimide (PI) substrate using inkjet printing to construct a flexible pixel array (pixel pitch 50μm). After 1000 bending cycles (radius of curvature 5 mm), the photocurrent retention rate remained above 90%. Its dark current in the NIR was only X A/pixel (value missing in source), making it suitable for flexible applications like epidermal pulse monitoring and industrial pipe endoscopy. The device was fabricated using all-solution processes at temperatures below 100 ℃, without damaging the substrate, showing broad prospects in flexible electronics manufacturing [12].

5. Challenges and future development directions

The many advantages of PbS semiconductor QD sensors, stability issues in the environment remain a significant obstacle to their application. The reason is that PbS QDs are relatively easily degraded by light, oxygen, and moisture, causing the surface ligands on the high-surface-area PbS to lose their protective encapsulation and detach, leading to a decrease in quantum efficiency. Furthermore, in some sensors where the response to PbS has inherent sensitivity, the presence of external impurities can also reduce selectivity to varying degrees. In some sensors, lattice mismatch at heterojunction interfaces can cause carrier recombination, reducing sensor accuracy and signal-to-noise ratio.

To address these sensor challenges, future development could focus on core-shell structures (e.g., Cd-free shells, graded bandgap engineering) and composite systems with two-dimensional materials (such as graphene). Such heterostructures can improve stability, broaden the spectral response range, and increase carrier transport rates. Broader markets should be explored in medical diagnostics (NIR in vivo imaging, biomarkers), the Industrial Internet of Things (IIoT gas detection, smart devices), and flexible electronics, promoting developments in biocompatibility, self-powered integration, and low-cost large-scale fabrication.

6. Conclusion

This comprehensive review systematically explores the fundamental properties, synthesis methods, application scenarios, challenges, and future prospects of lead sulfide (PbS) semiconductor Quantum Dot (QD)-based sensors. As zero-dimensional nanomaterials, PbS QDs exhibit unique advantages in sensing applications, including size-tunable quantum confinement effects, high specific surface area, efficient near-infrared (NIR) photoluminescence, and modifiable surfaces. These characteristics enable precise regulation of optical/electrical properties and strong interaction with target analytes, forming the basis for high-performance sensor design.

The review highlights diverse synthesis strategies for PbS QDs, such as organic phase synthesis, cation exchange, and pyrolysis, each enabling controlled size, bandgap, and monodispersity for specific applications. In sensor applications, PbS QDs have demonstrated remarkable performance: in biosensors, they enable high-sensitivity detection of biomolecules (e.g., SARS-CoV-2 biomarkers with detection limits down to 9.58 fg/ml); in photoelectric sensors, heterojunction structures and photonic integration enhance light absorption and carrier extraction efficiency (e.g., flexible photodetectors with 97% carrier extraction and 20 ns response time); in gas sensors, UV-light enhanced heterojunctions achieve ppb-level detection of triethylamine; and in image sensors, solution-processed PbS QDs enable wide-spectrum imaging (450–1550 nm) with cost-effectiveness and flexibility.

Notably, PbS QD sensors face critical challenges, including environmental instability (degradation by light/oxygen/moisture), lattice mismatch-induced carrier recombination in heterojunctions, and selectivity issues. Future research directions are proposed: core–shell structure engineering (e.g., gradient bandgap design), hybridization with two-dimensional materials (e.g., graphene) to enhance stability and carrier transport, low-temperature solution processing for flexible device fabrication, and machine-learning-optimized sensor arrays for multi-parameter detection. These advancements will facilitate the transition of PbS QD sensors from theoretical research to industrial applications in biomedical diagnostics, smart environmental monitoring, and flexible electronics, thereby breaking through traditional sensing bottlenecks and improving detection performance.

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