



Review Sensing Utilities of Cesium Lead Halide Perovskites and Composites: A Comprehensive Review

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Abstract: Recently, the utilization of metal halide perovskites in sensing and their application in environmental studies have reached a new height. Among the different metal halide perovskites, cesium lead halide perovskites (CsPb X_3 ; X = Cl, Br, and I) and composites have attracted great interest in sensing applications owing to their exceptional optoelectronic properties. Most $CsPbX_3$ nanostructures and composites possess great structural stability, luminescence, and electrical properties for developing distinct optical and photonic devices. When exposed to light, heat, and water, CsPbX₃ and composites can display stable sensing utilities. Many CsPbX₃ and composites have been reported as probes in the detection of diverse analytes, such as metal ions, anions, important chemical species, humidity, temperature, radiation photodetection, and so forth. So far, the sensing studies of metal halide perovskites covering all metallic and organic-inorganic perovskites have already been reviewed in many studies. Nevertheless, a detailed review of the sensing utilities of CsPbX₃ and composites could be helpful for researchers who are looking for innovative designs using these nanomaterials. Herein, we deliver a thorough review of the sensing utilities of CsPbX₃ and composites, in the quantitation of metal ions, anions, chemicals, explosives, bioanalytes, pesticides, fungicides, cellular imaging, volatile organic compounds (VOCs), toxic gases, humidity, temperature, radiation, and photodetection. Furthermore, this review also covers the synthetic pathways, design requirements, advantages, limitations, and future directions for this material.

Keywords: cesium lead halides; analyte detection; environmental monitoring; cellular imaging; fluorescent quantification; chemical sensors; real analysis; pesticides; herbicides; photodetection

1. Introduction

To protect the ecosystem, the detection, quantification, and removal of environmental contaminants play a vital role [1–3]. Thus, the synthesis and fabrication of novel nanomaterials and nanocomposites are important in developing various analytical methods [4–8]. Metal halide perovskites (including all inorganic and organic–inorganic perovskites) and their composites, in particular, have been demonstrated as unique probes in diverse analyte quantitation [9,10]. However, most halide perovskites suffer from chemical/structural instability caused by exposure to moisture, oxygen, and high temperature [9–11]. To resolve the instability problem, the development of all inorganic perovskites was proposed to make them sustainable under harsh conditions [12]. Furthermore, the use of all inorganic halide perovskites (such as inorganic metal oxides, lead-free metal halides, and cesium



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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/). lead halides) in analyte detection displayed exceptional performance in real-time applications [13]. Among all inorganic perovskites, cesium lead halides (CsPbX₃; X = Cl, Br and I) and composites have been widely demonstrated in photovoltaic applications and in the detection/quantification of metal ions, anions, chemicals, explosives, bioanalytes, pesticides, fungicides, cellular imaging, volatile organic compounds (VOCs), toxic gases, humidity, temperature, and radiation [14–19].

The distinct sensor responses of CsPbX₃ can be attributed to its excellent electro-optical properties, which benefit the development of numerous semiconducting and sensing utilities [18,19]. For instance, CsPbX₃ displays high chemical stability at higher temperatures (at >350 °C) and exhibits bright emission with high PLQY reaching >90% (PLQY= photoluminescence quantum yield) [20]. The bandgap of CsPbX₃ (lies between 1.7 and 3 eV) can be adjusted across the visible spectrum by tuning the X-site ion and composition ratios to attain red-to-blue emission [21–23]. Depending on the temperature and the size of halide (X) ions, CsPbX₃ could possess different crystal phases, such as cubic (Pm-3m, α), tetragonal (P4/mbm, β), and orthorhombic (Pnam γ and Pnma δ (noted as non-perovskite) phases [24,25]. Likewise, the surface morphology and potentials may vary when absorbing diverse analytes (moisture, gaseous species, environmental contaminants, bioanalytes, etc.) [26–28]. Variations in photoluminescence/absorption, phase transformation, and changes in the surface morphology and charge potentials of CsPbX₃ can be considered as sensor responses [29–33] when detecting analytes. These sensors can be further enhanced by combining perovskites with suitable/proper nanomaterials [34–43].

The electro-optical properties and sensor responses of CsPbX₃ and composites may vary depending on their distinct nanostructures. For example, CsPbX₃-based sensor probes/composites in QD structures with various sizes may possess diverse bandgaps and display red-to-blue wide optical properties [34], which facilitates the design of dualmode sensors. Subsequently, CsPbX₃ nanocrystals (NCs) also display unique magnetic and optoelectronic properties. The facile synthesis of NCs allows them to be adopted in distinct applications, such as solar cells and in vitro/in vivo applications [35]. Due to their structural features, such as hardness, diffusivity, density, enhanced ductility/toughness, elasticity, and conductivity/thermal properties, CsPbX₃ NCs can be effectively applied in energy-related studies. For example, Hu et al. defined the use of CsPbBr₃ NCs as single-photon emitters [36]. Metal nanoclusters (MNCs) showed exceptional physicochemical properties, such as surface modifiability, surface-to-volume ratio, number of atoms, biocompatibility, photothermal stability, etc. [37]. Therefore, conjugating with CsPbX₃ may enhance the performance of the target-specific sensors. Because the reduced dimensionality of nanowires (NWs) can significantly improve electric/heat transport compared with bulk wires, they have great potential as temperature and chemoresistive sensors [38,39]. For instance, Zhai and co-workers reported the solvothermal synthesis of $CsPbX_3$ (X = Cl, Br) NWs and demonstrated them in photodetector applications [40]. Regarding twodimensional materials, nanosheets (NSs) have been demonstrated as effective sensors due to their exceptional physical, chemical, optical, mechanical, electronic, and magnetic properties [41]. Lv et al. demonstrated the generalized colloidal synthesis of two-dimensional cesium lead halide perovskite nanosheets in photodetector applications [42]. Furthermore, nanoparticles with high surface-to-volume ratios were employed in multiple sensors, which can be operated at distinct solvent environments and elevated temperatures [43]. Based on the above reasons, CsPbX₃ probes/composites derived from QDs, NCs, MNCs, NWs, NSs, and NPs require detailed review.

The exceptional optical properties, unique structural/crystalline features, and electronic structures of CsPbX₃ (X = Cl, Br, and I) are considered important material properties for electrochemical, thermal, and chemoresistive sensing studies. To date, numerous optical sensors made of CsPbX₃ (X = Cl, Br, and I) and composites have been thoroughly investigated with exceptional applicability [9–15]. This can be attributed to their distinct and high PLQY in red-to-blue luminescence. However, there have been reports on the electrochemical, thermal, and chemoresistive sensing performance of CsPbX₃ (X = Cl, Br,

and I) and composites [9–15] that require further clarification for future research. Heavy metal ions and anions are well-known environmental contaminants that are involved in cellular processes, and, at high concentrations, they may become harmful to living beings as well [44–46]. Chemicals and explosives also contaminate the environment; thus, their detection methods are available in many reports [47–49]. Toxic gases and VOCs are noted as vital industrial contaminants; thus, their quantitation has been explored by numerous researchers [50,51]. Exposure to radiation, temperature, and high humidity may harm living tissues and beings, and therefore researchers have developed sensors for photo, radiation, and photodetection [52–54]. Bioanalytes, drugs, fungicides, and pesticides play crucial roles in food cycles and sustain the living environment; thus, numerous reports are available for their identification [55–58]. Based on the aforementioned important issues, many researchers have adopted CsPbX₃ (X = Cl, Br, and I) and composites for the optical, electrochemical, chemoresistive, and thermal detection of analytes. The progress and challenges in developing these sensors are reviewed in this article.

Numerous sensors are reported that involve the use of CsPbX₃ and composites toward the detection of metal ions, anions, chemicals, explosives, bioanalytes, pesticides, fungicides, cellular imaging, VOCs, toxic gases, humidity, temperature, X-rays, and photons (light). Many reviews covering halide perovskite-based sensors, including hybrid halide perovskites and all inorganic halide perovskites, are available [9,10,59–64]. However, most reviews do not provide much detail in sensor studies of CsPbX₃-based composites and the underlying sensor mechanisms. Therefore, the focus of this article is to review the sensing utilities of CsPbX₃ and composites toward diverse analytes (see Figure 1) and provide valuable information on the synthetic pathways, design requirements, advantages, limitations, and future directions.



Figure 1. Schematic representation of $CsPbX_3$ (X = Cl, Br, and I) and composite-based sensors used in metal ion and anion sensors, bioanalyte and drug monitoring, pesticide detection, cell imaging, etc.

2. Role of Structural Stability and Optoelectronic Properties in Sensors

CsPbX₃ crystals following the stoichiometry ABX₃ have an undistorted cubic structure composed of Pb²⁺ surrounded octahedrally by 'X' anions (X = Cl, Br, and I) and a larger Cs⁺ cation with a 12-fold cuboctahedral coordination [65]. CsPbX₃ in a cubic crystal structure can be stable only if the values of the Goldschmidt tolerance factor are between 0.9 and 1 [66]. The Goldschmidt tolerance factor of CsPbX₃ is determined from t = $(R_A + R_X)/\sqrt{2}$ ($R_B + R_X$), where R_A , R_B , and R_X are the ionic radii of Cs⁺, Pb²⁺, and halide (X) ions,

respectively. When the values of the tolerance factor lie between 0.7 and 0.9, the CsPb X_3 crystal may exist in distorted cubic structures with variations in symmetries/phases [65–67]. The structural distortion and instability of $CsPbX_3$ may arise from external factors, such as temperature, quantum size moisture, etc. [68,69]. For example, phase transitions among cubic, monoclinic, tetragonal, or orthorhombic phases occur in the CsPbX₃ crystal at a temperature range between 300 and 600 K [70]. Similar to the variations in particle sizes and compositions, the phase transformation in the CsPbX3 may also result in broad emission covering the entire visible range (from blue to red), which can be utilized to develop analyte sensors. For example, Protesescu et al. [71] demonstrated CsPbX₃ NCs with tunable bandgap energies by controlling the quantum size and colloidal compositions of NCs, as shown in Figure 2. When exposed to moisture, humidity, gaseous environment, and the doping of foreign materials, structural distortions via surface-mediated absorption, oxidation, reduction, etc., could occur in CsPbX₃, which can be regarded as sensor responses. The stability of hybrid halide perovskites also follows a similar trend as CsPbX₃-based materials [9]. However, metal oxide perovskites show slightly better stability than that of $CsPbX_3$ and hybrid halide perovskites [9–12].



Figure 2. Colloidal perovskite CsPbX₃ NCs (X = Cl, Br, and I) exhibit size- and composition-tunable bandgap energies covering the entire visible spectral region with narrow and bright emission; colloidal solutions in toluene under UV lamp (λ = 365 nm) is shown in the upper corner of the figure (permission obtained from Ref. [71]).

Owing to its exceptional optoelectronic properties, CsPbX₃ can be applied in analyte quantification by monitoring its responses in photoluminescence, absorbance, conductivity, temperature, etc. Moreover, CsPbX₃ possesses bright blue-to-red emission, depending on the halide (X) concentration, and displays high PLQY (can reach over 90%). Therefore, CsPbX₃ and composites can also be utilized in the quantification of halides [72]. CsPbX₃ and composites can display unique absorbance and colorimetric responses in the presence/absence of specific analytes [73]. The density functional theory calculations conducted by Y. Kang and co-workers [74] showed that different halide (X) ions in CsPbX₃ can lead to changes in intrinsic carrier mobility by a factor of 3 to 5, depending on the carrier concentration, which is between 10^{15} and 10^{18} cm⁻³. Their work also concluded that, in terms of carrier mobility, the preferred carrier type (electron or hole) also depends on halide (X). Kawano et al. investigated the halogen ion dependence on the low thermal conductivity of cesium halide perovskites using first-principle phonon calculations [75]. E. G. Ripka

and co-workers reported variations in surface-ligand binding potential due to the halide ion exchange to afford diverse emissions and PLQY [76]. The changes in intrinsic carrier mobility, thermal conductivity, and surface-ligand binding potential can be adopted in designing various electrochemical, temperature, and colloidal sensors for the detection of specific analytes. However, some of the reported sensors were attributed to a combination of carrier mobility and surface-ligand binding. For instance, exposing CsPbX₃ to gaseous or VOC analytes resulted in variations in conductivity, but the underlying mechanism was attributed to the efficacy of surface-ligand binding in the modification of oxidation or reduction [77–79].

3. CsPbX₃ (X = Cl, Br, and I) and Composites toward Metal Ion Detection

Due to the importance of heavy metal ion detection in environmental protection, the use of CsPbX₃ (X = Cl, Br, and I) and composites in metal ion sensors have been widely reported by many researchers, which are described in this section. Wu and co-workers demonstrated the PL-based detection of Cu^{2+} in the presence of ytterbium acetate (Yb(OAc)₃) by engaging one-dimensional (1D)-CsPbCl₃ NCs in the device [80]. The CsPbCl₃ NCs were synthesized using the hot-injection method and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). Yb(OAc)₃ induces morphology changes from weakly emissive 1D CsPbCl₃ NCs (PLQY = 2.1%) to highly luminescent 1D CsPbCl₃ NWs (PLQY = 17.3%), which are low in defect density and high in conductivity. The PLQY depends on the size of nanostructures (due to bandgap variations), which can be adjusted with metal doping. The doping of Yb³⁺ in 1D-CsPbCl₃ NWs resulted in a higher aspect ratio, uniformity, and lower number of defects compared with undoped ones; thus, Yb-doped 1D-CsPbCl₃ NWs showed high PLQYs. The enhanced defective and rough surface morphologies of 1D-CsPbCl₃ NCs effectively hindered light absorption and electron/charge transport, thereby lowering the PLQY. In the presence of acetate ion (AcO⁻; present in Yb(OAc)₃), the steric hindrance was reduced by the copper-based counter-ion pair, which enhanced the adsorption of Cu²⁺ on the surface of the CsPbCl₃ NCs and resulted in PL quenching. The linear regression of Cu^{2+} detection was observed between 0 and 1 μ M $(\mu M = \text{micromole} (10^{-6} \text{ M}))$ with an LOD of 0.06 nM (nM = nanomole $(10^{-9} \text{ M}))$. This work is informative and reveals much detail on the role of $Yb(OAc)_3$, underlying the dynamic quenching mechanism, surface-mediated analyte interaction, and feasible information of electron transfer/charge trap between CsPbCl₃ and Cu²⁺. However, it lacks real-time applications, which should be demonstrated before commercialization.

Sheng et al. reported the use of CsPbBr₃ QDs in the quantification of Yb³⁺ and Cu²⁺ [81]. CsPbBr₃ QDs were synthesized using the hot-injection method, with a PLQY of 63%, and showed enhancement in PL with Yb³⁺ and PL quenching with Cu²⁺, as seen in Figure 3. The linear PL quenching range of Cu²⁺ is between 2 nM and 2 μ M, with an estimated LOD of 2 nM. This work is impressive in reporting Cu²⁺ detection in edible oils but lacks detailed investigations on the underlying mechanisms. Liu et al. also described the use of CsPbBr₃ QDs (PLQY = 90%) toward the luminescent detection of Cu²⁺ [82]. CsPbBr₃ QDs were synthesized via the hot-injection method and displayed PL quenching between 0 and 100 nM, with an LOD of 0.1 nM. The detection of Cu²⁺ was carried out in organic media hexane following a dynamic quenching mechanism. This is a follow-up work of previous reports with additional validation on selectivity and time-resolved studies.

To avoid using organic media in sensor investigations, Kar and co-workers reported that the use of poly(vinyl pyrrolidone), n-isopropylacrylamide-coated CsPbBr₃ NCs (PVP-NIPAM-CsPbBr₃ NCs) for aqueous media facilitated the discrimination of Cu²⁺ [83]. Firstly, SiO₂-coated CsPbBr₃ NCs and PVP-NIPAM-CsPbBr₃ NCs were synthesized via ligand-ligand-assisted reprecipitation (LARP) method to achieve a maximum PLQY of 93%. The PVP-NIPAM-CsPbBr₃ NCs showed improved stability and dispersity in water compared to silica-coated NCs, with redshifted emission peaks around 513–515 nm. The NCs displayed linear PL quenching between 0 and 412 μ M, with a calculated LOD of 18.6 μ M, as seen in

Figure 4. This is an inspiring work that can be readily extended to biological studies. Li et al. reported the use of green-fluorescent CsPbBr₃ (CPB) QDs for Cu²⁺ quantification using phase transfer [84]. A strong organic ligand (oleylamine, OAm) was added to selectively transfer Cu²⁺ from water to cyclohexane, which led to fluorescent quenching. The PL emission was quenched linearly between 1 μ M and 10 mM. This is an innovative method that enables Cu²⁺ detection via phase transfer with a short response time (1 min). However, no real applications were reported in this work. Moreover, Song and co-workers developed long-wavelength-pass filters consisting of CsPbBr₃ and CsPb(Cl/Br)₃ QDs using a Cu²⁺ quenching strategy [85]. However, no clear real-time applications were demonstrated in this work.



Figure 3. (a) The effect of different metal ions on the PL intensity of CsPbBr₃ QDs. The concentration of metal ions and CsPbBr₃ QDs are 2.0×10^{-6} and $\approx 1.0 \times 10^{-9}$ M, respectively. The PL peak intensity is normalized by CsPbBr₃ QDs without adding metal ions (the "blank" column). (b) Photo of CsPbBr₃ QDs in cyclohexane under ultraviolet light excitation with and without Cu²⁺. (c) PL spectra of CsPbBr₃ QDs at different [Cu²⁺] concentrations and (d) PL intensity of CsPbBr3 QDs ($\lambda_{ex} = 365$ nm) as a function of [Cu²⁺] and [Yb³⁺] (permission obtained from Ref. [81]).

Li et al. proposed the utilization of macroporous CsPbBr₃-(SH)polyHIPE NCs for the ultrasensitive detection of Cu²⁺ via PL quenching [86]. In this work, CsPbBr₃ NCs were synthesized via the hot-injection method, with a PLQY of ~98%. The as-synthesized NCs were then composited with (SH)polyHIPE (generated from the monomers trimethylolpropane triacrylate (TMPTA) and trimethylolpropane tris(3-mercaptopropionate) (TMPTMP)). The linear regression of PL quenching was recorded between 10 fM and 10 mM, with an LOD of 10 fM. Although this work is supported by density functional theory (DFT) calculations, it lacks real-time applications. Gao and co-workers developed a CsPbBr₃ QD-based fluorescence-enhanced microfluidic sensor for the in situ detection of Cu²⁺ in lubricating

oil [87]. As displayed in Figure 5a, the polymethyl methacrylate opal photonic crystal (PMMA OPC) film is a microfluidic sensor substrate, which displays high sensitivity and low LOD with Cu²⁺. When coupling with OPCs, CsPbBr₃ QDs synthesized through the hot-injection method showed a 26-fold enhancement in PL intensity (at 496-526 nm under 450 nm excitation). When adding Cu^{2+} in lubricating oil, the PL intensity of PMMA OPC/CsPbBr₃ QD composites was quenched with Cu²⁺ concentrations of 1 nM-10 mM and an LOD of 0.4 nM, as shown in Figure 5b. The CsPbI₃ QD/SiO₂ IOPC (inverse opal photonic crystal) composite was further explored for the on-site rapid detection of Cu^{2+} [88]. CsPbI₃ QDs synthesized with a hot-injection method displayed PL emission at 693 nm under 405 nm excitation. SiO_2 IOPCs were introduced into the chip wells to couple with the CsPbI₃ QDs, which further enhanced the PL emission by 22 folds. After the addition of Cu²⁺ in lubricating oil to the above composites, a linear PL quenching was observed in the ranges of 0–20 nM and 20–50 nM, with an LOD of 0.34 nM. Both reports [87,88] show distinct performance in terms of mechanical durability, operating temperatures (5 °C to 50 °C), reusability of chips, etc. Advancing in this research direction will require further demonstrations of practical applications.



Figure 4. Images of the PbN-4 NC solution under a UV lamp (**a**) before and after adding different metal ions as marked in the figure. (**b**) Chart representing the comparison of the PL intensity of PbN-4 NCs that persisted after the addition of subsequent metal ions. (**c**) Emission spectra of PbN-4 NCs in the presence of different concentrations of Cu^{2+} solutions as shown in the legends. (**d**) The linear curve represents decreasing in the PL intensity of PbN-4 NCs after adding different concentrations of Cu^{2+} solution (permission obtained from Ref. [83]).

Zhang and co-workers proposed the utilization of organic cross-linker hexamethylene diisocyanate (HDI)-reinforced small-sized CsPbBr₃@SiO₂-E NPs (size ≤ 50 nm) toward the fluorescent sequential detection of Cu²⁺ and S²⁻ [89]. CsPbBr₃ NCs (size = 6.8 nm; emission at 515 nm) were first synthesized using a hot-injection technique and then conjugated via a three-step synthetic path to afford CsPbBr₃@SiO₂-E NPs (emission peak at 508 nm; PLQY = 90%), where 'E' stands for enhanced performance. The linear PL quenching/recovery of CsPbBr₃@SiO₂-E NPs with Cu²⁺ and S²⁻ were observed in ranges of 0–5 μ M and 5–10 μ M (for Cu²⁺) and 0–120 μ M (for S²⁻), with corresponding LODs of

0.16 μ M (for Cu²⁺) and 8.8 μ M (for S²⁻). This work requires further support with real-time investigations. The CsPbBr₃ QDs (PLQY = 88%) were encapsulated in polymethyl methacrylate (PMMA) fiber membrane (d \approx 400 nm) to afford CPBQD/PMMA FM for detecting trypsin, Cu²⁺, and pH [90]. The CPBQD/PMMA FM and cyclam interacted effectively to capture Cu^{2+} , with a linear range of 1 fM–1 M (fM = femtomole (10⁻¹⁵ M)) and an LOD of 1 fM. Moreover, fluorescence resonance energy transfer (FRET) between CPBQD and Cu²⁺ plays a vital role, resulting in PL quenching. Trypsin detection by CPBQD/PMMA FM via PL quenching was attained in the presence of peptide CF6 (Cys-Pro-Arg-Gly-R6G). Similarly, CPBQD/PMMA FM and R6G were combined to display pH-mediated fluorescent quenching. This is a unique work with exceptional sensor investigations. However, it can be improved further by supporting additional real-time applications. Ahmed et al. proposed a two-step surfactant-free procedure for producing a CsPbBr₃ QD-embedded zinc(II) imidazole-4,5-dicarboxylate metal-organic framework (MOF) for the luminescent detection of Cu²⁺ [91]. The PL emission of CsPbBr₃@MOF composites at 519 nm (under 360 nm excitation; PLQY = 39.2%) was quenched linearly between 100 and 600 nM, with an estimated LOD of 63 nM. PL quenching occurred through dynamic quenching and electron transfer with a Stern–Volmer quenching constant (K_{SV}) of 1.55×10^5 M⁻¹. Although this report is an impressive work, it lacks real-sample investigation.



Figure 5. (a) The workstation setup for the detection system of microfluidic sensor. (b) The schematic of the formation of PMMA OPCs/c composites and Cu^{2+} detection (permission obtained from Ref. [87]).

Wang et al. reported the use of a liquid–liquid extraction technique for the visual detection of Hg^{2+} in aqueous media [92]. In their study, the luminescent CsPbBr₃ NCs

(PL emission at 520 nm under 380 nm excitation) were synthesized using the hot-injection method to engage in the liquid–liquid-extraction-based visual detection of Hg^{2+} . When adding Hg^{2+} dissolved in water into CsPbBr₃ NCs in carbon tetrachloride (CCl₄), the colorimetric PL emission quenching at 520 nm via liquid–liquid extraction was observed, as displayed in Figure 6. The linear regression of Hg^{2+} was recorded between 50 nM and 10 μ M, with an estimated LOD of 35.65 nM. This work requires further investigations into the underlying mechanism and real-time applications.



Figure 6. Illustration of liquid–liquid extraction and visual detection of Hg²⁺ using CsPbBr₃ PNCs (permission obtained from Ref. [92]).

Jiang et al. proposed a two-step precipitation method to synthesize emissive CsPbBr₃ crystals (PL emission at 525 nm under 395 nm excitation) toward Hg²⁺ detection [93]. When detecting Hg²⁺, both CsPbBr₃ NCs and Hg²⁺ were co-precipitated in aqueous solution. The CsPbBr₃ precursor was firstly dissolved in an aqueous solution containing Hg²⁺ (0-1000 nM) and then dropped onto a hydrophilic polydimethylsiloxane (PDMS) substrate with a microwell array. When the substrate was heated at 25 °C for 3 min, co-precipitation occurred, which resulted in PL quenching via Hg²⁺ doping into the CsPbBr₃ lattice. The linear regression of Hg²⁺ was observed between 5 and 100 nM, with an estimated LOD of 0.1 nM. This work demonstrated an innovative technique and provided detailed studies on interference, pH effect, and underlying mechanisms toward Hg^{2+} detection. However, the cost-effectiveness and real-time applications of this method require more work. Through ligand engineering and silica encapsulation, a stable fluorescent CsPbBr₃-mPEG@SiO₂ composite (PL emission at 520 nm under 330 nm excitation; PLQY = 67.5%) was synthesized and adopted in the sequential detection of Hg²⁺ and glutathione (GSH) in aqueous solution via PL quenching and recovery, respectively [94]. Shu and co-workers demonstrated that the existence of 73% of the PL emission of NCs could last over 30 days in aqueous media. The PL quenching and recovery responses were attributed to the electron transfer process between NCs and Hg²⁺ and the effective interaction between Hg²⁺ and GSH. The linear PL responses of Hg²⁺ and GSH were observed in the ranges of 1–50 nM and 1–10 μ M, with LODs of 0.08 nM and 0.19 µM, respectively. This work was successfully applied in tab and serum sample analysis; therefore, it can be regarded as a remarkable work in Hg^{2+} and GSH detection.

Guo et al. developed a nucleation growth method for producing CsPbBr₃ NCs (PL emission at 518 nm under >360 nm excitation; PLQY > 89%) at a large scale and adopted as-synthesized NCs for detecting Zn²⁺ [95]. The PL emission of CsPbBr₃ NCs was quenched linearly between 0 and 40 μ M in the presence of Zn²⁺. The PL quenching was not due to the replacement of Pb²⁺ in the CsPbBr₃ matrix but was caused by the Zn–oleic complex formation. The surface defects created led to the self-assembly of CsPbBr₃ nanocubes into nanorods, thereby resulting in PL quenching. George and co-workers reported the use of alpha-amino butyric acid (A-ABA)-capped CsPbBr₃ QDs (M PQDs) for developing

Co²⁺ sensors [96]. The M PQDs were synthesized using the hot-injection method, which displayed PL emission at 489 nm. The PL emission of the M PQDs was quenched in Co²⁺ concentrations of 0–100 nM, with an LOD of 0.8 μ M. This report uncovered that PL quenching was due to FRET-facilitated dynamic quenching and the inner filter effect (IFE). This is the only report on IFE-based PQD sensors using metal ions, but it lacks information in real-time applications. Halali et al. reported uranyl (UO₂²⁺) ion detection using green emissive CsPbBr₃ PQDs (synthesized using the hot-injection method) [97]. When adding UO₂²⁺, the PL emission at 518 nm was quenched linearly in UO₂²⁺ concentrations of 0–3.3 μ M, with a calculated LOD of 83.33 nM. Extensive mechanistic studies revealed that the PL quenching was due to the electrostatic interaction and adsorption of UO₂²⁺ over the surface of QDs. To support this work, further research on the interference and application studies is necessary.

Polyvinylpyrrolidone (PVP) polymer shell-grown silica-coated Zn-doped CsPbBr₃ NCs (polymer-coated Zn-doped CsPbBr₃/SiO₂ core/shell NCs (PVP-0 NCs, PVP-2.5 NCs, PVP-5 NCs, PVP-7.5 NCs, and PVP-10 NCs)) were synthesized with the hot-injection method for detecting In³⁺ in water [98]. The double-coating method enhanced the water stability, dispersibility, and emission properties of the NCs. Among the various PVP shell-grown silica-coated Zn-doped CsPbBr₃ NCs, PVP-5 NCs (PLQY = 88%) were more stable at higher temperatures and showed stronger luminescence and greater selectivity to In³⁺. When adding In³⁺, the PL emission of the PVP-5 NCs at 511 nm was quenched in In^{3+} concentrations of 0–104 μ M, with an estimated LOD of 11 μ M. The PL quenching was associated with the replacement of Pb^{2+} by In^{3+} . This report is noteworthy but lacks evidence for the proposed mechanism and real-time applications. Pandey et al. employed the $CsPbBr_3 - Ti_3C_2T_x$ MXene QD/QD heterojunction for the PL-based detection of Cd²⁺ [99]. CsPbBr₃ QDs were synthesized using the hot-injection method and then were composited with $Ti_3C_2T_x$ MXene in toluene. The PL emission of CsPbBr₃- $Ti_3C_2T_x$ MXene QDs at 505 nm (under 410 nm excitation) was quenched via charge transfer when adding Cd^{2+} . The linear PL quenching of the QD composite was observed in Cd^{2+} concentrations of 99-590 µM with no information on the value of LOD. This work also demonstrated an on-off-on PL probe for cadmium ion detection, but more investigations are necessary to justify the underlying quenching (static/dynamic) mechanisms. Hsieh and co-workers proposed the use of (3-aminopropyl) triethoxysilane (APTES)0coated CsPbBr₃-CsPb₂Br₅ QDs toward the PL-based detection of Fe^{3+} , as illustrated in Figure 7 [100]. Through the ligand-assisted reprecipitation method, APTES-coated CsPbBr₃-CsPb₂Br₅ QDs were synthesized. The PL emission of the QDs at 520 nm was quenched rapidly (response time = 8 sat 40 °C) in the presence of Fe³⁺. The linear PL responses of QDs to Fe³⁺ were observed in Fe^{3+} concentrations of 10 μ M–10 mM with an LOD of 10 μ M. This is a well-organized work with excellent results in response time and temperature, but it lacks supportive data on mechanistic investigations. Table 1 summarizes the synthetic route, PLQY, linear range, detection limit, and application of $CsPbX_3$ (X = Cl, Br, and I) and composites for metal ion detection.

Table 1. The synthetic route, PLQY, linear range, detection limit, and application of $CsPbX_3$ (X = Cl, Br, and I) and composites toward metal ion detection.

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
CsPbCl ₃ NCs and CsPbCl ₃ NWs	Hot-injection method; 2.1% and 17.3%	Cu ²⁺	PL quenching	0–1 µM	0.06 nM	NA	[80]
CSPbBr3 QDs	Hot-injection method; 63%	Cu ²⁺	PL quenching	2 nM–2 μM	2 nM	Edible oils	[81]

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
CSPbBr ₃ QDs	Hot-injection method; 90%	Cu ²⁺	PL quenching	0–100 nM	0.1 nM	NA	[82]
Silica-coated CsPbCl ₃ NCs	ligand-assisted reprecipitation (LARP) method; 93%	Cu ²⁺	PL quenching	0–412 μM	18.6 µM	Natural water systems	[83]
CsPbBr ₃ QDs	Hot-injection method; NA	Cu ²⁺	PL quenching	1 μM–10 mM	NA	NA	[84]
CsPbBr ₃ -(SH) polyHIPE composite	Hot-injection method; ~98%	Cu ²⁺	PL quenching	10 fM-10 mM	10 fM	NA	[86]
PMMA OPCs/CsPbBr ₃ QD composites	Hot-injection method; NA	Cu ²⁺	PL quench- ing/Microfluidic detection	1 nM-10 mM	0.4 nM	Lubricating oils	[87]
CsPbI ₃ QD/S iO ₂ IOPCs	Hot-injection method; NA	Cu ²⁺	PL quench- ing/Microfluidic detection	0–20 nM and 20–50 nM	0.34 nM	Lubricating oils	[88]
CsPbBr3@SiO2-E NPs	Hot injection followed by 3-step synthetic modification; 90%	Cu ²⁺ /S ²⁻	PL quenching/PL Recovery	$\begin{array}{c} 0{-}5\;\mu M \text{ and} \\ 5{-}10\;\mu M (\text{for} \\ Cu^{2+}) \text{ and} \\ 0{-}120\;\mu M \\ (\text{for } S^{2-}) \end{array}$	0.16 μ M (for Cu ²⁺) and 8.8 μ M (for S ²⁻)	NA	[89]
CsPbBr ₃ QD/PMMA fiber membranes	Hot injec- tion/Electrospinning method; 88%	Cu ²⁺	PL quenching	1 fM-1 M	1 fM	NA	[90]
CsPbBr ₃ @MOF QDs	two step surfactant free procedure; 39.2%	Cu ²⁺	PL quenching	100–600 nM	63 nM	NA	[91]
CsPbBr ₃ NCs	Hot-injection method; NA	Hg ²⁺	PL quenching	50 nM–10 μM	35.65 nM	NA	[92]
CsPbBr ₃ Crystals	two-step precipitation method; NA	Hg ²⁺	PL quenching	5–100 nM	0.1 nM	NA	[93]
CsPbBr ₃ - mPEG@SiO ₂ NCs	Ligand engineering and silica encapsulation method; 67.5%	Hg ²⁺ /GSH	PL quenching/PL Recovery	0.1–50 nM (for Hg ²⁺) and 1–10 μM (for GSH)	0.08 nM (for Hg ²⁺) and 0.19 μM (for GSH)	Tap water and Serum analysis	[94]
CsPbBr ₃ NCs	Nucleation growth synthesis; >89%	Zn ²⁺	PL quenching	0–40 µM	NA	NA	[95]
alpha-amino butyric acid (A-ABA)-capped CsPbBr ₃ QDs (M PQDs)	Hot-injection method; NA	Co ²⁺	PL quenching	0–100 nM	0.8 µM	NA	[96]
CsPbBr ₃ QDs	Hot-injection method; NA	UO2 ²⁺	PL quenching	0–3.3 μM	83.33 nM	NA	[97]

Table 1. Cont.

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
PVP shell-grown silica-coated Zn-doped CsPbBr ₃ NCs	Hot-injection method; 88%	In ³⁺	PL quenching	0–104 µM	11 µM	NA	[98]
CsPbBr ₃ -Ti ₃ C ₂ Tx MXene QD/QD heterojunction	Hot-injection method; NA	Cd ²⁺	PL quenching	99–590 μM	99 µM	NA	[99]
APTES-coated CsPbBr ₃ - CsPb ₂ Br ₅ QDs	ligand-assisted reprecipitation method; NA	Fe ³⁺	PL quenching	10 μM– 10 mM	10 µM	NA	[100]

Table 1. Cont.

NA = not available; μ M = micromole (10⁻⁶ M); nM = nanomole (10⁻⁹ M); fM = femtomole (10⁻¹⁵ M).



Figure 7. (a) Emission spectra and (b) normalized emission intensity of AP-PQD in the presence of different Fe³⁺ concentrations. (c) Photographs of AP-PQD dispersed in ethanol containing Fe³⁺ under ambient light and 365 nm UV light. (d) Intensity ratio of AP-PQD in the presence of different Fe³⁺ concentrations (permission obtained from Ref. [100]).

Critical Comments on CsPbX₃ (X = Cl, Br, and I)-Based Metal Ion Detection

Based on the existing results, it is noted that as-synthesized CsPbX₃ QDs, NCs, and NWs display high specific selectivity to Cu²⁺ through feasible energy transfer between the probes and Cu^{2+} [80–82]. Furthermore, it was clarified that Yb³⁺ doping enhanced the selectivity by reducing the surface defect [80,81], thereby suggesting the effectiveness of surface forces in sensors. Another critical issue in the use of $CsPbX_3$ (X = Cl, Br, and I) probes for metal ion detection, which requires more attention, is their stability in aquatic environments. To solve the stability issues, using polymer and ligand capping/coating on CsPbX₃ has been proposed [83,84,86,89,90], which may enhance the PLQY by avoiding surface exposure to environmental forces existing in water and air. However, whether this approach can be effective in exposure to Cu^{2+} in an aquatic environment remains an open question. The development of a pass filter consisting of CsPbBr₃ and CsPb(Cl/Br)₃ QDs was demonstrated for Cu^{2+} detection via PL quenching responses [85]. However, the development of such pass filters has not met commercial standards. It is a premature proposal and requires additional work. CsPbBr₃ QD/CsPbI₃ QDs were explored using the microfluidic technique, which facilitated the detection of Cu^{2+} [87,88]. However, the fabrication processes of such devices are rather complicated and require a well-equipped clean room environment, thereby restricting their advancement in most developing countries. Also, it is essential to determine whether this microfluidic method is effective in all environmental samples. The use of CsPbBr3 crystals, NCs, and QDs was also reported in the PL "turn-off" detection of Hg²⁺ and UO₂²⁺ [92–94,97]. Many of the available reports on CsPbX₃ (X = Cl, Br, and I)-based metal ion sensors confirmed their selectivity to Cu^{2+} ; however, the underlying mechanisms of detecting Hg^{2+} and UO_2^{2+} by CsPbBr₃ crystals, NCs, and QDs are still unclear. Likewise, the composites of $CsPbX_3$ (X = Cl, Br, and I) with other emerging nanomaterials, such as MOFs, Mxene, APTES, etc., have been proved to be effective in discriminating diverse heavy metal ions [91,94–96,98–100]. However, most of those reports did not address the feasible surface-facilitated detection mechanisms, which restricted the development of analytical devices. These results also raise the question of the reliability of CsPbX₃ (X = Cl, Br, and I)-based Cu^{2+} sensors. The reason behind the selective sensing of Cu²⁺ must be clarified by investigating the Pb²⁺ replacement mechanism, as well as the magnetic property (ferro-/ferri-electronic) changes. The crystalline and lattice features of the probes/compositions in the presence/absence of analytes are not considered from mechanistic aspects, which should be taken into account in future sensor designs. If the crystalline/lattice parameters of CsPbX₃ (X = Cl, Br, and I)-based probes are taken into account, it is highly feasible to design chemoresistive and electrochemical sensors for heavy metal quantification in real samples.

4. Anion Detection by $CsPbX_3$ (X = Cl, Br, and I) and Composites

Similar to metal ion quantification, the discrimination of anions was also demonstrated by perovskite nanomaterials, as described in this section. Jan et al. reported the synthesis of the CsPbBr₃ nanoplatelets (PLQY = 83.7%) via the hot-injection method, which displayed PL emission at above 475 nm under 350 nm excitation [101]. The PL peak was blueshifted when the CsPbBr₃ nanoplatelets were exposed to Cl⁻ (from a HCl source). The sensor response showed a linear range from 0.2 to 0.4 nM, with an LOD of 28 pM. The observed response was attributed to the anion exchange mechanism. Moreover, CsPbBr₃ nanoplatelets are also able to effectively detect the arsenate in the presence of hypochlorous acid (HOCl). The following reaction process (1) shows that As³⁺ is oxidized to produce Cl⁻:

$$AsO_3^{3-} + OCl^- \to AsO_4^{3-} + Cl^-$$
(1)

A blueshifting phenomenon in PL emission from the reaction induced by Cl⁻ species occurred via anion exchange, which showed a linear regression of 6.4–58 nM, with an LOD of 1 nM. This is an innovative work with dual-species recognition; however, it does not provide enough real-time applications. Thereafter, Huang et al. proposed the use of

CsPbBr₃ QDs for Cl⁻ detection in water [102]. The CsPbBr₃ QDs, with PL emission at 513 nm and a calculated PLQY value of 87%, were synthesized using the hot-injection method. When exposed to Cl⁻, the PL emission peak at 513 nm was blueshifted to 483 nm due to the anion exchange reaction with Br⁻. The shifting of the PL peak occurred in Cl⁻ concentrations of 10–200 μ M, with an estimated LOD of 4 μ M. This report was well supported by real-time water analysis; therefore, it can be regarded as a unique work. Shu and co-workers developed highly stable CsPbBr₃ NCs via amphiphilic polymer ligand-assisted synthesis [103]. Amphiphilic polymer octylamine-modified polyacrylic acid (OPA) was used as the capping agent to produce stable NCs, with PL emission at 520 nm and >40% PLQY. As displayed in Figure 8, the PL peak at 520 nm is blueshifted to 441 nm due to the anion exchange reaction in Cl⁻ concentrations of 1–80 mM, with an LOD of 0.34 mM. This report demonstrated Cl⁻ detection in sweat samples; thus, it is an innovative work. However, further research work is required for commercialization.



Figure 8. (**A**) Fluorescence spectra and corresponding fluorescence photographs of the CsPbBr₃/OPA + OAm NCs in the presence of different concentrations of chloride ions from 0 to 150 mM in an aqueous solution under 365 nm UV excitation. (**B**) The fitting curve of $\Delta\lambda$ plotted as a function of Cl⁻ concentration; inset: the corresponding calibration curve of $\Delta\lambda$ and Cl⁻ concentration from 1 to 80 mM. (**C**) Wavelength shift of different substances for the selectivity investigation of Cl⁻ sensing. (**D**) Fluorescence spectra of actual samples and samples after being spiked with different concentrations of Cl⁻; inset: the corresponding fluorescence photos of the samples (permission obtained from Ref. [103]).

Shortly after, Li et al. adopted CsPbBr₃ NCs for the luminescent colorimetric sensing of Cl^- in n-hexane via a halide exchange reaction [104]. The CsPbBr₃ NCs were synthesized using the hot-injection method, in which a rapid halide exchange reaction occurred at

pH = 1. The green emissive peak of the CsPbBr₃ NCs at 514 nm was blueshifted to a 452 nm peak (blue emission) in Cl⁻ concentrations of 10–130 mM, with an estimated LOD of 3 mM. This work was applied in Cl⁻ detection in sweat samples; hence, it is quite innovative. However, the values of the LOD must be further improved by combining other techniques. By taking advantage of the anion exchangeability of CsPbBr₃ NCs, Dutt and co-workers proposed the construction of a glass plate-/paper-strip-based test kit for discriminating Cl⁻ [105]. The PL emission peak of the kit at 509 nm was slowly blueshifted to 478 nm because of the anion exchange reaction. The linear regression of Cl⁻ was observed between 100 μ M and 10 mM with an LOD of 100 μ M. This work requires more supportive evidence for possible commercialization.

Recently, Zhang and co-workers developed β-cyclodextrin (β-CD)-stabilized, arginine (Arg)-added CsPbBr₃ NCs (ACD-PNCs; PLQY = 82%) via ligand-assisted synthesis and utilized them in discriminating Cl⁻ and I⁻ through a ligand exchange mechanism [106]. β -CD capping, together with the addition of Arg, helped to stabilize the PNCs. The green emission of ACD-PNCs was blue/redshifted from 508 nm to 424 nm (blue emission) and 511 nm to 637 nm (red emission), respectively, in the presence of Cl^{-} and I^{-} . The linear regression of Cl⁻ and I⁻ detection was observed in the ranges of 0.04–0.8 mM and 0.04–1.16 mM, with calculated LODs of 3.2 μ M and 9 μ M, respectively. This is a unique work that provides a comparative study with earlier reports. However, perspectives on further work are not mentioned. As discussed in many studies related to anion exchange reactions, CsPBBr₃ can act as exceptional probes toward the quantification of Cl^-/HCl , I⁻, and F⁻ [107,108]. An alcohol-dispersed CsPbBr₃@SiO₂ PNCC nanocomposite was proposed for discriminating Cl^{-} in an aqueous phase [109]. The green emissive peak at 506 nm was blueshifted to 447 nm through the homogeneous halide exchange between CsPbBr₃@SiO₂ PNCCs and Cl⁻. The recovery studies of Cl⁻ in sea sand samples (with a linear range of 0–3%) attested to the reliability of this work, with an LOD of 0.05 mg/g. Moreover, the anion exchange between CsPbBr₃@SiO₂ PNCCs and Cl⁻ occurred in the absence of magnetic stirring or pH regulation, which was a novel observation.

Fu et al. proposed the use of the NH₂-functionalized CsPbBr₃ NCs for detecting I⁻ [110]. These NH₂-functionalized NCs were synthesized in ethanol by using 3-aminopropyltriethoxysilane (APTES) as ligands. In contrast to the traditional halide exchange-based I⁻ sensors of CsPbBr₃, the luminescence of the NH₂-PNCs in ethanol/water at 510 nm was quenched, as shown in Figure 9a. Linear regression is observed in I⁻ concentrations of 4–28 μ M, with an LOD of 1 μ M, as seen in Figure 9b. I⁻ showed higher selectivity among all other interferences, but this report lacks supporting evidence on the PL quenching response of the unshifted peak.

Park and co-workers fabricated a CsPbBr₃ QD/cellulose composite as an early diagnosis sensor for Cl^- and I^- [111]. The CsPbBr₃ QD/cellulose composite was synthesized via a hot-injection method to form monodispersed CsPbBr₃ QDs with high selectivity to Cl⁻ and I^- . The detection of CI^- and I^- in aqueous media was confirmed by observing a color change from green to blue and from green to red, respectively. The color change occurred within 5 s because of the halide exchange reaction. The linear responses of the CsPbBr₃ QD/cellulose composite to Cl⁻ and I⁻ were recorded at 0.1 mM–1 M, with calculated LODs of 2.56 mM (for Cl⁻) and 4.11 mM (for I⁻), respectively. In terms of real-time applications, this work can be regarded as a unique report on medical device fabrication. The halogen ion exchange reaction of CsPbBr₃ and composites brings an additional advantage of the effective discrimination of edible oils. Zhang et al. demonstrated the discrimination of edible oils by using octadecylammonium iodide (ODAI) and ZnI₂ as anion exchangers [112]. This colorimetric sensing strategy can be applied in detecting edible oil mixtures with 100% accuracy, but further research is required for commercialization. Wang et al. described the employment of tetraphenylporphyrin (TPPS)-modified CsPbBr₃ NCs (CsPbBr₃/TPPS nanocomposite) for the quantification of sulfide (S²⁻) [113]. The CsPbBr₃/TPPS nanocomposite possessed good water stability and dual-emission properties. As shown in Figure 10, the CsPbBr₃/TPPS nanocomposite displays strong green emission at 520 nm and moderate

red emission from the TPPS at 650 nm. When adding S^{2–}, the PL emission at 520 nm was quenched linearly in S^{2–} concentrations of 0.2–15 nM, with an LOD of 0.05 nM. This was attributed to the destruction of CsPbBr₃ NCs via the formation of more stable PbS. This work also reported the real-time water recovery study (>95%), which showed a relative standard deviation of <3%, thereby opening a new direction for future research. Table 2 summarizes the synthetic route, PLQY, linear range, LOD, and application of CsPbX₃ (X = Cl, Br, and I) and composites toward the detection of anionic species.



Figure 9. (a) Fluorescence spectra of NH₂-PNCs at various concentrations of I⁻ (0–60 μ M). (b) Linear fitting curve of I₀/I of the fluorescence of NH₂-PNCs and concentrations of I⁻ (permission obtained from Ref. [110]).



Figure 10. Schematic illustration of CsPbBr₃/TPPS nanocomposite-based ratiometric fluorescence detection of sulfide ion (permission obtained from Ref. [113]).

Table 2. The synthetic route, PLQY, linear range, detection limit, and application of $CsPbX_3$ (X = Cl, Br, and I) and composites toward the detection of anionic species.

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
CsPbBr ₃ nanoplatelets	Hot-injection method; 83.7%	Cl ⁻ and As ³⁺	PL peak shift	0.2–0.4 nM and 6.4–58 nM	28 pM and 1 nM	NA	[101]
CsPbBr ₃ QDs	Hot-injection method; 87%	Cl-	PL peak shift	10–200 μM	4 μΜ	Real-time water analysis	[102]

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
CsPbBr ₃ NCs	Ligand-assisted synthesis; >40%	Cl-	PL peak shift	1–80 mM	0.34 mM	Human sweat sample analysis	[103]
CsPbBr ₃ NCs	Hot-injection method; NA	Cl-	PL peak shift	10–130 mM	3 mM	Human sweat sample analysis	[104]
CsPbBr ₃ NCs	Hot-injection method; NA	Cl-	PL peak shift	100 μM–10 mM	100 µM	Glass/Paper- strip analysis	[105]
β-cyclodextrin stabilized, Arginine added CsPbBr ₃ NCs (ACD-PNCs)	Ligand-assisted synthesis; 82%	Cl ⁻ and I ⁻	PL peak shift	0.04–0.8 mM and 0.04–1.16 mM	3.2 μM and 9 μM	Human saliva, sweat, and test-strip analysis	[106]
CsPbBr ₃ @SiO ₂ NCs	Room- temperature synthesis; NA	Cl-	PL peak shift	0–3%	0.05 mg/g	Sand Analysis	[109]
NH ₂ -functionalized CsPbBr ₃ NCs	Hot-injection method; NA	Cl-	PL Quenching	4–28 μM	1 μΜ	NA	[110]
CsPbBr ₃ QD/Cellulose composite	Hot-injection method; NA	Cl [–] and I [–]	PL peak shift	0.1 mM–1 M	2.56 mM (For Cl ⁻) and 4.11 mM (For I ⁻)	Real-time water analysis	[111]
Tetraphenylporphy- rin tetrasulfonic acid (TPPS)-modified CsPbBr ₃ NCs	Hot-injection method followed by compositing; NA	S ^{2–}	PL Quenching	0.2–15 nM	0.05 nM	Real-time water analysis	[113]

Table 2. Cont.

NA = not available; μ M = micromole (10⁻⁶ M); nM = nanomole (10⁻⁹ M); mM = millimole (10⁻³ M); mg = milligram; g = gram.

Critical View on CsPbX₃ (X = Cl, Br, and I)-Based Anion Sensors

 $CsPbX_3$ (X = Cl, Br, and I)-based probes/composites have been reported for discriminating Cl⁻, Br⁻, and I⁻ to display red/blueshifted PL emissive peaks via anion exchange, as noted in Table 2 [101–112]. According to these sensing studies, the presence of anions in the aquatic environment may also lead to a rapid anion exchange due to the disturbed structural parameters. These issues should be addressed with in-depth investigations. Surface stabilization by using suitable capping agents may change lattice features, resulting in an enhanced PLQY; thus, the proposed anion-sensing performance by $CsPbX_3$ (X = Cl, Br, and I)-based probes/composites is not yet confirmed and requires further research. The real question is how can the anion-sensing performance be confirmed if the sensing medium itself could affect the stability of the proposed CsPbX₃ (X = Cl, Br, and I)-based probes/composites. The reaction-based sensing of S^{2-} using tetraphenylporphyrin tetrasulfonic acid (TPPS)-modified CsPbBr₃ NCs was also observed [113], which showed dependence on composition concentrations. Therefore, the optimization of composition concentrations is regarded as a high-priority task and requires detailed investigations. Due to the instability issues of $CsPbX_3$ (X = Cl, Br, and I)-based probes, anion discrimination to distinct competing matrices in real water samples becomes more urgent.

5. CsPb X_3 (X = Cl, Br, and I) and Composites for the Recognition of Chemicals and Explosives

Similar to the quantification of metal ions and anions, $CsPbX_3$ (X = Cl, Br, and I) and composites have been widely applied in the discrimination of chemicals and explosives.

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Yin and co-workers reported the use of CsPbBr₃ NCs (synthesized with the hot-injection method; PL at 510–520 nm) in the quantification of iodomethane (CH₃I) via the halide exchange reaction in the presence of oleylamine (OLA) [114]. The presence of OLA induced the nucleophilic substitution of CH₃I to release iodide species. As illustrated in Figure 11, the iodide exchange occurs rapidly within <5 s, resulting in a redshift of PL (nearly 150 nm; original PL at 660–670 nm). The selectivity of CsPbBr₃ NCs toward CH₃I was high with this portable approach. The linear range of CH₃I detection is between 0.7 and 70 μ M with an LOD of 0.2 \pm 0.07 μ M. Based on the results, this work can be regarded as innovative. Shortly after, Feng et al. described the use of yttrium single-atom-doped cesium lead bromide nanocrystals (Y-SA/CsPbBr₃ NCs) for detecting CH₃I [115]. The Y single-atom deposition was carried out using a photo-assisted method. In the presence of OLA, the PL peak of CH₃I was redshifted due to the halide exchange reaction. The linear range of CH₃I detection was between 5.6 and 157 μ M, with an LOD of 0.3 μ M. Except for the anchoring of the Y single atom, this is a follow-up work of an earlier report [114], hence requiring more research efforts to confirm its novelty.



Figure 11. Reaction mechanisms and the spectroscopic response of CsPbBr₃ perovskite nanocrystals (PNCs) to CH₃I. (**a**) Oleylamine (OLA, 0.96 mM) or CH₃I (20,000 ppbv solution) were introduced separately into PNC dispersions in toluene. The emission images under 365 nm UV light were recorded after 100 min, showing no change in emission. (**b**) OLA-pretreated CH₃I solutions (CH₃I concentration: 20,000 ppbv) were added to a PNC dispersion in toluene, with the emission color observed under 365 nm UV light before and 20 s after addition. The hypothesized reaction mechanism occurs when CH₃I induces the alkylation of OLA via the SN² mechanism and stops at dimethyl analog formation. (**c**) UV–visible absorption spectra of PNCs exposed to varying amounts of CH₃I. (**d**) Emission spectra of CsPbBr₃ PNCs as a function of the amount of added CH₃I; inset: redshift of PNC PL emission as a function of CH₃I concentration. Linear fitting of results from 100 to 10,000 ppbv is shown as a red line with R² = 0.997. (**e**) CIE chart converted from the PL spectra of PNCs exposed to varying amounts of CH₃I. Note: Spectra in c, d were recorded 20 s after CH₃I addition at room temperature to ensure the reaction was complete (permission opted from Ref. [114]).

Xie et al. reported a paper-based microfluidic colorimetric assay for dichloromethane/ dibromo methane (CH₂Cl₂/CH₂Br₂) in the presence of trialkyl phosphines (TOP) by using CsPbX₃ (X = Cl, Br, or I) nanocrystals [116]. When adding TOP or through UV-photoninduced electron transfer, the homogeneous nucleophilic substitution could be enhanced to afford a colorimetric fluorescent response with corresponding peak shifts. In the presence of CH₂Cl₂, the CsPbBr₃ NCs displayed a linear peak shift (from 510 nm to 460 nm) in CH₂Cl₂ concentrations of 0–0.9 M, with an LOD of 48 mM. Similarly, In the presence of CH₂Br₂, CsPbBr_{0.5}I_{2.5} displayed a linear PL peak shift (from 660 nm to 560 nm) in CH₂Br₂ concentrations of 7.2–21.0 mM, with an LOD of 1.7 mM. Although the results of this work look appealing, improvement in LODs is required before commercialization. Saikia et al. used cetyltrimethylammonium bromide (CTAB)-passivated CsPbBr₃ to effectively discriminate ethanol and methanol [117]. Due to the different interaction modes with CTAB, CsPbBr₃ displayed diverse PL "turn-off/turn-on" responses with LODs down to 9.3 ppb. This technique has been validated in petrol and cough syrup samples; therefore, it is quite innovative.

Bahtiar et al. described the employment of CsPbBr₃ NCs for quantifying the benzoyl peroxide (PBO) concentration in solutions [118]. When adding oleylammonium iodide (OLAM-I), the PL emission of CsPbBr₃ NCs at 515 nm was redshifted to 660 nm via the halide exchange reaction. When BPO was added to the above solution, the original PL emission was blueshifted within 1-2 min. Zhang and co-workers also used luminescent CsPbBr₃ NCs (synthesized with the hot-injection method; PLQY = 87%) to detect BPO [119]. The linear range of BPO detection was observed between 0 μ M and 120 μ M, with an LOD of 0.13 μ M. The applicability of both reports was demonstrated in white flour and noodles. Thus, this is a unique method for BPO detection. Huangfu et al. confirmed the highly responsive photoluminescence sensing performance of CsPbBr₃ quantum dots (QDs) for total polar material (TPM) identification in edible oils [120]. As seen in Figure 12, the CsPbBr₃ QDs display diverse colorimetric and PL emissive responses to individual polar solvents (dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), methanol, acetonitrile, ethanol, 1-propanol, acetone, ethyl acetate, chloroform, dichloromethane, and toluene). This TPM detection was effectively applied in edible oils, such as olive oil, soybean oil, and sunflower oil. Hence, it is regarded as an innovative method for the real-time quality assessment of edible oil.



Figure 12. Photos of the effect of different polar solvents on CsPbBr₃ QD solution. The solvents are arranged basically in the order of increasing dipole moment: (1) DMSO, (2) DMF, (3) methanol, (4) acetonitrile, (5) ethanol, (6) 1-propanol, (7) acetone, (8) ethyl acetate, (9) chloroform, (10) dichloromethane, and (11) toluene; (**a**) under ambient light, (**b**) under 365 nm UV light (permission obtained from Ref. [120]).

Zhao and co-workers developed orange-emitting oil-soluble CsPbBr_{1.5}I_{1.5} QDs for detecting excessive acid number (AN), 3-chloro-1,2-propanediol (3-MCPD), and moisture content (MC) for edible oil quality assessment [121]. The PL emission of the CsPbBr_{1.5}I_{1.5} QDs at 609 nm was quenched when detecting excessive acid number (AN). The peak at 609 nm was blueshifted to 583 nm when 3-MCPD was detected. For MC detection, mesoporous silica-coated CsPbBr_{1.5}I_{1.5} QDs were adopted as ratiometric sensors to develop water-stable green-emitting CsPbBr₃ nanosheet (NS) probes. The LODs were determined for the detection of AN, 3-MCPD, and MC as 0.71 mg KOH/g, 39.8 µg/mL, and 0.45%, respectively. Based on these results, this work can be regarded as innovative. Aamir et al. demonstrated the use of CsPbBr₃ microcrystals for the PL-based detection of nitrophenol [122]. The PL emission was quenched rapidly due to the π - π stacking interaction of the benzene ring with CsPbBr₃ microcrystals. PL emission was quenched linearly in nitrophenol concentrations of 0.1–0.6 mM. This study reported a preliminary result, thereby requiring more research work.

Chen et al. reported the use of CsPbX₃ QDs (Br/I; synthesized via the hot-injection method; PLQY = 52.88% and 46.18%, respectively) for the highly selective detection of explosive picric acid (PA) [123]. In which, the green/red fluorescence of CsPbX₃ (Br/I) at 510 nm/675 nm was quenched in the presence of PA. The linear regression of CsPbX₃ (Br/I) to PA was in the ranges of 0–180 nM and 0–270 nM, with estimated LODs of 0.8 nM and 1.9 nM, respectively. Based on the supported evidence, the authors speculated that the electrostatic-assisted energy transfer is the possible sensor mechanism. Figure 13 displays a schematic model of the CsPbBr₃ QD-based quenching response to PA and its paper-strip application. This is outstanding work, but additional research is necessary for commercialization. Aznar-Gadea and co-workers described the consumption of molecularly imprinted CsPbBr₃ nanocomposites for rapid explosive taggant detection at the gaseous stage [124].



Figure 13. Schematic for the sensitive fluorescence detection of PA based on perovskite quantum dots and its paper-strip applications (permission obtained from Ref. [123]).

A molecularly imprinted polymer (MIP) sensor was fabricated by embedding CsPbBr₃ NCs in polycaprolactone (PCL). When exposed to template molecules, such as 3-nitrotoluene (3-NT) and nitromethane (NM), PL quenching responses (>75%) were observed. The MIP sensor showed high selectivity to NT within 5 s, with an LOD of 0.218 mg mL⁻¹. This is a preliminary work; hence, it should be further extended for commercialization. Table 3 summarizes the synthetic route, PLQY, linear range, LOD, and application of CsPbX₃ (X = Cl, Br, and I) and composites toward the detection of chemicals and explosives.

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
CsPbBr ₃ NCs	Hot-injection method; NA	CH ₃ I	PL peak shift	0.7–70 μM	$\begin{array}{c} 0.2\pm 0.07\\ \mu M \end{array}$	NA	[114]
Yttrium single- atom-doped CsPbBr ₃ NCs	Hot-injection method; NA	CH ₃ I	PL peak shift	5.6–157 μM	0.3 μΜ	NA	[115]
CsPbX ₃ (X = Cl, Br, or I) NCs	Hot-injection method; NA	CH ₂ Cl ₂ and CH ₂ Br ₂	PL peak shift	0–0.9 M and 7.2–21 mM	48 mM and 1.7 mM	Microfluidic application	[116]
CsPbBr ₃ NCs	NA	Benzoyl peroxide	Peak shift and Ratiometric detection	NA	NA	Food sample analysis	[118]
CsPbBr ₃ NCs	Hot-injection method; 87%	Benzoyl peroxide	Peak shift and Ratiometric detection	0 μM–120 μM	0.13 μΜ	Food sample analysis	[119]
CsPbBr ₂ I microcrystals	Hot-injection method; NA	Nitrophenol	PL Quenching	0.1–0.6 mM	NA	NA	[122]
CsPbBr ₃ and CsPbI ₃ QDs	Hot-injection method; 52.88% and 46.18%, respectively	Picric acid	PL Quenching	0–180 nM and 0–270 nM, respectively	0.8 nM and 1.9 nM, respectively	Paper-strip analysis	[123]

Table 3. The synthetic route, PLQY, linear range, LOD, and application of $CsPbX_3$ (X = Cl, Br, and I) and composites toward the detection of chemicals and explosives.

NA = not available; μ M = micromole (10⁻⁶ M); nM = nanomole (10⁻⁹ M); mM = millimole (10⁻³ M).

Critical View on CsPbX₃ (X = Cl, Br, and I)-Based Chemical and Explosive Sensors

The detection/quantification of specialized chemicals, such as CH_3I , CH_2Cl_2 , CH_2Br_2 , benzoyl peroxide, and excessive acid number (AN), via anion exchange mechanisms [114–121] cannot be regarded as a specific quantification procedure because of its similarity to anion detection. This should be critically investigated to pursue the "state-of-the-art" sensing procedure. Since the observed ratiometric PL responses are also similar to those in the anion sensing studies, critical investigations are required for commercialization. Furthermore, discriminating explosives was demonstrated via the PL quenching response resulting from surface interaction and charge transfer between nitro-containing explosives and CsPbX₃ (X = Cl, Br, and I)-based probes or composites [122–124]. However, this also requires critical studies to justify the exact static/dynamic PL quenching responses.

6. CsPbX₃ (X = Cl, Br, and I) and Composites for the Quantification of Gaseous Analytes and Volatile Organic Compounds (VOCs)

Many CsPbX₃ (X = Cl, Br, and I) and composites have also been reported for the detection of gaseous analytes and VOCs, as described in this section. Huang et al. reported the oxygen-sensing performance of CsPbBr₃ NCs [125]. NCs have a porous structure, which allows for the rapid diffusion of O₂, resulting in PL quenching. The underlying sensor mechanism is that O₂ molecules are directly involved in the extraction of photogenerated electrons from the conduction band of CsPbBr₃ NCs. This work lacks in-depth sensor investigations, thereby requiring extensive research. Lin et al. developed Mn^{2+} -doped cesium lead chloride nanocrystals (Mn:CsPbCl₃ NCs) by using a heat-up strategy for sensing O₂ via luminescent dopants and the host–dopant energy transfer mechanism [126]. As seen in Figure 14a–e, upon exposure to O₂, the phosphorescence intensity of Mn:CsPbCl₃ NCs decreased linearly between 0 and 12% of O₂. High sensing reversibility, rapid signal response, and high photostability in air were also demonstrated. The estimated Stern–Volmer quench-



ing constant (K_{SV}) value following first-order kinetics was 0.0658% [O_2]⁻¹ ($R^2 = 0.9997$). This work is innovative, but it lacks practical applications.

Figure 14. Sensing responses of the $Mn_{0.175}$:CsPb_{0.825}Cl₃ film to O₂: (**a**) Phosphorescence spectra under different O₂ fractions (%). (**b**) The first-order reaction kinetics curves of the maximum phosphorescence intensities under different O₂ fractions (%). (**c**) Stern–Volmer plot under O₂ fractions between 0 and 12%. (**d**) Reversibility test under the alternating exposure to 100% O₂ or 100% N₂ (detected at 586 nm). (**e**) The response time curve within one cycle test. (**f**) Photostability test in air condition (excited at 365 nm) (permission obtained from Ref. [126]).

Brintakis and co-workers described the use of CsPbBr₃ nanocubes as self-powered ozone sensors, which showed higher sensitivity (54% in 187 ppb) and faster responses (between 100 s and 150 s) and recovery (between 250 s and 320 s) [127]. The sensor response of CsPbBr₃ nanocubes to O₃ was recorded between 4 and 2650 ppb (ppb = parts per billion). The as-synthesized CsPbBr₃ nanocubes were semiconductors with a certain resistance. When exposed to O₃, an accumulation layer of holes with lower resistance covering the whole surface of the nanocubes was formed resulting in an increase in electrical current. This is an innovative work, which has attracted many scientists to work in this direction. Park et al. fabricated cesium lead bromide nanofibers (CsPbBr₃ NFs) by attaching CsPbBr₃ NCs with cellulose nanofibers (CNFs) for N₂-sensing investigations [128]. When exposed to N₂ flow, the PL intensity of the CsPbBr₃ NFs at 520 nm was quenched linearly between 1 and 20 ppm (R₂ = 0.99433; ppm = parts per million) with an LOD of 1 ppm. The surface trapping of N₂ was proposed as the underlying mechanism for N₂ detection. This is a study on a conventional sensor, but further research is still necessary.

Nanocrystalline ZnO sensitized with CsPbBr₃ NCs for the photoresistive sensing of NO₂ gas was proposed by Chizhov and co-workers [129]. In a temperature range of 25–100 °C, the ZnO/CsPbBr₃ nanocomposite showed a linear sensor response between 0.5 and 3.0 ppm to NO₂. These sensing measurements were conducted under periodic blue LED illumination (light = t_{dark} = 20 s; LED = light emitting diode). At 1 ppm of NO₂ gas, it was found that the optimum temperature to provide the best reversibility of sensor measurements was 75 °C. Under periodic illumination, the increase in the electron concentration of ZnO led to the adsorption of oxidizing molecules over the surface. The photoexcited holes in CsPbBr₃ were involved in the redox reaction, resulting in a change in the electrical signal. This research is an impressive report, and it could be further developed for commercialization. Yueyue et al. demonstrated the use of CsPbBr₃ QD/ZnO MB nanocomposites (MBs = microballs) for NO₂ detection at room temperature [130]. In the

presence of diverse CsPbBr₃ QDs (0.5 wt%, 1.0 wt%, and 1.5 wt%) with ZnO MBs, the sensing responses to NO₂ were recorded. ZnO MB composited with 1.0 wt% QDs displayed a greater photoresistive response to NO₂ (for 5 ppm NO₂; R_{gas}/R_{air} = 53; response/recovery time = 63s/40s under 520 LED (1.2 W/m²) illumination). The adsorption and desorption of NO₂ over the ZnO surface were proposed as the underlying mechanism, and the QDs had minimal effect on the sensor mechanism. This is a well-developed study on NO₂-sensing studies of CsPbBr₃-ZnO conjugates, but more studies on the interference and real-time applications are required.

The ultrafast sensing of NO₂ was demonstrated using FA_{0.83}Cs_{0.17}PbI₃ (FAC) prepared via one-step spin-coating in ambient conditions [131]. When exposed to NO₂ (20, 10, 5, 2, 1, and 0.5 ppm), the photoresistive responses (R_{gas}/R_{air}) were measured as 2.64, 2, 1.52, 1.27, 1.17, 1.1, respectively. The optimum sensor response of NO_2 was recorded at 10 ppm, with a response/recovery time of 2 s/22 s. The strong oxidizing ability of NO_2 gas attracts electrons from FAC, which is a p-type semiconductor. The calculated values of the adsorption energy (E_{ads}) of NO₂ of FA⁺ and Cs⁺ in FACs are -0.37 and -0.60 eV, respectively, thereby allowing for the spontaneous adsorption of NO₂. It should be noted that NO₂ molecules attached to FACs may induce lattice distortion, which leads to a dipole moment and the migration of charge carriers. All these factors were involved in the sensing of NO₂. The roles of FA⁺ and Cs⁺ in detecting NO₂ were clearly justified. Further research in this direction is required to improve the sensitivity. Wang and co-workers combined ZnO nanorods with CsPbBr₃/Cs₄PbBr₆ particles to afford the CsPbBr₃/Cs₄PbBr₆/ZnO composite, which showed photoresistive sensor responses to NO (100 ppm), with the R_{gas}/R_{air} reaching 2296 (at 50 °C) and an LOD of 1 ppm [132]. The response and recovery time were determined as 1235 s and 173 s, respectively. NO gas attracts electrons from the surface of CsPbBr₃/Cs₄PbBr₆/ZnO to release O₂, which results in electrical signal changes. Although electrons were accumulated in the conduction band of ZnO, the diffusion of NO gas was hindered due to the covering layer of CsPbBr₃/Cs₄PbBr₆ particles. Therefore, a long response time was recorded. This work requires further research for the optimization of the response/recovery time and interference studies.

Chen et al. described the use of luminescent CsPbBr₃ QDs (synthesized via the sonication method) for the solution-mediated detection of hydrogen sulfide (H₂S) [133]. As seen in Figure 15A,B, the luminescent intensity of QDs at 520 nm was quenched linearly between 0 and 100 μ M with an LOD of 0.18 μ M. Note that the QDs exhibit a greater selectivity to H₂S among all the interfering species, as shown in Figure 15C. H₂S penetrated the surface of QDs and reacted with Pb²⁺ to form PbS, which resulted in fluorescent quenching. The applicability of this work was demonstrated in rat brain samples; therefore, it can be considered a unique report. Luo and co-workers synthesized a CsPbBr₃@CMO nanocomposite by encapsulating CsPbBr₃ QDs with cetyltrimethylammonium bromide and mineral oil via sonication. The composite was stable in water and was applied for detecting H₂S [134]. When adding H₂S, the PL emission of CsPbBr₃@CMO at 524 nm was quenched linearly in the range of 0.15–105 μ M, with an estimated LOD of 53 nM. The sensor response was attributed to the formation of PbS originating from H₂S and excessive Pb²⁺ present in CsPbBr₃ QDs. The high selectivity and applicability of CsPbBr₃@CMO to H₂S were confirmed by interference studies and rat brain investigations.

A water-soluble CsPbBr₃@sulfobutylether- β -cyclodextrins nanocomposite was synthesized via sonication and employed as a photothermal sensor [135]. The H₂S acted as a switch to trigger a photothermal response, which resulted in PL quenching (at 520 nm). The linear regression of H₂S was observed between 0.5 μ M and 6 mM with an LOD of 0.3 μ M. This work involved zebra fish-based in vivo studies, but it lacks interference investigations; therefore, further research is mandatory. Shan et al. reported the utilization of tributyltin oxide (TBTO)-capped CsPbBr₃ QDs (CsPbBr₃-Sn QDs) for the chemoresistive sensing of H₂S [136]. The sensor response (R_{gas}/R_{air}) at 100 ppm H₂S reached 6.69, with a response/recovery time of 278 s/730 s. The sensitivity of H₂S could reach 0.58 at 250 ppb. During the adsorption of H₂S, the charge distribution of the internal CsPbBr₃-Sn QDs

was affected by a metalloorganic TBTO molecule, thereby leading to enhanced sensing performance. On the other hand, the sensor performance was affected by the interaction between H_2S and $CsPbBr_3$ QDs through PbS formation. This is an innovative work, but the response still needs to be improved with more interference studies.



Figure 15. (**A**) Fluorescence spectra of CsPbBr₃ QDs upon the addition of different concentrations of H_2S . The concentration of H_2S from top to bottom was $0-100 \ \mu$ M. (**B**) A linear relationship between the fluorescence intensity of CsPbBr₃ QDs and H_2S concentration. (**C**) Changes in fluorescence intensity of CsPbBr₃ QDs in the presence of H_2S (100 μ M) and other interfering agents (1 mM) (permission obtained from Ref. [133]).

Chen et al. described the fabrication of photoresistive sensors comprising a porous network of CsPbBr₃, which can generate an open-circuit voltage of 0.87 V under visible light irradiation, to be employed in O_2 and VOC (acetone and ethanol) detection [137]. The device showed 100% photocurrent enhancement for O_2 with a corresponding response and recovery time of 17 s and 128 s under visible light irradiation. At 1 ppm of acetone/ethanol (at 30 °C; illumination density = 37.8 mW cm⁻²), the device displayed sensor responses $(I_{VOC}/I_{air} - 1)$ of 0.03 and 0.025 with a response/recovery time of >200 s/400 s, respectively. The sensor response was attributed to surface lattice changes. This work needs further optimization to improve the sensor response and response/recovery time before commercialization. Xuan et al. proposed the use of stable ZnO-coated CsPbBr₃ NCs (CsPbBr₃@ZnO NCs, synthesized using an in situ technique) for the photoresistive detection of heptanal (breath biomarker) at room temperature [138]. The sensor response of CsPbBr₃@ZnO NCs at 200 ppm heptanal was measured as S = 0.36 (S = $I_h - I_0/I_0$, where I_h and I_0 represent the current values in the presence and absence of heptanal gas, respectively) with response/recovery time of 36.5 s/5.3 s. Note that the LODs were down to 2 ppm in air and 3 ppm under artificial conditions. The heptanal-induced lattice distortion was attributed as the underlying mechanism for the sensor response. This method can facilitate the early detection of lung cancer and COVID-19. This is an innovative work and should be extensively studied with interfering species toward biomedical applications. CsPbBr₂I was also reported as a self-powered sensor for reducing and oxidizing gas molecules via surface adsorption and desorption [139]. Because this device detects multiple gaseous analytes, the possibility of an interfering effect cannot be ruled out.

Liu and co-workers reported triethylamine (TEA) detection by using CsPbBr₃- decorated ZnO polyhedrons derived from ZIF-8 [140]. ZnO-CsPbBr₃ showed a higher photoresistive sensor response to TEA (~60 for 100 ppm at 180 °C) than pristine ZnO and ZnO NP-CsPbBr₃. Note that the ZnO-CsPbBr₃ also displayed shorter response and recovery times of 2 s and 18 s with an LOD of 5 ppb. The sensor response is due to the adsorption of oxygen molecules in the air onto the surface of ZnO-CsPbBr₃, which generates oxygen anions to initiate a redox reaction when exposed to TEA. Based on the reported sensing performance, this work is innovative, but it requires more research to optimize interference studies. Xu et al. demonstrated the sensing performance of CsPbBr₃ to ethanolamine (EA), in which a high response (R_{gas}/R_{air} = 29.87 for 100 ppm EA) with a response/recovery time of 62 s/782 s and an LOD of 21ppb were reported [141]. Figure 16 shows the EA sensing performance of CsPbBr₃, reversibility, and linear ranges to EA. Following the reaction Formulas (2) and (3), the adsorbed O_2 molecules on the CsPbBr₃ surface generate O_2^- anions, which further reduce EA to generate sensor signals.

$$O_2(gas) + e^- \to O_2^- (ads)$$
⁽²⁾

 $H_2NCH_2CH_2OH + 3O_2^- \rightarrow NH_2OH + 2CO_2 + 2H_2O + 3e^-$ (3)



Figure 16. Gas sensitivity test of the CsPbBr₃ gas sensor at 13% RH: (**a**) Selective response to 100 ppm of different test gases. (**b**) Response curve to different concentrations of EA at RT. The error bars were taken from 5 sets of data. (**c**) Dynamic response curve; the inset shows that the response is linearly related to the low concentration of EA of less than 50 ppm. (**d**) Repeatable response curve of the CsPbBr₃ sensor to 50 ppm EA at RT (permission obtained from Ref. [141]).

Shortly after, the same research group as in Ref. [141] demonstrated using the 3mercaptopropionic acid (MPA)-regulated heterojunction of CsPbBr₃ NPs/ZnO NPs for detecting EA [142]. The hydrophilic groups in MPA enhance the stable anchoring of ZnO over the CsPbBr₃ surface via hydrogen bond-facilitated MPA network structures. The O₂ molecules anchored on ZnO generated O₂⁻ species, which interacted with EA via a redox reaction to generate a sensor signal. At 100 ppm of EA, CsPbBr₃-2MPA/ZnO displayed a chemoresistive sensor response of 13.23 with a response/recovery time of 50 s/698 s and an LOD of 31 ppb. This work is innovative, judging from its supportive evidence in interference studies and the justification of the underlying mechanism. Nevertheless, further optimization to maximize the sensor signal is still required. CsPbBr₃ NC-anchored aminefunctionalized graphene oxide (GO) was demonstrated in the electrochemiluminescence (ECL)-based detection of cupric oleate in acetonitrile containing 10 mM of tripropylamine (TPrA) [143]. The ECL response for the cupric oleate showed a decreasing trend in the range of $10^{-18}-10^{-16}$ M with LODs down to the attomolar (10^{-18} M) level. This is a preliminary study, thereby requiring additional efforts. Thiophene sulfides are one of the harmful contaminants of air pollutants; hence, their detection becomes vital. Feng and co-workers proposed the use of CsPbBr₃ NCs and CsPbBr₃/SiO₂ NCs for detecting diverse thiophene sulfides [144]. Benzothiophene (BT), dibenzothiophene (DBT), 2-methylbenzothiophene (2-MeBT), 3-methylthiophene (3-MeBT), and thiophene (TP) were discriminated using the fluorescent quenching method, as seen in Figure 17. The linear regression of BT, DBT, 2-MeBT, and TP detection was observed between 10 and 50 ppm. As for t3-MTP, linearity was observed between 20 and 50 ppm. The fluorescence of perovskite NCs can be effectively weakened by thiophene sulfides to varying degrees due to the different interactions between thiophene sulfides and CsPbBr₃/SiO₂ NCs. Hence, this method can be adopted for both quantitative and qualitative detection of thiophene sulfides. This work is impressive in terms of its qualitative and quantitative measurements.



Figure 17. Schematic illustration of the discrimination principle of the fluorescent sensor array for thiophene sulfides based on two perovskite NCs (permission obtained from Ref. [144]).

A method involving dynamic passivation over the surface of CsPbBr₃ QDs (synthesized using the hot-injection method) was proposed by Huang et al. for the PL-enhanced detection of ammonia (NH₃) [145]. In this study, the luminescence of purified QD film was enhanced when exposed to NH₃. The linear range of PL enhancement at 610 nm was between 25 and 300 ppm with an LOD of 8.85 ppm. The photoluminescent response and recovery times were determined as 10 s and 30 s, respectively, at room temperature. In particular, this innovative work explains the analysis at room temperature. Following a similar approach, the employment of CsPbBr_{1.5}Cl_{1.5} QDs, CsPbBr₃ QDs, and CsPbBr_{1.5}I_{1.5} QD films for the PL "turn-on" detection of ammonia (NH_3) was demonstrated [146]. As illustrated in Figure 18, the QD films display exceptional selectivity among other interferences. All these films display good linear behavior (25–200 ppm) and LODs of \approx 20 ppm. The uniqueness of this passivation method is well demonstrated by these reports, and hence it can be extended for developing commercialized devices for the detection of ammonia (NH₃). Similar to the "turn-on" detection, a few CsPbX₃-conjugated materials were also proposed for the discrimination and quantification of NH_3 via PL quenching responses. Humidity-resistant CsPbBr₃–SiO₂ nanocomposites, porous nanofibers/nanocomposites (CsPbBr₃ NFs and CsPbBr₃/BNNF; BNNF = boron nitride nanofiber), and stable CsPbBr₃ QDs grown within Fe-doped zeolite X were proposed for the PL-quenched detection of NH_3 [147–150]. The adsorption and desorption of NH_3 over the surface of these nanocomposites resulted in reversible cycles with given linear ranges and LODs. Table 4 summarizes the synthetic route, PLQY, linear ranges, LODs, and applications of CsPbX₃ (X = Cl, Br, and I) and composites toward the detection of gas and VOCs.

Figure 18. (**a**–**c**) The responses of CsPbBr_{1.5}Cl_{1.5}, CsPbBr₃, and CsPbBr_{1.5}I_{1.5} perovskite QD film sensors to various gases (permission obtained from Ref. [146]).

Table 4. The synthetic route, PLQY, linear range, LOD, and application of $CsPbX_3$ (X = Cl, Br, and I) and composites toward the detection of gas and VOCs.

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
Mn:CsPbCl ₃ NCs	Heat-up strategy; NA	O ₂	PL quenching	0–12%	NA	NA	[126]
CsPbBr ₃ NFs	Hot-injection method; NA	N ₂	PL quenching	1–20 ppm	1 ppm	NA	[128]
CsPbBr ₃ QDs	Sonication Method; NA	H ₂ S	PL quenching	0–100 µM	0.18 µM	Rat brain studies	[133]
CsPbBr ₃ @CMO	Sonication followed by compositing method; NA	H ₂ S	PL quenching	0.15–105 μΜ	53 nM	Rat brain studies	[134]
CsPbBr3@SBE-β- CD nanocomposite	Sonication followed by compositing method; NA	H ₂ S	PL quenching	0.5 μM– 6 mM	0.19 μΜ	Zebrafish studies	[136]
CsPbBr3/NCM composite	Hot injection followed by EDC–NHS method; NA	tripropyla- mine (TPrA) and Cesium oleate	Electrochem- iluminescence (ECL) signals	10 mM and NA	NA and 1 aM	NA	[143]
CsPbBr ₃ /SiO ₂ NCs	Precursor injection followed by compositing method; NA	Thiophene Sulfides	PL quenching	10–50 ppm	$\approx 10 \text{ ppm}$	NA	[144]
CsPbBr ₃ QD film	Hot-injection method; NA	NH ₃	PL enhancement	25–300 ppm	8.85 ppm	Film-based sensor study	[145]
$CsPbX_3$ (X = Cl, Br, I or mixed halogen) QD film	Hot-injection method; NA	NH ₃	PL enhancement	25–200 ppm	\approx 20 ppm	Film-based sensor study	[146]
CsPbBr ₃ -SiO ₂ nanocomposites on PVDF membrane	controllable strategy; NA	NH ₃	PL quenching	2160– 3600 ppm	NA	Test paper study	[147]
CsPbBr ₃ NFs	Hot-injection method followed by electrospinning; NA	NH ₃	PL quenching	528 μM– 1.76 mM	<0.5 mM	NA	[148]

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
CsPbBr ₃ /BNNF composites	Hot-injection method followed by compositing method; ~54%	NH ₃	PL quenching	NA	NA	NA	[149]
CsPbX ₃ (X = Cl, Br, and I) QDs @Fe/X-n	Hydrothermal crystallization followed by in situ growth of QDs; NA	NH ₃	PL quenching	0–10 mL	NA	NA	[150]

Table 4. Cont.

NA = not available; mM = millimole (10^{-3} M); μ M = micromole (10^{-6} M); nM = nanomole (10^{-9} M); aM = attomole (10^{-18} M); ppm= parts per million.

Critical View on the Detection of $CsPbX_3$ (X = Cl, Br, and I)-Based Gases and VOCs

Combining CsPbX₃ (X = Cl, Br, and I) with different materials can result in composited materials with exceptional electro-optical properties and less defect, which can be adopted in the design of PL-based probes, electrochemiluminescence probes, chemoresistive sensors for discriminating N₂, O₂, H₂S, tripropylamine (TPrA), thiophene sulfides, and NH₃ [125–150]. To achieve the above goal, compositing ratios need to be optimized. Changes in the compositing ratios may significantly affect selectivity, thereby requiring careful/critical adjustments. The detection of H₂S was demonstrated in rat brain and zebrafish studies [133–135], but there is no clear indication of how to overcome the toxicity induced by Pb²⁺ in CsPbX₃. The film- or test-strip-based sensing of NH₃ mostly displayed dependence on the crystalline and morphological features of CsPbX₃ (X = Cl, Br, and I) and composites. Thus, optimizing the crystallinity/morphology of thin film is critical to attaining the best results.

7. Humidity, Temperature, and Radiation/Photodetection by $CsPbX_3$ (X = Cl, Br, and I) and Composites

Humidity and moisture are the main causes resulting in perovskite material degradation, which affects the practical use and commercialization of perovskite-based energy devices [151]. The water molecules in the air react with the metal halide perovskite surface, which rapidly affects the morphology and uniformity, resulting in changes in optical properties and conductivity [152]. The above effect is the major mechanism of humidity-sensing responses. Doping with specified metal ions can improve the environmental stability of metal halide perovskites and reduce the humidity effect on the surface/morphology [153]. Due to the structural distortion (phase change) and instability of CsPbBr₃, its composites can be effectively employed for the trace detection of water and humidity (%RH). For example, dimethyl aminoterephthalate-functionalized CsPbBr₃ QDs (CsPbBr₃@DMT-NH₂ QDs) were synthesized with a low-temperature method and engaged in trace water detection in edible oils [154]. The PL emission at 530 nm was quenched in trace water (0.05–5%; v/v) with ratiometric enhancement at 445 nm. The LOD (3σ /slope) and limit of quantification (LOQ; 10σ /slope) were 0.01% and 0.04%, respectively. The involvement of the IFE, FRET, aggregation of QDs, and disintegration were proposed as the underlying mechanisms. This work is notable and can be extended to detect water traces in oils and chemicals. Thereafter, Xiang and co-workers described the luminescent quenching response of CsPbBr₃ to trace water in herbal medicines [155]. The PL intensity at 503 nm was quenched linearly with water contents of 1–17%. The values of LODs in Seutellaria baicalensis and Astragalus flavone were 0.75% and 0.67%, respectively.

These materials also show a great response to varying humid conditions with a linear behavior between 33 and 98% RHs and an estimated LOD of 12% RH, as visualized in

Figure 19. A phase change from CsPbBr₃ to CsPb₂Br₅ was attributed as the mechanism for the observed PL quenching response to water and RH. The recovery of RH in the above herbals was in the range of 96.7–102.5%; therefore, this is noted as an inspiring work. The utilization of CsPbBr₃ NPs in impedance-based humidity-sensing (under 20 mV) studies was also proposed [156]. The CsPbBr₃ NPs were operative in the humidity range of 11–95% with a response/recovery time of 2.8 s/9.7 s and a sensitivity of 1.56% RH. This is also an inspiring work that can be further explored in commercial electrochemical device fabrication.

Figure 19. (**A**) PL images of paper substrates loading CsPbBr₃ perovskite. (**B**) PL images of papersubstrate-loading CsPbBr₃ exposed to different RHs. (**C**) Humidity-dependent PL spectra of CsPbBr₃ perovskite loaded on paper substrates. (**D**) Calibration curve for detecting different RHs, n = 3(permission obtained from Ref. [155]).

Variations in temperature led to changes in phase and grain sizes [157], which can be adopted in temperature sensors via monitoring changes in I–V responses, PL intensity, absorbance, etc. On the other hand, alterations in temperature also affected the grain uniformity and morphologies of CsPbX₃ and composites [158], resulting in changes in the PL intensity and current density. However, the doping of metal ions may also improve the temperature sensitivity of CsPbX₃ and composites [159], as illustrated in this section. The doping of metal ions may enhance the sensitivity of CsPbX₃ and composites. For example, Chang et al. described the temperature-sensing ability of Mn²⁺-doped CsPbCl₃ QDs (CsPbCl₃:0.1Mn²⁺ QDs; PLQY = 47.3%) via a dual-mode luminescent response at 298–353 K [160]. In this study, the stability of QDs was improved by replacing Pb²⁺ with Mn²⁺. For the 6% Mn²⁺-doped CsPbCl₃ QDs, the PL intensity at 410 nm and 600 nm was quenched considerably compared with those of undoped CsPbCl₃ QDs (quenching was observed at 410 nm only), as seen in Figure 20.

Figure 20. Temperature-dependent emission spectra of (**a**) $CsPbCl_3$ and (**b**) $CsPbCl_3:6\%$ Mn^{2+} QDs in the range of 298 K–353 K. The integrated emission intensity centered at (**c**) approximately 410 nm and (**d**) approximately 600 nm as a function of temperature (permission opted from Ref. [160]).

The 6% Mn^{2+} -doped CsPbCl₃:QDs displayed 83% and 22% quenching at 410 nm and 600 nm, respectively. Using the fluorescence intensity ratio (FIR) and full width at half-maximum (FWHM), the maximum relative sensitivity (SR) of CsPbCl₃:0% Mn^{2+} was 7.38% K⁻¹ at 298 K and 2.13% K⁻¹ at 353 K. Although this is a follow-up work of earlier reports [161,162], which also demonstrated the temperature-sensing ability through the dual-mode fluorescent response, its results are impressive. Moreover, Mn^{2+} -doped CsPbCl₃@glass [161] and Mn^{2+} -doped CsPbCl₃ NCs [162] were employed as dual-mode luminescent sensors in temperature ranges of 80–293 K and 80–30 K, respectively.

Similar to Mn^{2+} doping, Eu^{3+} -doped cesium lead halide perovskite glasses (Eu^{3+} : CsPbCl₂Br₁ QDs and Eu^{3+} :CsPbBr₃ QDs) were also used as effective materials in optical temperature-sensing studies [163,164]. With increasing temperature from 80 K to 440 K and 93 K to 383 K, both Eu^{3+} :CsPbCl₂Br₁ QDs and Eu^{3+} :CsPbBr₃ QD glasses displayed blueshifted PL quenching at 458 nm (excitation at 395 nm) and 519 nm (excitation at 394 nm), respectively. For Eu^{3+} :CsPbCl₂Br₁ QD glass, the absolute temperature sensitivity maxima (S_a) and the relative temperature sensitivity (S_r) were established as 0.0315 K⁻¹ and 3.097%/K, respectively. Similarly, the S_a and S_r values of Eu^{3+} :CsPbBr₃ QD oxyhalide glass were 0.0224 K⁻¹ and 2.25% K⁻¹. Figure 21 shows the optical quenching response of one of the Eu^{3+} :CsPbBr₃ QD oxyhalide glass samples (S3) between 93 K and 383 K. These results also suggest that metal doping can enhance the temperature-sensing ability of cesium lead halide perovskites and composites for future device development.

CsPbCl_xBr_{3-x} NCs confined in hollow mesoporous silica (CsPbCl_{1.2}Br_{1.8} NCs@h-SiO₂) and integrated with K₂SiF₆:Mn⁴⁺ phosphor in the EVA polymer matrix (EVA = ethylene–vinyl acetate) were proposed by Huang and co-workers for reversible temperature sensing [165]. The high density of halide vacancies played a vital role in temperature sensing between 30.0 °C and 45.0 °C. The temperature sensitivity was established as 13.44% °C⁻¹ at 37.0 °C. This is an inspiring work that investigates defects in sensor performance. Similarly, microencapsulated CsPbBr₃ NCs with K₂SiF₆:Mn⁴⁺ phosphor (CsPbBr₃-KSF-PS film) showed temperature sensitivity between 30 °C and 70 °C, with the S_r value reaching 0.31% °C⁻¹ at

45 °C [166]. A highly stable film with its fluorescence visible to the naked eye (green-to-red fluorescence) was achieved by optimizing the CsPbBr₃ and KSF ratio and applied for temperature sensing. Lu et al. developed dual-phase compounds containing CsPbBr₃ QDs (emission at 529 nm) and NaYF₄:Ho³⁺ NPs (emission at 647 nm and 751 nm) for conducting optical temperature sensing between 293 and 433 K at an excitation wavelength of 447 nm [167]. The nonradiative recombination between the energy band and the defective surface led to the thermal quenching of CsPbBr₃. S_a and S_r values of 385 K⁻¹ and 5.13% K⁻¹ were reported in this work. This is an interesting report among all the studies on temperature sensors.

Figure 21. (a) Temperature-dependent PL spectra of Eu^{3+} -doped PQDs@glass sample (S3). (b) Temperature-dependent PL spectra of CsPbBr₃ PQD emission. (c) Integrated emission intensity of CsPbBr₃ PQDs and Eu^{3+} as a function of temperature (permission obtained from Ref. [164]).

The use of cesium lead halides and composites in radiation/photo detection was proposed by numerous researchers [168–180]. Ti/Ni/CsPbBr₃/Ni/Ti (with ER of 5.70% at 8250 V·cm⁻¹; ER = energy resolution) [153], single crystals of CsPbBr₃ (with diverse hole mobilities) [169–172,175], In/LiF/CPB/Au detectors [173], CsPbBr₃ QDs embedded in P₃HT:PC₆₁BM (P₃HT:PC₆₁BM:QD; a bulk heterojunction photodiode) [174], CsPbBr₃ microcrystals on ITO functional substrate [176], a single-crystalline thin film of CsPbBr₃ (CsPbBr₃ SCF; switching ratio = 3.2×10^3 , and response time = 200/300 ns) [177], CsPbBr₃/RGO nanocomposites (RGO = reduced graphene oxide) [178], CsPbBr₃ QD/ZnO NWs nanocomposites [179], and ZnONW/CsPbBr₃ QD/graphene heterojunction were demonstrated for X-ray, radiation, and photodetection. Ion migration, photon-exciton coupling, electron-hole diffusion, and strain-based mechanisms were proposed as the underlying mechanisms for the radiation/photodetection. Most of the proposed cesium lead halide-based composites showed exceptional performance. For example, P₃HT:PC₆₁BM:QD [174] displayed good current density and X-ray photocurrent response by optimizing the weight ratio, as depicted in Figure 22. Since there are several reviews available on the radiation/photodetection performance of perovskites [14–19,32,61,63], they will not be discussed here.

Figure 22. (a) Dark J–V curves of the hybrid OPD with different weight ratios of $P_3HT:PC_{61}BM:QD$. (b) Dark current densities of hybrid OPDs under -3 V bias. (c) The X-ray response of the device with the weight ratio of 1:1:1 under various bias voltages. (d) The X-ray response of the hybrid OPDs with different QD weight ratios (dose rate: 27.14 mGy s⁻¹). (e) X-ray photocurrent of devices with different QD weight ratios under a reversed bias varying from -0.1 to -5 V. (f) The linear response of the OPD device with a weight ratio of 1:1:2 at different dose rates (permission obtained from Ref. [174]).

Critical View on the Detection of $CsPbX_3$ (X = Cl, Br, and I)-Based Humidity, Temperature, and Radiation/Photodetection

The low stability and degradation of CsPbX₃ (X = Cl, Br, and I) and composites were adopted as sensor responses for humidity detection [151–156]. However, reports on = humidity sensors also discussed the recovery, which is problematic due to the environmental instability issue of the CsPbX₃ (X = Cl, Br, and I) and composites. Thus, CsPbX₃ (X = Cl, Br, and I) and composite-based recovery of humidity sensors must be carefully examined. Phase transitions may occur in CsPbX₃ (X = Cl, Br, and I) and composites during temperature sensing [157–167]; thus, in-depth investigations are critical in many cases involving phase transitions. Likewise, doping of ions, such as Mn²⁺, may enhance the phase changes, which requires a more careful examination. When detecting photon/radiation, lattice defects could be generated in CsPbX₃ (X = Cl, Br, and I). This problem can be alleviated by using composites with diverse materials [168–180]. However, the compositing ratios must be critically evaluated to achieve better sensing results.

8. CsPb X_3 (X = Cl, Br, and I) and Composites in the Detection of Bioanalytes, Drugs, Fungicides, and Pesticides

Cesium lead halides and composites were applied in discriminating biologically significant analytes, as described in this section. Niu and co-workers constructed a dualemitting nanoprobe consisting of CsPbBr3 NCs and red-emissive Cu NCs (CsPbBr3@Cu nanohybrid) for the luminescent detection of hydrogen peroxide (H_2O_2) and glucose [181]. CsPbBr₃@Cu nanohybrid with PL emission centered at 517 nm and 645 nm displayed ratiometric responses to H_2O_2 and glucose. A linear ratiometric response at F_{645}/F_{517} was observed in the ranges of 0.2–100 μ M and 2.0–170.0 μ M with LODs of 0.07 μ M and $0.8 \,\mu$ M, respectively, when recognizing H₂O₂ and glucose. The electron-transfer-induced redox reaction was considered to be the underlying sensor mechanism. This method was also demonstrated for glucose detection in human serum samples with an impressive RSD value of < 4%. The TiO₂/CsPbBr₁ ₅I₁ ₅ composite film and CsPbCl₃/TiO₂ served as inverse opal electrodes for the photoelectrochemical discrimination of dopamine (DA) and alpha-fetoprotein (AFP), respectively [182,183]. Slow volatilization was used to fabricate electrodes. The detection of DA showed a linear response between 0.1 and 250 μ M, with an LOD of 12 nM, and the detection was also demonstrated in human serum samples [167]. Therefore, it is noted as an impressive report. On the contrary, the detection of AFP showed a linear regression between 0.08 and 980 ng/mL with an LOD of 30 pg/mL [183]. However, this report lacks information on real-time applications.

Saikia et al. reported the utilization of CsPbBr₃ microcrystals (via one-pot synthesis; PLQY = 60%) as a sensing probe for the fluorometric detection of uric acid (UA) via hydrogen bonding interactions [184]. The PL of CsPbBr₃ microcrystals at 520 nm (green to blue) was dynamically quenched within a response time of 30 s in the presence of UA. The linear regression of UA was observed between UA concentrations of 3.1 nM and 1.33 μ M with an LOD of 0.063 ppm. This is a remarkable work with applications in human serum samples. Wang and co-workers described a ratiometric fluorescent approach for sensing acetylcholinesterase (AChE; 57 kDa protein; dispenses nerve impulse spread) by using the CsPbBr₃ NC-TPPS nanocomposite (synthesized via self-assembly strategy; PLQY = 60%; TPPS = Tetraphenylporphyrin tetrasulfonic acid) [185]. The ratiometric response at F_{520}/F_{650} to AChE showed a linear response between 0.05 and 1.0 U/L, with an LOD of 0.0042 U/L. Investigations of AChE quantification in human serum samples displayed >95% recovery, with an RSD of <4%. This is an interesting work with low interfering effects and real-time applicability. CsPbBr₃ QDs and CsPbBr₃ QD/MoS₂ (MoS₂ = molybdenum sulfide) nanoflakes were proposed as chemiluminescence biosensors for human hepatitis B, immunodeficiency virus, and AFP via the sandwich complex formation [186]. In this work, the CsPbBr₃ QD/MoS₂ nanoflakes were fabricated by including a parylene-C passivation layer. This is an interesting photosensor for multianalyte detection, which can be extended for commercialization.

Hu et al. reported the use of water-stable CsPbX₃ (X = Br/I) as a probe for the sensitive detection of penicillamine (PA) [187]. Firstly, CsPbBr₃ (PL maxima at 525 nm) interacted with iodide via an anion exchange reaction to afford CsPbX₃ (X = Br/I), which displayed PL emission at 580 nm. As shown in Figure 23, the PL intensity increases accompanied by a blueshift when adding PA between 5.0 and 35.0 nM. The linear regression of PA quantification was observed between 5.0 and 35.0 nM, with LOD values of 1.19 nM (PL intensity vs. PA concentration) and 5.47 nM (PL peak shift vs. PA concentration). Based on the results from high-angle annular dark-field (HAADF) imaging and multiple investigations with organic S-containing substances, the interaction of the sulfhydryl group present in penicillamine with iodide is identified as the underlying sensor mechanism. This is an inspiring work in detecting PA in water. Through a one-pot synthetic method, stable carboxyl group-functionalized CsPbBr₃–COOH QDs were developed by using amino-

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poly(ethylene glycol)-carboxyl and perfluorooctyltriethoxylsilane as ligands and were engaged in the PL "turn-on" detection of Mycobacterium tuberculosis (Mtb) [188].

Figure 23. Detection of D-PA by CsPbX₃ (Br/I) PNCs: (a) The 3D photoluminescence spectrum. (b) The 2D photoluminescence spectra and photos of corresponding samples at 365 nm (inset). The linear relationship between (c) relative intensity of photoluminescence and D-PA concentration, (d) photoluminescence wavelength shift, and D-PA concentration (permission obtained from Ref. [187]).

CsPbBr₃–COOH QDs were composited with MoS₂ and deoxy nucleic acid (DNA) to afford CsPbBr₃ QD-DNA/MoS₂ for the effective detection of Mtb via PL enhancement. Mtb showed a linear response between 0.2 and 4.0 nM, with an LOD of 51.9 pM. This work involved the clinical analysis of tuberculosis pathogens and thereby is noted as an innovative work. CsPbBr₃ QDs composited with MoS₂ and passivated with parylene (C, N, and F) were utilized in microbial detection [189] and photo-sensing of bioanalytes. An anodic electrochemiluminescence-based assay of alkaline phosphatase (LOD = 0.714 mU L⁻¹; mU = milli units) was also proposed using CsPbBr₃ QDs [190]. In both reports, charge/ electron transport plays a vital role in the detection mechanism.

Li and co-workers used phospholipid-coated CsPbBr₃ NCs for the effective detection of pore-forming biotoxins and prostate-specific antigens via dual-readout assays [191,192]. By using fluorometric and electrochemical assays, the pore-forming biotoxins were detected by CsPbBr₃ NCs@PL, which showed a linear regression between 50 nM and 150 μ M with an LOD of 50 nM [160]. Likewise, the detection of prostate-specific antigens by CsPbBr₃ NCs@PL displayed a linear PL enhancement and colorimetric response in the ranges of 0.01–80 ng/mL and 0.1–15 ng/mL, with calculated LODs of 0.081 ng/mL and 0.29 ng/mL, respectively [192]. Both reports were applied in bacterial and clinical analyses, and they can be noted as innovative bioanalytical research. Qi et al. designed a composite consisting of of aptamer-functionalized CsPbBr₃ NCs and magnetic nanoparticles of Fe₃O₄ (MNPs), namely the "Apt-PNCs@cDNA-MNPs" material, for detecting peanut allergen Ara h1 in food samples [193]. In their study, the CsPbBr₃ NCs were employed as PL labeling probes for collecting fluorescent data. Also, the interaction of Ara h1 with aptamer resulted in PL recovery. The Apt-PNCs@cDNA-MNPs showed linear PL enhancement between 0.1 and 100 ng/mL, with an estimated LOD of 0.04 ng/mL. In terms of the reported real-time studies in food samples, this research can be regarded as inspiring work and should be extended toward food safety monitoring.

Similar to bioanalytes, cesium lead halide perovskites were also employed in the selective and sensitive quantification of drugs. 3-Aminopropyltriethoxysilane-functionalized CsPbBr₃ QDs (APTES-IPQDs), mesoporous silica nanoparticle-composited CsPbBr₃ QDs (LMSNs@IPQDs), perofluorooctyltriethyloxylsilane fluorocarbon-assembled Cs₄PbBr₆/CsPbBr₃ NPs (CPB-PFOS), molecularly imprinted CsPbBr₃ QDs (IPQDs@MIPs), and CsPbBr₃ QD/BN composites (BN = boron nitride) were used in detecting tetracycline (TC; antibiotic drug) by means of photoinduced electron transfer (PET) or the inner-filter effect (IFE) mechanism [194–198]. All these materials displayed linear TC detection ranges in micro- to millimolar levels with estimated LODs at a nanomolar or micromolar concentration, as listed in Table 5. Moreover, these reports can further attest to the applicability of TC detection in food, water, and soil samples for possible commercialization. Figure 24 illustrates the PL quenching response of CPB-PFOS to TC and the related linear response [196].

Figure 24. (a) Response of FL intensity of different concentrations of CPB-PFOS aqueous solution in the presence of 25 mM of TC, where F and F₀ are FL intensity with and without TC, respectively. (b) The spectra of an aqueous solution of 5% (v/v) of CPB-PFOS samples with different concentrations of TC under an excitation of 355 nm wavelength. (c) Relationship between TC concentration and FL intensity log((F₀ – F)/F₀) = 3.281 + 0.7259 × log(C_{TC}(M)) with R² = 0.986 (permission opted from Ref. [196]).

Shi et al. described the sensing utility of CsPbBr₃ NCs toward the quantification of ciprofloxacin hydrochloride (an antibiotic) via PL peak shifting induced by anion exchange [199]. In the presence of ciprofloxacin hydrochloride, the transformation from CsPbBr₃ NCs to CsPbBr_(3-x)Cl_x NCs occurred together with a corresponding peak shift from 513 nm to 442 nm via anion exchange. The PL peak shift was achieved between 0.8 and 50 mM, with an LOD of 0.1 mM. Though this work was applied in colorimetric paper-strip analysis, additional research is still required to lower the LODs. Through an in situ hot-injection method, CsPbBr₃-loaded MIP nanogels were developed and employed for discriminating roxithromycin (ROX; an antibiotic) via PL quenching responses [200]. The nanogels showed linear PL quenching behavior between 100 pM and 100 nM, with an LOD of 20.6 pM in detecting ROX. Phase transformation and structural decomposition were

proposed as the mechanisms underlying ROX detection. This work was applied in animalderived food analysis, and hence it can be regarded as an inspiring work toward biomedical applications. Salari and co-workers adopted CsPbBr₃ QDs (PLQY = 42%) in an organic phase, together with Fe(II) and K₂S₂O₈, in an aqueous medium for the chemiluminescencebased detection of cefazolin (CFZ; an antibiotic) [201]. A chemiluminescence response of CsPbBr₃ QDs in the presence of Fe(II) and K₂S₂O₈ was observed in CFZ concentrations of 25–300 nM with an LOD of 9.6 nM at pH 7. This report was demonstrated with recoveries of >90% in multiple real samples, such as human plasma, urine, water, and milk samples. Although this is an interesting work, further research must be conducted to optimize experimental conditions.

Water-stable luminescent $CsPbBr_3/Cs_4PbBr_6$ NCs were synthesized using a water emulsion technique and demonstrated for sensing folic acid (FA; vitamin B) [202]. The $CsPbBr_3/Cs_4PbBr_6$ NCs showed a linear PL quenching response between 10 and 800 μ M of FA, with an LOD of 1.695 μ M. The quenching response was attributed to the electrostatic mechanism between NCs and FA. This work was demonstrated through a urine sample-based recovery (>99% with <0.5% RSD). It is a preliminary work on cesium lead halide-based FA detection. He et al. fabricated molecularly imprinted polymer-encoded $CsPbX_3$ (X = Cl, Br, and I) microspheres for quantitatively detecting Sudan I (a food colorimetric enhancer) [203]. The PL emission of CsPbBr₃, CsPbCl_{1.5}Br_{1.5}, and CsPbI₂Br microspheres was recorded at 463 nm, 508 nm, and 644 nm, respectively. Interestingly, MIP-CsPbBr₃ microspheres showed a greater response to Sudan I than nonimprinted ones (NIP-CsPbBr₃), as shown in Figure 25. A linear range of between 2 and 604 nM with an estimated LOD of 1.21 nM was recorded for detecting Sudan I by MIP-CsPbBr₃. This work was effectively applied in foodstuffs (egg and chili), which showed >95% recovery. Therefore, it can be utilized in commercial food safety monitoring. Thereafter, barium sulfate-coated cesium lead bromide nanocrystals (CsPbBr₃ NCs@BaSO₄) were proposed for the PL-enhanced quantitation of melamine [204]. The PL emission of CsPbBr₃ NCs@BaSO₄ was quenched via the IFE when adding Au NPs. When adding melamine to the above conjugate, the PL emission was restored to the original intensity via the weakening of the IFE. A linear detection range of melamine was recorded between 5 nM and 5 μ M with an LOD of 0.42 nM. Through using this method, >95% recoveries of melamine in raw milk samples were achieved with <4% RSDs. This is an inspiring and innovative work for melamine monitoring. Su et al. fabricated a $CsPbBr_3/a-TiO_2/FTO$ electrode for the photoelectrochemical immunoassay of aflatoxin B1 (AFB₁; a carcinogen) by compositing $CsPbBr_3$ NCs with amorphous titanium dioxide (TiO₂) [205]. A linear regression of AFB₁ detection by CsPbBr₃/a-TiO₂/FTO electrode was observed between 32 pM and 48 nM with an LOD of 9 pM. This work was confirmed by recoveries (ranging between 90.2% and 109.0%) in peanut and corn samples; therefore, it can be regarded as one of the most inspiring photoelectrochemical analytical methods.

The employment of CsPbX₃ (X = C, Br, and I) and composites toward the quantification of pesticides, insecticides, and fungicides has also been demonstrated by many researchers. CsPbBr₃ QDs (PLQY = 96%), CsPbBr₃ QD-coated MIPs (PLQY = 92%), CsPbI₃ QDs (PLQY = 27%), MIP/CsPbBr₃ QD composites, and MIP-mesoporous silica-embedded CsPbBr₃ QDs were demonstrated for discriminating ziram (a fungicide), omethoate (an organophosphorus insecticide), clodinafop (an herbicide), phoxim (an organophosphate insecticide), and dichlorvos (2,2-dichlorovinyl dimethyl phosphate; an insecticide), respectively, via PL quenching responses [206–210]. These composites were developed using diverse methods, such as room-temperature-controlled synthesis, the slow hydrolysis of the capping agent, microwave synthesis, self-assembly, etc. It should be noted that cesium lead halide composites have displayed exceptional linear regression with excellent LODs and have been applied in real-time food stuff/soil analysis, as detailed in Table 5. Moreover, all these composites showed negligible interfering effects from competing species, which is rather unique. For example, the MIP/CsPbBr₃ QD composite [209] displayed greater selectivity than other interferences, as seen in Figure 26. Table 5 summarizes the synthetic

route, PLQY, linear range, detection limit, and application of $CsPbX_3$ (X = Cl, Br, and I) and composites toward the detection of bioanalytes, drugs, fungicides, and pesticides.

Figure 25. Effect of different concentrations of Sudan I (0–300 μ g L⁻¹) on the fluorescence spectra of (**a**) MIP-CsPbBr₃ and (**b**) NIP-CsPbBr₃ probe; insets of (**a**,**b**) represent the corresponding calibration curve; fluorescence response of MIP-CsPbBr₃ probe on (**c**) Sudan I, structural analogs, amino acids, and (**d**) some ions (permission obtained from Ref. [203]).

Figure 26. Response performance of the MIP/QDs and NIP/QDs to different OPPs (0.13 μ M; OPPS = organophosphorus pesticides) (permission opted from Ref. [209]).

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Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
CsPbBr ₃ @Cu nanohybrid	In situ synthesis; NA	H ₂ O ₂ and Glucose	Ratiometric PL response	0.2–100 μM and 2–120 μM	0.07 μM and 0.8 μM	Human serum analysis	[181]
TiO ₂ /CsPbBr _{1.5} I _{1.5} composite film	Slow volatilization method; NA	Dopamine (DA)	Photoelectro- chemical (PEC) detection	0.1–250 μM	12 nM	Human serum analysis	[182]
TiO ₂ IOPCs/CsPbCl ₃	slow volatilization method; NA	alpha- fetoprotein (AFP)	Photoelectro- chemical (PEC) detection	0.08– 980 ng/mL	30 pg/mL	NA	[183]
CsPbBr ₃ microcrystals	one-pot synthesis method; 60%	Uric acid (UA)	PL quenching	3.1 nM–1.33 μM	0.063 ppm	Human blood serum analysis	[184]
CsPbBr ₃ NC-TPPS nanocomposite	Self-assembly strategy; 60%	Acetylcho- linesterase (AChE)	PL quenching	0.05–1.0 U/L	0.0042 U/L	Human serum analysis	[185]
CsPbX ₃ (X = Br/I) PNCs	Anion exchange method; NA	Penicill- amine	PL enhancement	5.0–35.0 nM	1.19 nM and 5. 47 nM	NA	[187]
CsPbBr ₃ QD-DNA/MoS ₂ NS	One-pot synthetic method; NA	Mycobac- terium tubercu- losis (Mtb)	PL enhancement	0.2–4.0 nM	51.9 pM	Clinical tuberculosis pathogen analysis	[188]
CsPbBr ₃ NCs@PL	Film hydration method; NA	Pore- forming biotoxins	PL quenching	50 nM– 150 μM	50 nM	Bacterial study	[191]
Phospholipid- coated CsPbBr ₃ NCs	Film hydration method; NA	Prostate- specific antigen (PSA)	PL enhancement and colorimetric sensing	0.01– 80 ng/mL and 0.1– 15 ng/mL	0.081 ng/mL and 0.29 ng/mL	Clinical sample analysis	[192]
Apt-PNCs@cDNA- MNPs	One-pot synthesis, magnetic stirring, and sonication; NA	Peanut allergen Ara h1	PL enhancement	0.1– 100 ng/mL	0.04 ng/mL	Food sample analysis	[193]
APTES- functionalized CsPbBr ₃ QDs	Slow hydrolysis of the capping agent; 46.86%	Tetracycline	PL quenching	0.5–15.0 μM	76 nM	Soil sample analysis	[194]
LMSNs@CsPbBr ₃ QDs	Water emulsion followed by homogeneous mixing; ~54%	Tetracycline	PL quenching	0.7–15 μΜ	93 nM	Water sample analysis	[195]
Cs ₄ PbBr ₆ /CsPbBr ₃ NPs	Temperature- controlled synthesis; NA	Tetracycline	PL quenching	0.4–10 μM	76 nM	Food sample analysis	[196]

Table 5. The synthetic route, PLQY, linear range, detection limit, and application of $CsPbX_3$ (X = Cl, Br, and I) and composites toward the detection of bioanalytes, drugs, fungicides, and pesticides.

Composition	Synthetic Route; PLQY (%)	Analyte	Method of Detection	Linear Regression	Detection Limit (LOD)	Applications	Ref.
Molecularly imprinted CsPbBr ₃ QDs	Water emulsion followed by homogeneous mixing; NA	Tetracycline	PL quenching	0.2–5 μΜ	28 nM	Water sample analysis	[197]
CsPbBr ₃ @BN	Hot injection followed by calcination; NA	Tetracycline	PL quenching	0–99 μM	14.6 μΜ	Honey and milk samples analysis	[198]
CsPbBr ₃ NCs	Hot-injection method; NA	Ciproflox- acin hydrochlo- ride	PL peak shift	0.8–50 mM	0.1 mM	Paper-strip analysis	[199]
CsPbB _{r3} -loaded MIP nanogels	In situ hot-injection method; NA	Roxithro- mycin	PL quenching	100 pM– 100 nM	20.6 pM	Animal-derived food product analysis	[200]
CsPbBr ₃ QDs	ligand-assisted reprecipitation method; 42%	Cefazolin	Chemilumin- escence	25–300 nM	9.6 nM	Human plasma, urine, water, and milk samples analysis	[201]
Water-stable fluorescent CsPbBr ₃ /Cs ₄ PbBr ₆ NCs	Water emulsion method; NA	Folic acid	PL quenching	10–800 μM	1.695 µM	Urine sample analysis	[202]
MIP-CsPbX ₃ (X = Cl, Br, and I) fluorescent- encoding microspheres	Encoding of MIPs with CsPbX ₃ QDs: NA	Sudan I	PL quenching	2-604 nM	1.21 nM	Food sample analysis	[203]
CsPbBr ₃ NCs@BaSO4	Aqueous emulsion process; 80.3%	Melamine	PL enhancement	5 nM–5 μM	0.42 nM	Spiked dairy sample analysis	[204]
CsPbBr ₃ /a- TiO ₂ /FTO	Hot injection followed by compositing; NA	Aflatoxin B1 (AFB ₁)	Photoelectro- chemical im- munoassay	32 pM-48 nM	9 pM	Food sample analysis	[205]
CsPbBr ₃ QDs	Room- temperature- controlled synthesis; 96%	Ziram	PL quenching	0.1–50 ppm	0.086 ppm	Food sample analysis	[206]
CsPbBr ₃ QDs coated MIPs	Slow hydrolysis of the capping agent; 92%	Omethoate	PL quenching	0–1.9 µM	88 nM	soil and cabbage samples analysis	[207]
CsPbI ₃ QDs	Microwave synthesis; 27%	Clodinafop	PL quenching	0.1–5 μM	34.7 nM	Food sample analysis	[208]
MIP/CsPbBr ₃ QD composite	Hot injection followed by self-assembly method; NA	Phoxim	PL quenching	16.8– 335.4 nM	4.9 nM	Food sample analysis	[209]
MIP-mesoporous silica-embedded CsPbBr ₃ QDs	Multiple synthetic methods; NA	Dichlorvos	PL quenching	23–110 nM	5.7 nM	Food sample analysis	[210]

Table 5. Cont.

NA = not available; mM = millimole (10^{-3} M); μ M = micromole (10^{-6} M); nM = manomole (10^{-9} M); pM = picomole (10^{-12} M); ng = microgram (10^{-9} g); pg = picogram (10^{-12} g); ppm = parts per million.

Critical View on the Detection of $CsPbX_3$ (X = Cl, Br, and I)-Based Bioanalytes, Drugs, Fungicides, and Pesticides

The stability of CsPbX₃ (X = Cl, Br, and I) in water is the main issue for discriminating bioanalytes, drugs, fungicides, and pesticides [181–210]. To avoid the above complications, compositing CsPbX₃ (X = Cl, Br, and I) with other materials, such as APTES, BN, and MIPs has been proposed. However, there are still a few probes that require critical evaluation in terms of structural degradation in aqueous media. Water-stable CsPbBr₃/Cs₄PbBr₆ NCs were proposed for detecting folic acid [202], but how long can the proposed structure remain stable is still under debate. Another controversial issue regarding CsPbX₃ (X = Cl, Br, and I) and composite-based biomolecule sensing is how to avoid the toxicity of Pb²⁺ in food sample analysis. Consequently, the sensor's selectivity to specific analytes requires careful investigation in many reports. Detecting pesticides and fungicides in real samples using CsPbX₃ (X = Cl, Br, and I) and composites needs critical analysis to overcome the toxicity induced by Pb²⁺.

9. Cellular Imaging Applications of CsPbX₃ (X = Cl, Br, and I) and Composites

Getachew et al. and Kar et al. described the cellular imaging utility of magnesiumand zinc-doped cesium lead halides, namely CsMg_xPb_{1-x}I₃ QDs and zinc-doped CsPbBr₃- Cs_4PbBr_6 nanocomposites [211,212]. The doping of metal ions in perovskite quantum dots could result in stability and biocompatibility improvement. In CsMg_xPb_{1-x}I₃ QDs, Mg^{2+} partially substituted Pb^{2+} in the CsPbI₃ framework [211]. When encapsulating CsMgxPb_{1-x}I₃ QDs with gadolinium-conjugated pluronic 127 (PF127-Gd), PQD@Gd nanoagents were achieved, which were applied in ROS detection in cancer cells and photocatalytic studies. The Zn^{2+} doping in CsPbBr₃-Cs₄PbBr₆ NCs (emission at 494–506; nm, ; PLQY = 88%) improved the stability compared to bare NCs in highly polar solvents [212]. Moreover, the zinc-doped ensemble showed greater biocompatibility, thereby becoming effective in cellular imaging, as visualized in Figure 27. In this report, silicacoated CsPbBr₃-Cs₄PbBr₆@(OA)₂PbBr₄ (core-shell NCs synthesized via the LARP method using (3-amino-propyl)trimethoxysilane [APTMS]) without zinc doping were labeled as NC-0. The NCs with 20%, 40%, 60%, and 80% zinc doping were labeled as NC-20, NC-40, NC-60, and NC-80, respectively. NC-40 was engaged in cellular imaging studies because of its exceptional biocompatibility and stability. Similarly, CsPbBr₃@SiO₂ core-shell, CsPbBr₃/SiO₂/mPEG-DSPE NCs (mPEG-DSPE = polyethylene glycol-grafted phospholipid), and phTEOS-TMOS@CsPbBr₃ NCs (TMOS and phTEOS represent the alkoxysilanes) were also demonstrated in bioimaging studies [213–215]. SiO₂-coated CsPbBr₃ core–shell structures reduced the toxicity and made NCs more effective for in vitro cellular imaging [213]. Hydrophobic CsPbBr₃/SiO₂ encapsulated with mPEG-DSPE showed better water stability and photostability; thus, they can be applied in multiphoton bioimaging [214]. CsPbBr₃ NCs coated with alkoxysilanes showed improved stability, water dispersibility, and lower toxicity and thus can be used in two-photon cellular imaging studies [215].

Many research groups reported the preparation of encapsulated CsPbX₃ (X = C, Br, and I) and composites with a polymer matrix to maintain the structural and emission stability of cesium lead halides. Methoxypolyethylene glycol amine-capped CsPbBr₃ NCs (CsPbBr₃/mPEG-NH₂ NCs), polyvinylidene fluoride (PVDF)-encapsulated CsPbBr₃, poly-vinyl pyrrolidone (PVP)-capped CsPbX₃ NCs, poly(lactic-co-glycolic acid) (PLGA)-encapsulated CsPbBr₃ QDs, and polystyrene-block-poly(acrylic acid) (PS-b-PAA) were developed with high water stability, greater biocompatibility, and low toxicity; thus, they can be applied in long-term cellular imaging studies [216–220]. For cellular imaging of cesium lead halide perovskites, Lou et al. synthesized insoluble CsPbBr₃/CsPb₂Br₅-composited NCs (PLQY = 80%) via water-assisted chemical transformations and HeLa cellular imaging studies [221]. Judging from the synthetic simplicity and low toxicity, this work can be regarded as inspiring. However, more investigations on structural stability and PL emission are required.

Figure 27. Biocompatibility of NC-40 with mammalian cells. NCs (blue) are internalized by cells and do not associate with mitochondria (green) or lysosomes (red). Higher concentrations of NCs have a detrimental effect on cells as mitochondrial and lysosomal structures become atypical. NCs, nanocrystals (permission obtained from Ref. [212]).

Critical View on CsPbX₃ (X = Cl, Br, and I)-Based Cellular Imaging

It has been argued that cellular imaging using CsPbX₃ (X = Cl, Br, and I) could be hindered due to the unstable emission properties of CsPbX₃ in aqueous media. To avoid the instability issue, capping CsPbX₃ (X = Cl, Br, and I) with suitable ligands, such as 3-amino-propyl)trimethoxysilane (APTMS), polyethylene glycol-grafted phospholipid (mPEG-DSPE), and alkoxysilanes (TMOS and phTEOS) has been proposed. This capping could not only reduce toxicity due to Pb²⁺ but can also improve biocompatibility [211–215]. However, careful optimization is still required. Polymer capping, metal doping, and surface coating were also used to improve the biocompatibility of CsPbX₃ (X = Cl, Br, and I) in cellular imaging studies [216–221]. Nevertheless, critical assessments of toxicity profiles when applying these composites in cellular imaging still require much attention.

10. Advantages and Limitations

The employment of $CsPbX_3$ (X = Cl, Br, and I) and composites in sensing investigations has certain advantages and limitations, as noted below.

10.1. Advantages

- 1. Due to the unique structural features, tuning the photophysical properties of $CsPbX_3$ (X = Cl, Br, and I) and anion exchange can result in red, green, and blue emission with an enhanced PLQY (reaches up to 98%); therefore, PL-based sensors with relevant colorimetric responses can benefit from the above properties.
- The greater carrier mobility of CsPbX₃ (X = Cl, Br, and I) can be adjusted by combining with other semiconducting materials (such as MoS₂, graphene, mxenes, etc.), which is advantageous to the fabrication of heterojunction devices and electrodes for photo/chemoresistive and electrochemical detection of a specific analyte [222–225].

- 3. The capping and encapsulation of the proposed $CsPbX_3$ (X = Cl, Br, and I) system can enhance water stability, which allows for long-term tracking of bioanalytes.
- Core–shell/polymer encapsulation can produce a low-toxicity, biocompatible CsPbX₃ (X = Cl, Br, and I) conjugate, which can be applied in bioimaging with comparable performance to other lead-free perovskites and luminescent organic probes [226–229].
- 5. Advancing sensing studies in real samples is highly feasible with capped/functionalized CsPbX₃ (X = Cl, Br, and I) nanostructures; therefore, their performance can be comparable to other nanoprobes (nanoparticles, nanoclusters, nanowires, nanocomposites, etc.) [230–235].

10.2. Limitations

- 1. Many stable CsPbX₃ (X = Cl, Br, and I) and composites are fabricated using multiple synthetic steps, which require precision optimization. However, optimizing synthesis processes is time-consuming, which restricts the use of CsPbX₃ (X = Cl, Br, and I) as sensor probes.
- CsPbX₃ (X = Cl, Br, and I) and composites can degrade rapidly when exposed to air moisture, elevated temperature, humid conditions, etc., thereby limiting their sensing utility in harsh conditions [236–238].
- The major contributing factor for the sensing performance of CsPbX₃ (X = Cl, Br, and I) and composites has been attributed to structural/phase transformation [239,240]. Thus, it is questionable if reversible cycles in analyte detection can be realized.
- 4. To investigate the precise underlying mechanism of the sensing response to a specific analyte, supporting lines of evidence through methods, such as TEM, XPS, dynamic light scattering spectra (DLS), Zeta potential, etc., are necessary. Thus, the cost-effectiveness of research is questionable, which limits such sensor development in developing or underdeveloped countries.
- 5. Since real water samples may contain certain numbers of ionic species, the reliability of metal ion quantification by $CsPbX_3$ (X = Cl, Br, and I) and composites in real samples is still questionable. This limits the application of $CsPbX_3$ (X = Cl, Br, and I) probes toward the detection of metal ions and anions.

11. Conclusions and Perspectives

This article provides a detailed review of the sensing performance of CsPbX₃ (X = Cl, Br, and I) and composites toward the detection of analytes, such as metal ions, anions, chemicals, explosives, gases, volatile organic compounds, bioanalytes, humidity, temperature, radiation, etc. In particular, the involved synthetic methods in developing CsPbX₃ (X = Cl, Br, and I)-based sensor probes, the linear detection range, LODs, and real-time applicability were also tabulated for a broad audience. Discussions on the mechanistic aspects of analyte detection, novelty, deficiencies, and feasible directions were also extrapolated for readers. Finally, the bioimaging applications of CsPbX₃ (X = Cl, Br, and I)-based composites were illustrated for future biomedical research.

The following questions/perspective points must be addressed or focused on in future research: (A) There are many reports available on the employment of CsPbX₃ (X = Cl, Br, and I)-based probes toward Cu²⁺ quantification; hence, a state-of-the-art procedure for fabricating commercial sensors must be developed; (B) to date, the detection of Cu²⁺, Hg²⁺, Co²⁺, Zn²⁺, Cd²⁺, UO₂²⁺, In³⁺, and Fe³⁺ have been demonstrated using CsPbX₃ (X = Cl, Br, and I)-based probes, but the research direction should be further extended toward the sensing of monovalent (M⁺) cations, divalent (M²⁺) cations, trivalent (M³⁺) cations, etc., by optimizing the functional/capping agents; (C) the method can be further fine-tuned to develop an effective procedure for the commercialization of anion-exchange-facilitated detection of Cl⁻ and I⁻ by CsPbBr₃ toward real-time monitoring; (D) the optimization of csPbX₃ (X = Cl, Br, and I)-based probes to existing anions, such as SO₄²⁻, PO₄²⁻, P₂O₇²⁻, CN⁻, SCN⁻, etc.; (E) the anion-exchange-directed detection of alkyl halides, benzoyl

peroxide, and solvent polarity by $CsPbX_3$ (X = Cl, Br, and I) and composites requires in-depth investigation to confirm its novelty; (F) advancing CsPbX₃ (X = Cl, Br, and I) and composites toward the detection of toxic gases, such as carbon monoxide (CO), carbon dioxide (CO_2) , phosgene $(COCl_2)$, etc., must be the focus in future research; (G) numerous reports on CsPbBr₃-based NH₃ sensors are available; therefore, fabricating commercial NH₃-sensing devices must be the focus in future research; (H) research on humidity, temperature, radiation, and photodetection using $CsPbX_3$ (X = Cl, Br, and I) and composites can be expanded to include other nanostructures, such as graphene, metalorganic frameworks, nanosheets, nanotubes, etc.; (I) few reports are available on detecting essential bioanalytes, drugs, fungicides, and pesticides using CsPb X_3 (X = Cl, Br, and I) and composites; thus, more attention is required in this research direction; (J) in-depth (in vitro/in vivo) cellular imaging, tracking, and the underlying mechanisms of the imaging responses of CsPbX₃ (X = Cl, Br, and I) and composites and the construction of low-toxicity probes must be carried out in future research; (K) the majority of $CsPbX_3$ (X = Cl, Br, and I) and composite-based sensor reports lack theoretical support from density functional theory (DFT) calculations, which should be included in new sensor designs.

Apart from the above open questions and possible future research directions, sensing studies that involve composites of $CsPbX_3$ (X = Cl, Br, and I) toward the detection of diverse analytes require more innovative approaches to realize real-time applications. Many scientists are currently working on developing a "state-of-the-art" sensor procedure for the detection of diverse analytes. Thus, innovative breakthroughs can be expected in the near future.

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