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Highly DUV to NIR-II responsive broadband quantum dots heterojunction photodetectors by integrating quantum cutting luminescent concentrators

Nan Ding¹, Wen Xu^{1✉}, Hailong Liu¹, Yuhan Jing¹, Zewen Wang¹, Yanan Ji¹, Jinlei Wu¹, Long Shao¹, Ge Zhu^{1✉} and Bin Dong^{1✉}

Abstract

Low-cost, high-performance, and uncooled broadband photodetectors (PDs) have potential applications in optical communication etc., but it still remains a huge challenge to realize deep UV (DUV) to the second near-infrared (NIR-II) detection for a single broadband PD. Herein, a single PD affording broadband spectral response from 200 to 1700 nm is achieved with a vertical configuration based on quantum dots (QDs) heterojunction and quantum cutting luminescent concentrators (QC-LC). A broadband quantum dots heterojunction as absorption layer was designed by integrating CsPbI₃:Ho³⁺ perovskite quantum dots (PQDs) and PbS QDs to realize the spectral response from 400 to 1700 nm. The QC-LC by employing CsPbCl₃:Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs as luminescent conversion layer to collect and concentrate photon energy for boosting the DUV-UV (200–400 nm) photons response of PDs by waveguide effect. Such broadband PD displays good stability, and outstanding sensitivity with the detectivity of 3.19×10^{12} Jones at 260 nm, 1.05×10^{13} Jones at 460 nm and 2.23×10^{12} Jones at 1550 nm, respectively. The findings provide a new strategy to construct broadband detector, offering more opportunities in future optoelectronic devices.

Introduction

Photodetectors (PDs) with the ability to capture optical signals and convert them into electrical signals, are significance in optoelectronic applications^{1–4}. Particularly, uncooled broadband PDs capable of covering the near infrared (NIR) region with low-cost and high-performance are vital components for optical communication, national security, military monitoring, and bioimaging^{5–7}. Currently, the commercial broadband PDs were fabricated by mature materials with narrow bandgap, such as silicon (Si), indium gallium arsenide (InGaAs), and mercury cadmium telluride (HgCdTe) etc. With the rapid development of detection technology, they achieved

excellent response within visible to short-wave-NIR (eg., Si PDs)⁸ or the second near-infrared (NIR-II) region (eg., InGaAs PDs)⁹. However, to our knowledge, few of them are targeted to realize high performance in the whole region spanning from deep ultraviolet (DUV) to NIR-II. Previously, to construct fully spectral responsive PDs, two or more PDs should be integrated into one system, inevitably bringing about large size, high price, and especially for incomparable responsiveness among different PDs. Meanwhile, these PDs usually encounter with complex fabrication process and low temperature working conditions etc. All of these cause huge difficulties in practical applications.

All inorganic lead halide (CsPbX₃, X = Cl, Br or I) perovskite quantum dots (PQDs) have attracted numerous attention in solar cells, light-emitting diodes (LEDs), lasers and PDs, owing to their excellent light sensitivity, tunable bandgap, large absorption coefficient, and high

Correspondence: Wen Xu (xuwen@dlnu.edu.cn) or Ge Zhu (zhuge@dlnu.edu.cn) or Bin Dong (dong@dlnu.edu.cn)

¹Key Laboratory of New Energy and Rare Earth Resource Utilization of State Ethnic Affairs Commission, School of Physics and Materials Engineering, Dalian Minzu University, 18 Liaohe West Road, Dalian 116600, China

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collection efficiency of carriers^{10–16}. Especially, iodine based PQDs process narrow bandgap (~ 1.73 eV) with a wide spectral response, exhibiting a great potential for photoactive layer to constructing broadband PDs^{17–19}. Nevertheless, the current PDs based on CsPbI₃ PQDs still suffer from low sensitivity, slow response time, and poor stability, due to the high trap density and susceptibility to UV light and oxygen^{20–22}. In addition, its responsive wavelength was concentrated in UV–Visible region (350 nm–750 nm), incapable of covering the DUV–UV (200 nm–350 nm) and NIR (>750 nm) because of the insensitivity for DUV–UV light and limitation of bandgap^{23,24}. Therefore, how to overcome the above issues as the main challenges for obtaining broadband and high performance PDs.

Doping with lanthanide ions (eg., Ce³⁺, Eu³⁺, Eu²⁺, Sm³⁺, Nd³⁺, Er³⁺) has emerged to boost the optical and electrical performance of PQDs, such as improving the photoluminescence quantum yields (PLQYs), enhancing UV- and long term- stability, and decreasing the trap density^{25–29}. It is mainly assigned to their unique spectroscopic properties and atomic radii suitable for the tolerance factor of PQDs^{13,27,30–32}. Meanwhile, a hybrid structure combining perovskites with the organic or inorganic narrower bandgap semiconductor materials (e.g., BTP-4Cl:PBDB-TF, PbSe, HgTe, PbS) is one of a promising strategy to achieve high performance broadband PDs with NIR spectral response^{33–35}. Among them, lead sulfide (PbS) quantum dots (QDs) with easily adjustable absorption range to the NIR-II region via the size dependent quantum confinement^{36,37}. Besides, it has large absorption coefficient ($\sim 10^6$ M⁻¹ cm⁻¹) and better chemical stability³⁸.

Aiming at the low DUV–UV response of PDs, the downshifting luminescence materials provide an effective route to convert DUV–UV light into visible or NIR photons, and subsequently being recaptured by the integrated PDs^{8,23}. Various luminescent conversion materials including the quantum cutting materials with the PLQYs of $\sim 200\%$ have been implemented to significantly improve the UV response of solar cells or PDs (eg., Si and perovskites)^{39,40}. But the huge photon energy loss by directly integrating with photoelectric devices always happens, stemming from the random emission direction of luminescent conversion materials. Luminescent concentrator (LC) devices with directional emission consisting of transparent polymer sheets doped with luminescent species can collect and concentrate photon energy to minimize the photons loss through waveguide effect.

In this work, high PLQYs (93.5%) and stability, and less defects of CsPbI₃:Ho³⁺ PQDs were synthesized, served as the UV–Visible photoresponsivity layer for broadband PDs. To broaden the NIR-II response of broadband PDs, the PbS QDs with Visible–NIR absorption region were directly assembled on the surface of CsPbI₃:Ho³⁺ PQDs to

form a heterojunction composite. Meanwhile, the Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ doped CsPbCl₃ PQDs with the high PLQYs ($\sim 179\%$) were incorporated into the polymethyl methacrylate to prepare a quantum cutting LC (QC–LC), which can convert DUV–UV light into NIR photons and subsequently being recaptured by the integrated PDs. This broadband PDs consists of QC–LC and CsPbI₃:Ho³⁺–PbS QDs heterojunction to realize the full spectrum response spanning from 200 nm–1700 nm, showing the detectivity of 3.19×10^{12} Jones at 260 nm, 1.05×10^{13} Jones at 460 nm, and 2.23×10^{12} Jones at 1550 nm. Furthermore, this broadband PDs demonstrate outstanding air- and UV-stability and high-contrast imaging applications.

Results

In general, the commercial broadband PDs (UV–NIR) usually by integrating two or more PDs (eg., GaN, Si, and InGaAs) for detecting DUV to UV, Visible to short-wave–NIR, and NIR light (Fig. 1a), respectively, which can bring complex fabrication process and higher costs. Herein, we successfully fabricated a broadband responsive PD from DUV to NIR-II (200 nm–1700 nm) with the device structures of CsPbCl₃:Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs doped polymethyl methacrylate QC–LC / FTO / SnO₂ / CsPbI₃:Ho³⁺–PbS QDs heterojunction / MoO₃ / Au, as shown in Fig. 1b. The corresponding cross-sectional scanning electron microscope (SEM) image of the broadband PD is displayed in Fig. S1. In such devices, the CsPbI₃:Ho³⁺ PQDs with outstanding optoelectronic performance is responsible for UV–Visible light (350 nm–700 nm). The PbS QDs were prepared through hot injection method exhibits broadband absorption from 500 nm to 1700 nm (Fig. 1c). Then, they were assembled on the surface of CsPbI₃:Ho³⁺ PQDs via mechanical stirring, serving as the NIR-II absorption material. Finally, QC–LC with the strong absorption from 200 nm to 400 nm and efficiently converts them into typical NIR emission of Yb³⁺ and Er³⁺ through quantum cutting process (Fig. 1d). Consequently, these NIR photons can be further reabsorbed by the CsPbI₃:Ho³⁺–PbS QDs heterojunction, thereby expanding the response in DUV to UV region (Fig. 1e).

To obtain the high performance and broadband response in a single PD, a series of optical and electrical experiments were conducted. Firstly, to improve the performance of PQDs, lanthanide ions (Ho³⁺) was selected as dopant to incorporate into CsPbI₃ PQDs prepared by modified hot injection method^{41–43}. As revealed in the transmission electron microscope (TEM) and high-resolution TEM (HR-TEM) images (Fig. 2a and S2–S4), the undoped CsPbI₃ and CsPbI₃:Ho³⁺ PQDs with the similar cubic shape were obtained. The average size of CsPbI₃ PQDs is ~ 11.6 nm, which gradually decreases to ~ 11.4 nm, ~ 11.1 nm, ~ 10.8 nm and ~ 10.5 nm with increasing Ho³⁺ concentrations from 1.4% to 8.3%,

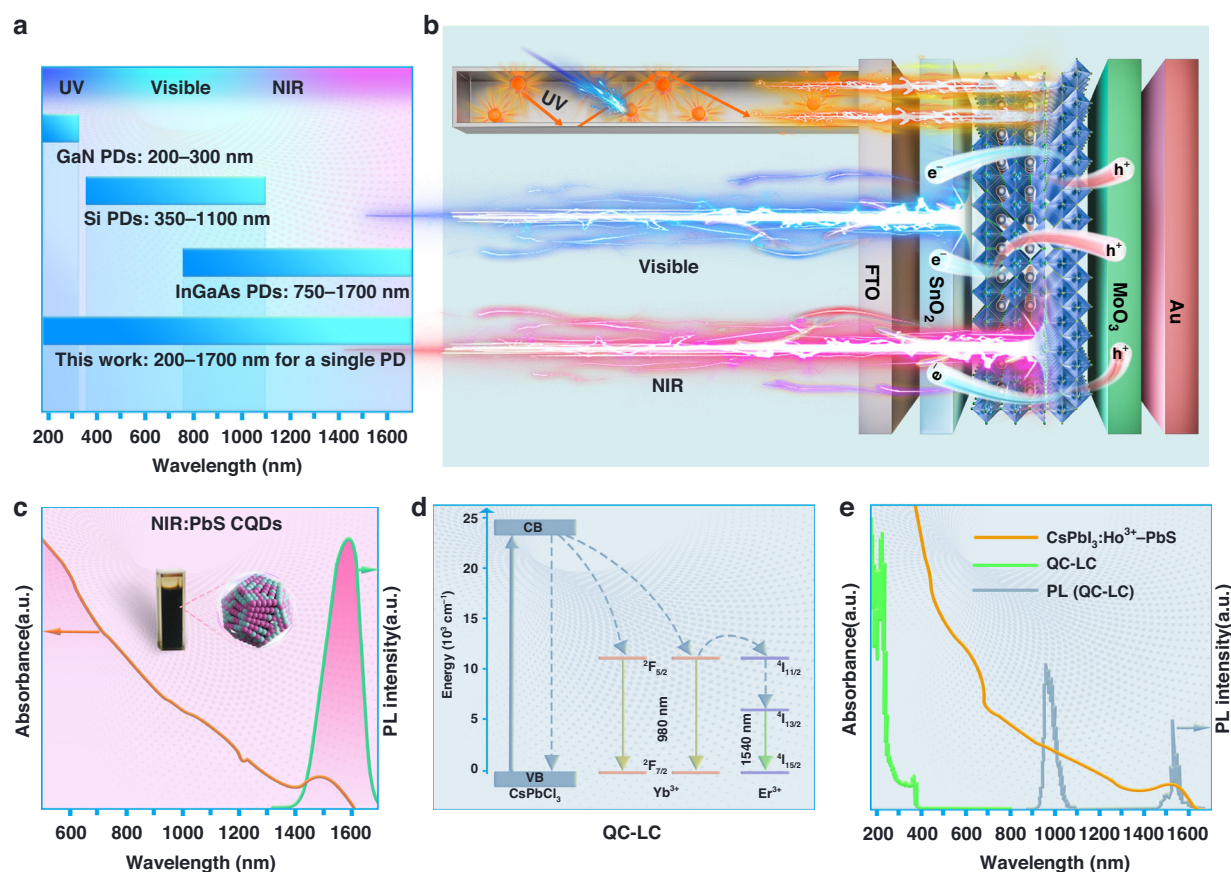
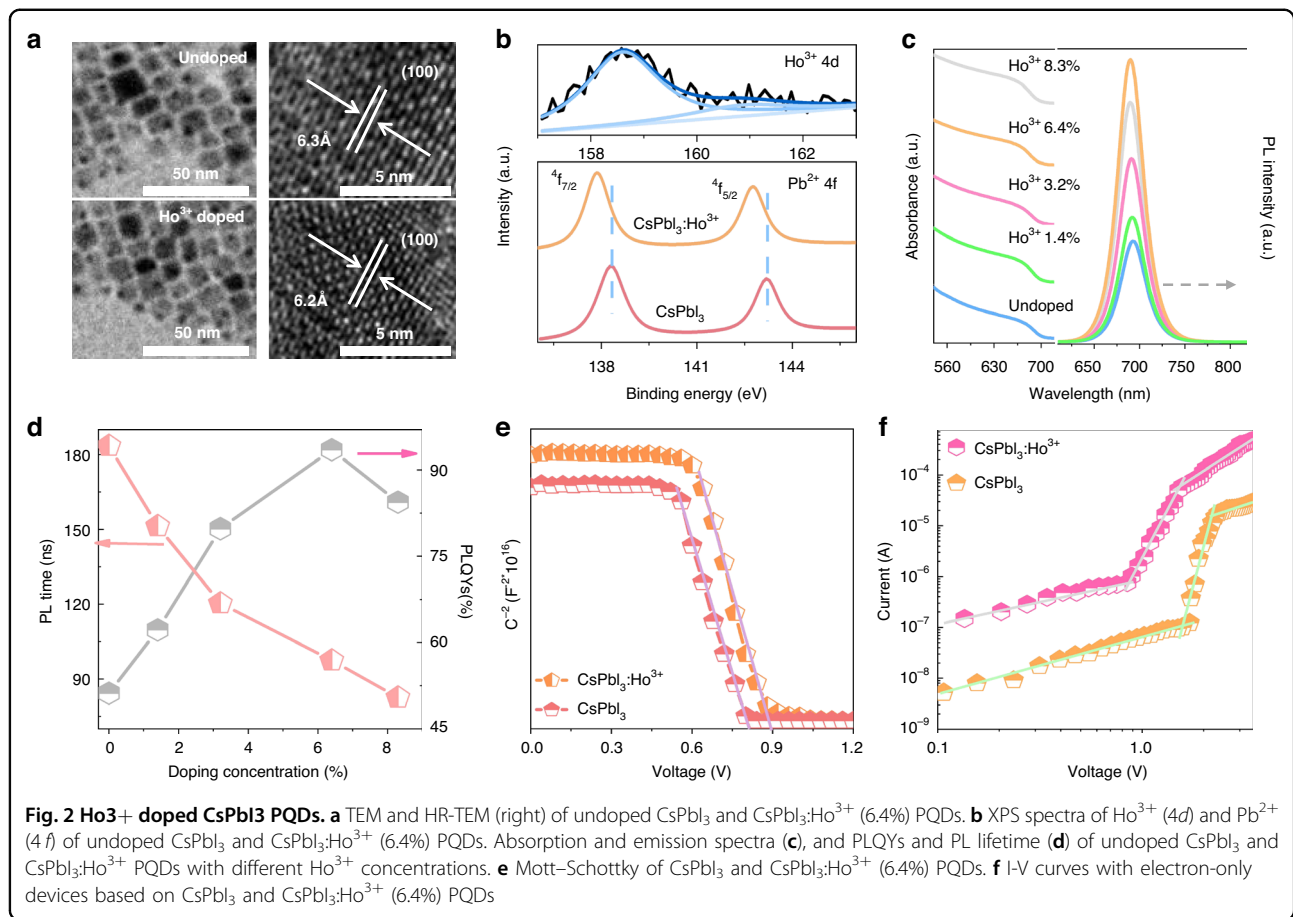


Fig. 1 DUV–NIR-II broadband PD. **a** The detection range for the commercial GaN PDs, Si PDs, InGaAs PDs, and this work. **b** Schematic of a broadband PD configuration. **c** Absorption and emission spectra of PbS QDs. Inset is the image of PbS QDs. **d** Energy level diagram of QC-LC. **e** Absorption spectra of QC-LC and CsPbI₃:Ho³⁺–PbS QDs, and emission spectra of QC-LC

respectively (Fig. S5). The practical Ho³⁺ doping concentration was identified by the inductively coupled plasma optical emission spectrometry (ICP–OES) and the X-ray photoelectron spectroscopy (XPS) (Table S1). The lattice distances of the (100) plane of undoped CsPbI₃ and CsPbI₃:Ho³⁺ PQDs are determined to be ~6.3 Å and ~6.2 Å. The lattice shrinkage is ascribed to the replacement of the larger radius of Pb²⁺ (~119 pm) by smaller size of Ho³⁺ (~90.1 pm)^{44–46}. The energy dispersive X-ray (EDX) mapping images demonstrate that all of the elements (cesium, lead, iodine, and holmium) exist in CsPbI₃:Ho³⁺ PQDs (Fig. S6). The X-ray diffraction (XRD) patterns in Fig. S7 shows that undoped CsPbI₃ and CsPbI₃:Ho³⁺ PQDs have the same cubic structure without impurity peak, and the (100) peaks of PQDs gradually shift to higher diffraction angle after Ho³⁺ doping. Meanwhile, the XPS survey spectra evidence that the appearance of Ho³⁺ 4d peaks in CsPbI₃:Ho³⁺ PQDs, and the peaks of Cs⁺ 3d, Pb²⁺ 4f, and I⁻ 3d are presented in undoped CsPbI₃ and CsPbI₃:Ho³⁺ PQDs (Fig. 2b and S8). Compared with the undoped CsPbI₃ PQDs, the binding

energy of Pb²⁺ 4f_{5/2} and 4f_{7/2} moves to lower energy after Ho³⁺ doping, while Cs⁺ 3d and I⁻ 3d shows slight changes. Based on the above observations, we confirm that Ho³⁺ ions are successfully doped into the CsPbI₃ PQDs and mainly replace the Pb²⁺ sites.

Figure 2c shows the absorption and emission spectra of pristine CsPbI₃ and CsPbI₃:Ho³⁺ PQDs with various Ho³⁺ doping concentration. The absorption peak of CsPbI₃ PQDs gradually blue shifts from 683 nm to 678 nm with increasing Ho³⁺ concentration. In line with the absorption peak variation, the exciton bandgap increases from 1.76 eV of pristine CsPbI₃ to 1.82 eV of CsPbI₃:Ho³⁺ (6.4%) (Fig. S9). It can be mainly due to the lattice contraction by substituting Pb²⁺ with Ho³⁺ (Supplementary Note 1)^{47,48}. Accordingly, the exciton emission peak of CsPbI₃ PQDs moves to high energy from 693 nm to 685 nm with Ho³⁺ doping (Fig. S10). Significantly, after Ho³⁺ doping, the emission intensity of CsPbI₃ PQDs rapidly enhances with the optimal Ho³⁺ concentration of 6.4%. The PLQYs of CsPbI₃:Ho³⁺ PQDs reaches remarkable 93.5% (Fig. 2d). In addition, the



exciton decay lifetimes gradually decrease from 183.5 ns of pristine CsPbI₃ PQDs to 82.6 ns of CsPbI₃:Ho³⁺ (8.3%) PQDs (Fig. S12). Then, the radiative rates (k_r) and non-radiative rates (k_{nr}) of CsPbI₃ and CsPbI₃:Ho³⁺ PQDs were calculated according to their PLQYs and PL decay lifetimes. As displayed in Table S2, the k_r of PQDs increases about 3.44 folds from $2.79 \times 10^6 \text{ s}^{-1}$ of undoped CsPbI₃ PQDs to $9.59 \times 10^6 \text{ s}^{-1}$ of CsPbI₃:Ho³⁺ (6.4%) PQDs. The k_{nr} of CsPbI₃ PQDs is $2.66 \times 10^6 \text{ s}^{-1}$, which decreases to $0.67 \times 10^6 \text{ s}^{-1}$ of CsPbI₃:Ho³⁺ (6.4%) PQDs. Compared to the undoped CsPbI₃ PQDs, the k_r process becomes dominant for CsPbI₃:Ho³⁺ PQDs, leading to the high emission efficiency of CsPbI₃:Ho³⁺ (6.4%) PQDs. Based to the formula⁴⁴:

$$k_r = \frac{ne^2\omega^2}{3\epsilon_0 m_0 c^3 f_0} \left(\frac{\mu}{M} E_b \right)^{1.5} \frac{1 - e^{-\frac{A\epsilon}{kT}}}{\Delta E} \quad (1)$$

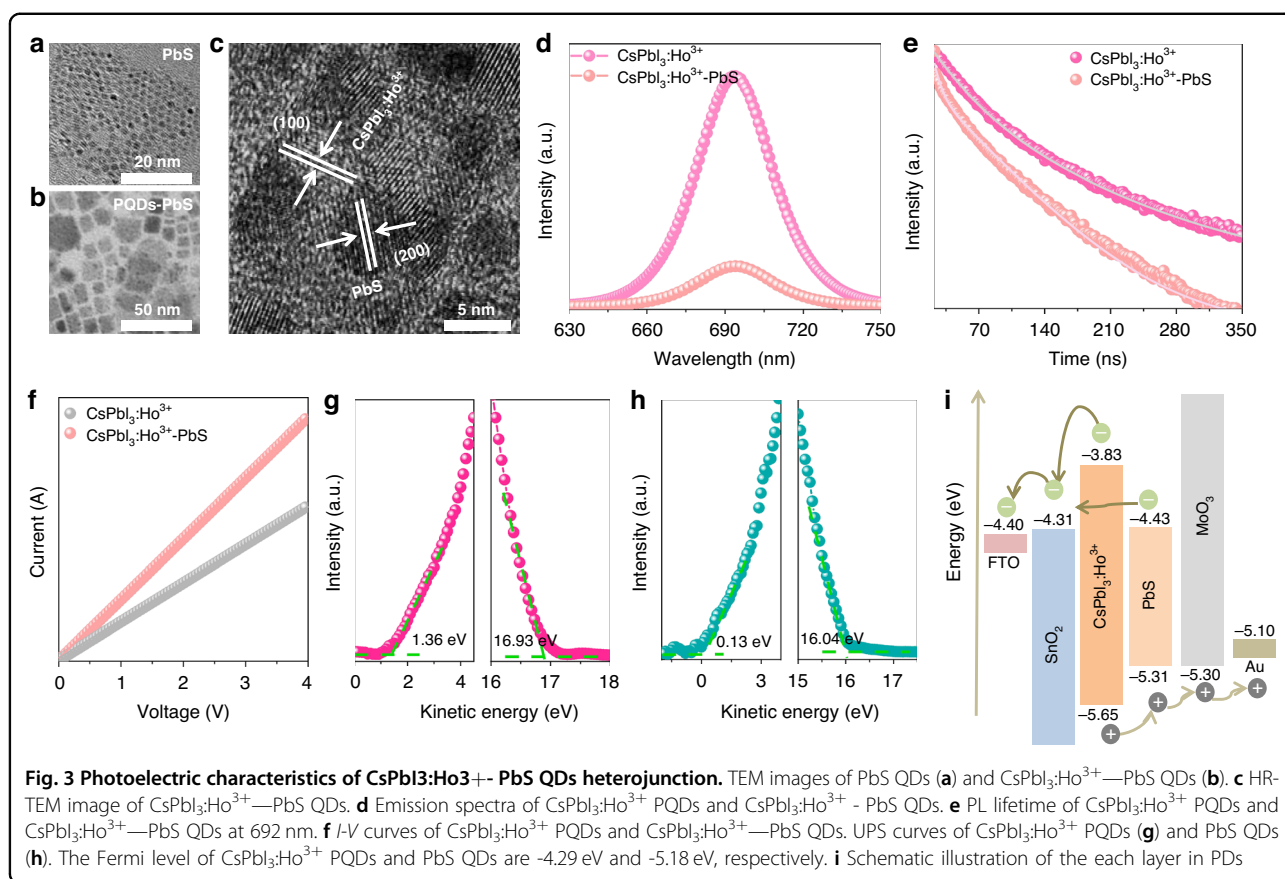
where μ , k , m_0 , ϵ_0 , ΔE , ω , and n are the equivalent mass of exciton, the Boltzmann's constant, the mass of exciton, the vacuum permittivity, the energy line width of PQDs, the optical transition frequency and the refractive index. The k_r can be mainly related to the exciton binding energy (E_b) of PQDs. The E_b is achieved from the temperature-

dependent PL intensity of PQDs by²¹:

$$I(T) = \frac{I_0}{1 + A \exp\left(\frac{-E_b}{kT}\right)} \quad (2)$$

where the I_0 is the PL intensity of PQDs at 0 K, A is the proportional constant. The E_b of CsPbI₃:Ho³⁺ (6.4%) PQDs is 32.8 meV (Fig. S13), and 20 meV for pristine CsPbI₃ PQDs⁴⁹. On the basis of Eq. (1), it suggests that the increasing k_r with Ho³⁺ doping is mainly originates from the increase of the E_b of PQDs.

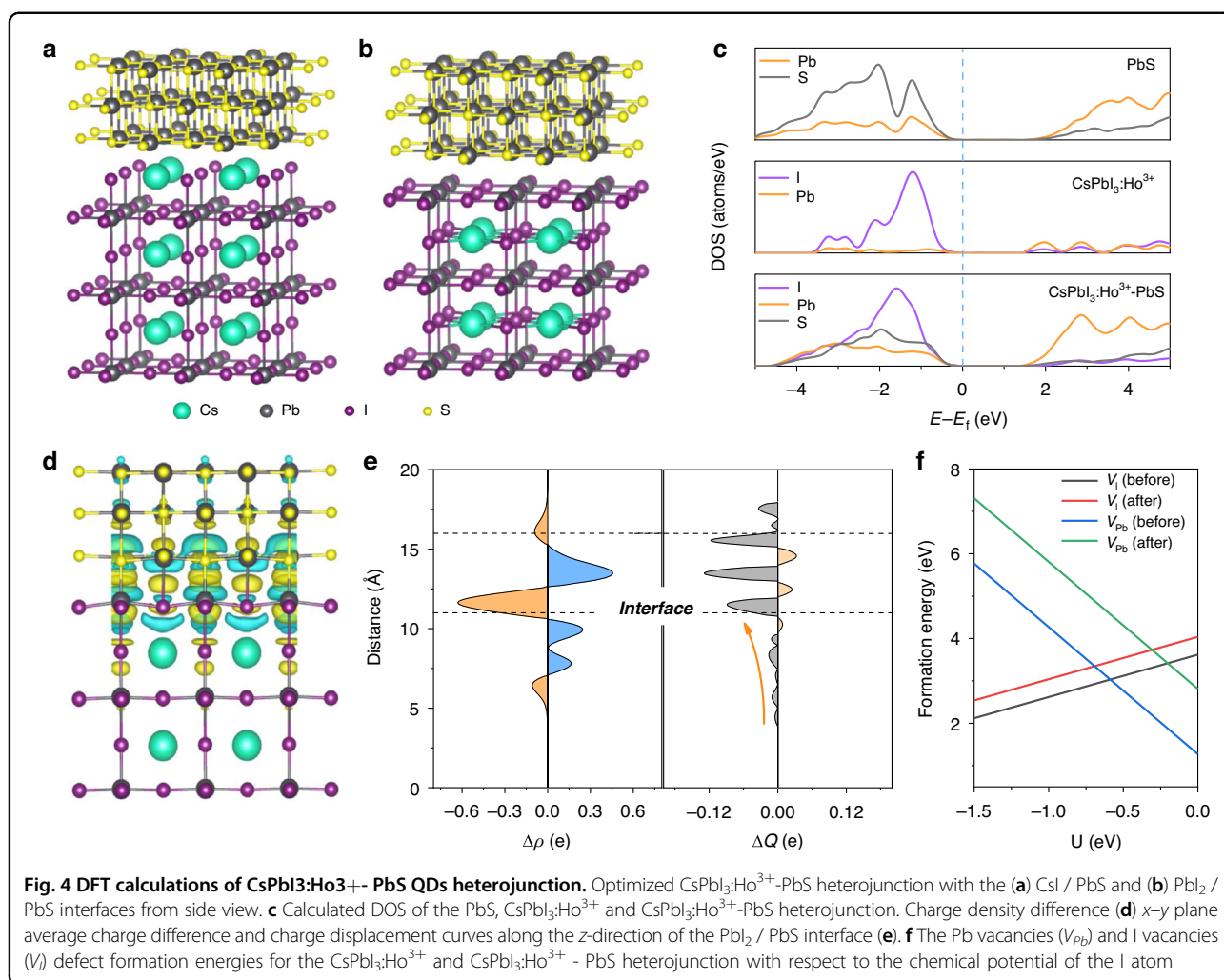
The role of Ho³⁺ on the electrical performance of PQDs films were investigated using I-V curves. As shown in Fig. S14 and Supplementary Note 2, the conductivity (σ) was determined to be $1.18 \times 10^{-6} \text{ S cm}^{-1}$ for the pristine CsPbI₃ PQDs, which increases to $3.54 \times 10^{-6} \text{ S cm}^{-1}$ in CsPbI₃:Ho³⁺ PQDs. The Mott-Schottky analysis was used to obtain the built-in potential (V_{bi}) of the devices through capacitance-voltage ($C-V$) measurements (Fig. 2e and Supplementary Note 3). The CsPbI₃:Ho³⁺ PQDs exhibits higher V_{bi} ($\sim 0.89 \text{ V}$) than that of the undoped CsPbI₃ PQDs ($\sim 0.81 \text{ V}$), indicating the decreased carrier accumulation and improved carrier transports in PQDs⁵⁰. Meanwhile, according



to the space charge limited current (SCLC) method, the trap density of undoped CsPbI₃ and CsPbI₃:Ho³⁺ PQRs were deduced to be $1.05 \times 10^{17} \text{ cm}^{-3}$ and $4.08 \times 10^{16} \text{ cm}^{-3}$ (Fig. 2f and Supplementary Note 4). It reduces 2.57 folds of CsPbI₃ PQRs with Ho³⁺ doping, dominating the decrease of k_{nr} for CsPbI₃:Ho³⁺ PQRs. The charge carrier mobility increases from $6.35 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ of pristine CsPbI₃ PQRs to $4.94 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ of CsPbI₃:Ho³⁺ PQRs. Furthermore, the air- and UV- stability of CsPbI₃ PQRs significantly improves after Ho³⁺ doping (Fig. S15). It can be seen that the emission intensity of undoped CsPbI₃ PQRs degrades rapidly, almost disappears after 8 days storage and 12 h UV irradiation. In contrast, the emission intensity of CsPbI₃:Ho³⁺ PQRs maintains about 95% and 90% of the original intensity after 50 days storage and 24 h UV radiation. The tolerance factor of CsPbI₃:Ho³⁺ PQRs was estimated to be 0.813, larger than that 0.807 of pristine CsPbI₃ PQRs (Fig. S16). Therefore, reduced trap density, boosted the carrier mobility and conductivity, enhanced the stability, and increased tolerance factor of CsPbI₃ PQRs with Ho³⁺ doping account for the improved performance for broadband PDs based on CsPbI₃:Ho³⁺ PQRs.

We next performed the optical and electrical analysis of CsPbI₃:Ho³⁺ PQRs by combining with PbS QDs. As shown in Fig. 3a and S17–S18, the PbS QDs exhibits

the cubic shape with an average diameter of $\sim 4.4 \text{ nm}$ were obtained by typical hot injection method⁵¹. Then, the smaller sized PbS QDs would attach on the CsPbI₃:Ho³⁺ PQRs surface to formation of a heterojunction composite by electrostatic interactions (Fig. 3b and S19). We further revealed the HR-TEM of CsPbI₃:Ho³⁺-PbS QDs heterojunction, in which the lattice plane of CsPbI₃:Ho³⁺ (100) and PbS (200) can be clearly identified (Fig. 3c). The CsPbI₃:Ho³⁺-PbS QDs heterojunction exhibits a complementary absorption in the visible to NIR-II region (400 nm–1700 nm), where the enhanced absorption within 400 nm–681 nm is corresponding to exciton absorption of CsPbI₃:Ho³⁺ PQRs (Fig. S20). The PL intensity of CsPbI₃:Ho³⁺ PQRs dramatically reduces after integrating with PbS QDs (Fig. 3d), accompanied by the shortening of exciton lifetime of CsPbI₃:Ho³⁺ PQRs from 97.5 ns to 62.3 ns for CsPbI₃:Ho³⁺-PbS QDs heterojunction (Fig. 3e). Those results indicate that the CsPbI₃:Ho³⁺-PbS QDs heterojunction can effective improve the carrier extraction and transfer. Meanwhile, the NIR emission of PbS QDs slightly increases for CsPbI₃:Ho³⁺-PbS QDs heterojunction under 808 nm excitation (Fig. S21), enabling the high responsivity of PDs in NIR region.



To further investigate the charge recombination dynamic of CsPbI₃:Ho³⁺ PQDs after combining with the PbS QDs, the *I-V* curves of CsPbI₃:Ho³⁺ PQDs and CsPbI₃:Ho³⁺-PbS QDs heterojunction were measured (Fig. 3f). It can be seen that CsPbI₃:Ho³⁺ - PbS QDs heterojunction obtains higher σ ($5.11 \times 10^{-6} \text{ S cm}^{-1}$), compared with the CsPbI₃:Ho³⁺ PQDs device ($3.54 \times 10^{-6} \text{ S cm}^{-1}$). The ultraviolet photoelectron spectroscopy (UPS) was employed to determine the energy levels of the CsPbI₃:Ho³⁺ PQDs and PbS QDs (Fig. 3g, h). The valence band maximum (VBM) and the conduction band minimum (CBM) of CsPbI₃:Ho³⁺ PQDs and PbS QDs are deduced to be -5.65 eV and -5.31 eV, and -3.83 eV and -4.43 eV, respectively. As illustrated in Fig. 3i, the band alignment between CsPbI₃:Ho³⁺ PQDs and PbS QDs enables them to form a heterojunction. Under visible light illumination, the generated electrons in CsPbI₃:Ho³⁺ PQDs tends to enter electron transport layer (ETL, SnO₂). While the holes move to PbS QDs, subsequently transfer to hole transport layer (HTL, MoO₃). Meanwhile, the PbS QDs captures the NIR light to produce electrons and

holes, the electrons transfer to ETL by CsPbI₃:Ho³⁺ PQDs, and the holes directly enter into HTL. Thus, the PDs combining CsPbI₃:Ho³⁺ PQDs with PbS QDs brings about the broadband response from visible to NIR-II.

The structural and photophysical interaction between of CsPbI₃:Ho³⁺ PQDs and PbS QDs were calculated through density functional theory (DFT) (Supplementary Note 5). Figure 4a, b shows the optimized CsPbI₃:Ho³⁺-PbS QDs heterojunction with the PbI₂ / PbS and CsI / PbS interfaces. The adhesive energies of PbI₂ / PbS interface (-3.22 eV) is smaller than that of the CsI / PbS interface (-2.07 eV), indicating that the PbI₂ / PbS is more stable interface structure⁵². The strong electron interface coupling between PbS and CsPbI₃:Ho³⁺ is revealed by the density of states (DOS) functional (Fig. 4c), where the significant overlap between the Pb 6*p* and I 5*p* states in CsPbI₃:Ho³⁺ PQDs with the S 2*p* orbital in PbS QDs. Furthermore, the bandgap of CsPbI₃:Ho³⁺-PbS QDs heterojunction shows a slight smaller than that of the CsPbI₃:Ho³⁺ PQDs, benefiting for the effectively transition of electrons from VBM to CBM. In order to

understand the charge distribution of the CsPbI₃:Ho³⁺—PbS QDs heterojunction interface, the charge density difference $\Delta\rho$ is obtained by⁵³:

$$\Delta\rho = \rho_{hete} - \rho_{PbS} - \rho_{PQDs} \quad (3)$$

where ρ_{hete} is the charge density of the fully relaxed CsPbI₃:Ho³⁺—PbS QDs heterojunction, ρ_{PbS} and ρ_{PQDs} are the isolated PbS QDs and CsPbI₃:Ho³⁺ PQDs slab. As shown in Fig. 4d, the charge depletions underneath Pb / I atoms for PbI₂ / PbS interface, which is favorable for efficient charge migration from CsPbI₃:Ho³⁺ PQDs to PbS QDs. Meanwhile, the x - y plane average charge difference Δq is calculated by⁵³:

$$\Delta q = \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} \Delta\rho d\chi \quad (4)$$

In general, the charge accumulation and depletion can be obtained based on the positive and negative Δq , respectively⁵⁴. Fig. 4e displays the Δq of PbI₂ / PbS interface, where a dipole can be produced between the CsPbI₃:Ho³⁺ PQDs surface and PbS QDs because of the charge accumulation and depletion, facilitating the charge separation and transport. Moreover, the charge displacement (CD) functional (ΔQ) can be achieved through integrating the x - y plane average charge difference Δq along the z direction⁵²:

$$\Delta Q = \int_{-\infty}^z \Delta q dz \quad (5)$$

where the positive ΔQ values indicates the charge transfer from the right to the left across the perpendicular plane through this direction and vice versa. The CD plot of PbI₂ / PbS interface along z direction present that the whole negative for CsPbI₃:Ho³⁺ PQDs side, which means that the charge transport from CsPbI₃:Ho³⁺ PQDs to PbS QDs. As shown in Fig. 4f, we calculated the defect formation energies of Pb²⁺ vacancies (V_{Pb}) and I⁻ vacancies (V_I) in CsPbI₃:Ho³⁺ PQDs and CsPbI₃:Ho³⁺—PbS QDs heterojunction, where the V_{Pb} and V_I exhibit higher defect formation energies after PbS QDs coupling, benefiting for the responsivity of PDs²³.

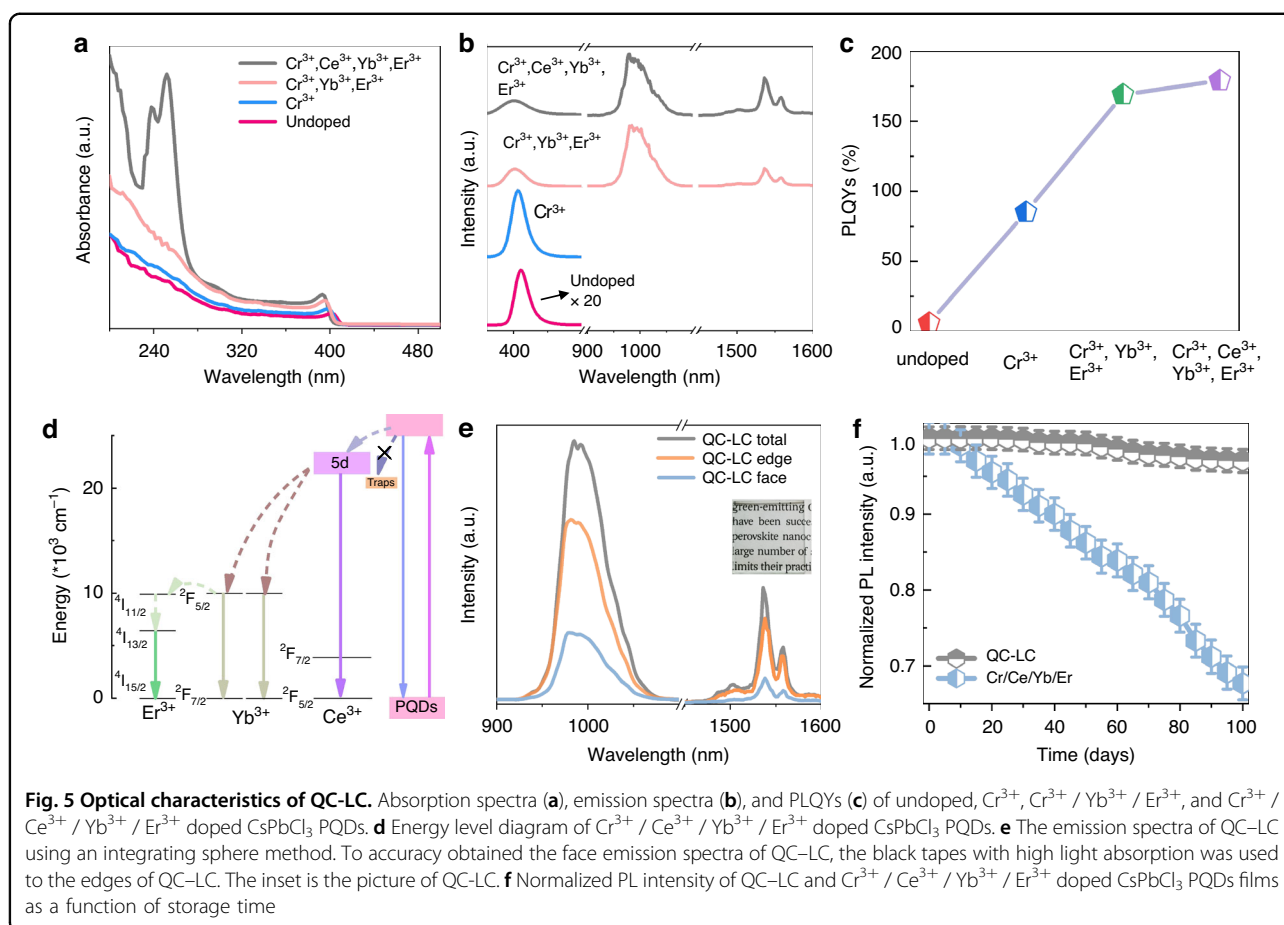
To fabricate QC—LC, the cubic and uniform Cr³⁺ / Ce³⁺ / Yb³⁺ / Er³⁺ doped CsPbCl₃ PQDs with the average diameter of ~8.4 nm were prepared through the hot-injection method (Fig. S22)⁵⁵. The Cr³⁺ and Ce³⁺ were selected to improve emission intensity and boost DUV absorption of CsPbCl₃ PQDs. The emission of Yb³⁺ and Er³⁺ ions locate within the absorption of CsPbI₃:Ho³⁺—PbS QDs heterojunction, and has high efficient quantum cutting behavior in CsPbCl₃ PQDs. All the elements (Cs, Pb, Cl, Cr, Ce, Yb, and Er) exist in Cr³⁺ / Ce³⁺ / Yb³⁺ / Er³⁺ doped CsPbCl₃ PQDs (Fig. S23). Figure 5a displays the UV—Visible absorption spectra of undoped, Cr³⁺ doped CsPbCl₃ PQDs, Cr³⁺ / Yb³⁺ / Er³⁺

doped CsPbCl₃ PQDs, and Cr³⁺ / Ce³⁺ / Yb³⁺ / Er³⁺ doped CsPbCl₃ PQDs. It can be seen that the absorption peak of CsPbCl₃ PQDs locates at 405 nm, and blue shifts to 391 nm after Cr³⁺ / Ce³⁺ / Yb³⁺ / Er³⁺ doping, ascribed to the lattice contraction of PQDs by substituting Pb²⁺ with the smaller size doping ions^{47,56}. Moreover, the absorption spectra of Cr³⁺ / Ce³⁺ / Yb³⁺ / Er³⁺ doped CsPbCl₃ PQDs present a significant enhancement within 200 nm—280 nm after Ce³⁺ doping, attributed to absorption contribution of $4f - 5d$ for Ce³⁺⁴². Fig. 5b shows the emission spectra of undoped CsPbCl₃ PQDs, CsPbCl₃:Cr³⁺ PQDs, CsPbCl₃:Cr³⁺, Yb³⁺, Er³⁺ PQDs, and CsPbCl₃:Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs. It is found that an obvious exciton emission band centering at 410 nm for CsPbCl₃ PQDs was observed under 365 nm excitation, which significant improvement after Cr³⁺ doping. Except for exciton emission, two additional emission peaks in CsPbCl₃:Cr³⁺, Yb³⁺, Er³⁺ and CsPbCl₃:Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs were identified, appearing at 980 nm and 1540 nm, assigned to Yb³⁺ (²F_{5/2} - ²F_{7/2}) and Er³⁺ (⁴I_{13/2} - ⁴I_{15/2}). Similarly to the previous reported, they originate from the quantum cutting energy transfer from CsPbCl₃ PQDs to Yb³⁺, and further Yb³⁺ to Er³⁺^{57,58}. Furthermore, the introduction of Ce³⁺ regards as an intermediate bridge to match the energy between CsPbCl₃ PQDs and NIR quantum cutting emission of Yb³⁺⁵⁹. Meanwhile, the PLQYs is estimated by²³:

$$PLQYs = \frac{N_{em}}{N_{abs}} = \frac{\int I_{sample}(\lambda) - I_{ref}(\lambda) d\lambda}{\int E_{ref}(\lambda) - E_{sample}(\lambda) d\lambda} \quad (6)$$

where N_{em} and N_{abs} are the number of emission and absorption photons of PQDs. I_{sample} and E_{sample} present the spectral intensity of the emitted light and excitation light of samples, and I_{ref} and E_{ref} are the spectral intensity of the emitted light and excitation light for a reference cuvette containing toluene. It should be highlighted that the PLQYs of CsPbCl₃:Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs reaches to 179% (Fig. 5c). The higher PLQYs are concluded in the following three aspects: (1) reduced k_{nr} of CsPbCl₃ PQDs after Cr³⁺ doping, (2) enhanced energy transfer from CsPbCl₃ PQDs to Yb³⁺ and improved DUV absorption after Ce³⁺, (3) NIR quantum cutting emission (²F_{5/2} - ²F_{7/2}) after Yb³⁺ doping. The energy transfer process for Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ doped CsPbCl₃ PQDs was represented in Fig. 5d.

Then, the CsPbCl₃:Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs were incorporated into a PMMA polymer matrix to form QC—LC. The performance of the QC—LC was achieved using an integrating sphere. As seen in Fig. 5e and S24, the QC—LC presents the similar emission spectra with CsPbCl₃:Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs and high transparency. Considering directly integrating one of edge of QC—LC with the PDs, the emission intensity of the edge, face, and total of LC were recorded (Fig. 5e). The emission intensity of the edge is higher than that of face, attributed to the waveguide effect of



QC-LC. The edge and face emission intensity ratio of the QC-LC was 73.61%, which is nearly to the ideal light trapping efficiency of 75%^{13,60}. Moreover, the stability of $\text{CsPbCl}_3:\text{Cr}^{3+}, \text{Ce}^{3+}, \text{Yb}^{3+}, \text{Er}^{3+}$ PQDs were also remarkably enhanced by incorporating them into LC, in which their PL intensity remains 97.5% after 100 days storage (Fig. 5f). Based on the high luminescence performance and stability and transparency, the QC-LC can be served as a converter to improve the DUV-UV responsivity for broadband PDs.

Figures 6a and S25 shows the photocurrent-time (I_p - t) response curves of FTO / SnO_2 / CsPbI_3 PQDs / MoO_3 / Au (PD1), FTO / SnO_2 / $\text{CsPbI}_3:\text{Ho}^{3+}$ PQDs / MoO_3 / Au (PD2), FTO / SnO_2 / $\text{CsPbI}_3:\text{Ho}^{3+}$ -PbS QDs heterojunction / MoO_3 / Au (PD3), and QC-LC / FTO / SnO_2 / $\text{CsPbI}_3:\text{Ho}^{3+}$ -PbS QDs heterojunction / MoO_3 / Au (PD4) in dark and 260 nm, 460 nm, and 1550 nm illumination at a bias of 0.5 V, respectively. It can be seen that the I_p reach to 3.09 μA of PD4, whereas only 0.84 μA for PD1 under 460 nm illumination. Compared with the PD1, the I_p of PD4 increase 3.68 folds for 460 nm, due to the reduce density of defects and boost carriers mobility after Ho^{3+} doping, and passivated surface vacancy by PbS QDs. Besides, the dark current (I_d) of PD1-PD4 were recorded in Fig. S26. The value of I_d was about 2.44 pA for PD1,

which decreases to 0.26 pA for PD4. Furthermore, the light to dark current ratio of PD4 was 1.19×10^7 , which further suggest the formation of uniform $\text{CsPbI}_3:\text{Ho}^{3+}$ -PbS QDs heterojunction film^{35,61}. Interestingly, the high I_p signals of DUV (0.91 μA of 260 nm) and NIR-II (0.64 μA of 1550 nm) were observed for PD4. The enhancement is mainly due to the strong absorption in the DUV region and extremely efficient NIR quantum cutting emission of QC-LC, and high performance NIR-II broadband absorption of PbS QDs. Figure 6b, c and S27-S28 shows the responsivity (R), detectivity (D^*), and external quantum efficiency (EQE) of PD1-PD4 (Supplementary Note 6). Compared to the PD1 with lower R (119.04 mA W^{-1}) and D^* (5.43×10^{11} Jones) and EQE (16.9%), the maximum R and D^* and EQE of the PD4 were calculated to be 596.62 mA W^{-1} and 1.05×10^{13} Jones and 84.6% under 460 nm illumination. Furthermore, these values of PD4 were largely enhanced in the DUV-UV and NIR-II region, realizing a broadband spectral response ranging from 200 nm to 1700 nm, where the R and D^* and EQE of PD4 were 180.6 mA W^{-1} and 164.5 mA W^{-1} , 3.19×10^{12} Jones and 2.23×10^{12} Jones, and 45.3% and 7.2% under 260 nm and 1550 nm, respectively. The statistical analysis on 25 devices for PD4 under

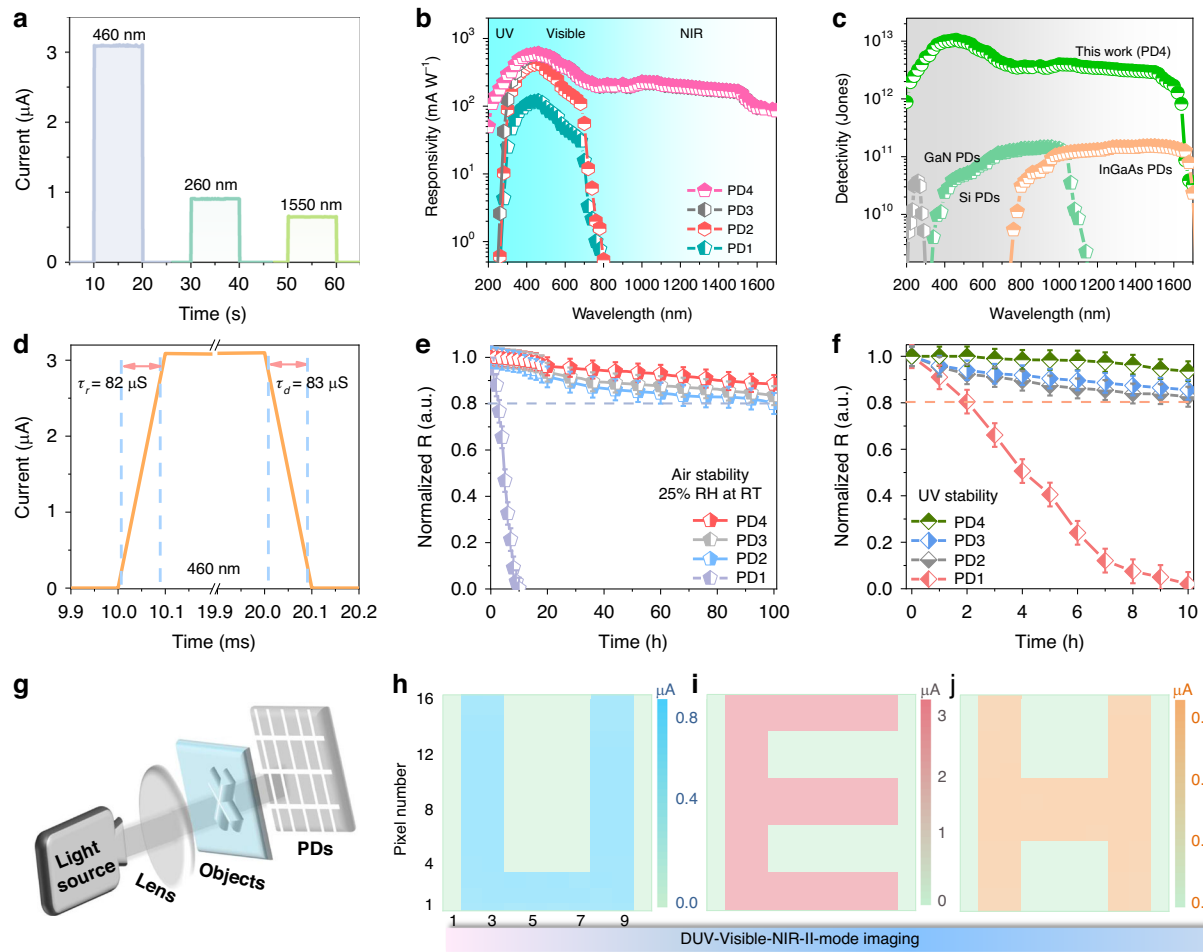


Fig. 6 Performances of PDs. **a** I_p - t curves of PD4 under the 260 nm, 460 nm, and 1550 nm illumination, respectively. **b** Responsivity of PD1–PD4. **c** Detectivity of this work (PD4), GaN PDs, Si PDs and InGaAs PDs, respectively. **d** Response time of the PD4 under 460 nm illumination. **e, f** The evolution of responsivity under 25% RH at room temperature and UV radiation. **g** Schematic diagram of imaging arrays. DUV–Visible–NIR–II mode imaging output for “U, E, H” mask under 260 nm (**h**), 460 nm (**i**) and 1550 nm (**j**), respectively

260 nm, 460 nm, and 1550 nm illumination, respectively, showing the excellent repeatability of this broadband PDs (Fig. S29). Importantly, the D^* of PD4 improves two orders that of commercial GaN PDs and Si PDs and InGaAs PDs under the same detection condition. Meanwhile, the noise current (I_n) of PD4 (2.34×10^{-14} A Hz $^{-1/2}$) was lower than that of PD1 (8.33×10^{-14} A Hz $^{-1/2}$) at 1 Hz in Fig. S30. According to the noise-equivalent power (NEP) equation, the D^* can also be calculation by ref. ⁶:

$$D^* = \frac{\sqrt{SB}}{NEP} (\text{cmHz}^{-1/2} \text{W}^{-1} \text{ or Jones}) \quad (7)$$

$$NEP = \frac{I_n}{R} \quad (8)$$

where S and B are the active layer area and the electrical bandwidth. The D^* of PD4 was obtained to be 7.71×10^{11}

Jones of 260 nm, 2.55×10^{12} Jones of 460 nm, and 5.23×10^{11} Jones of 1550 nm, respectively (Fig. S31). Compared with the PD1, the D^* of PD2–PD4 shows the consistent increases trend for it calculated by the dark current, indicating a great potential for weak light detection.

The photon-response times of PDs are exhibited in Fig. 6d and S33–S34. The rise (τ_r) and decay times (τ_d) of the PD4 were measured to be $\sim 82 \mu\text{s}$ and $\sim 83 \mu\text{s}$ under 460 nm illumination, much faster than that of the PD1 ($\sim 202 \mu\text{s}$ and $\sim 223 \mu\text{s}$). The fast response time can be attributed to the restrained defects after Ho^{3+} doping, and the enhanced charge extraction and transport by integrating with PbS QDs. Figure S35 represent the relative response trend versus the frequency of 460 nm light. The -3dB bandwidth of PD4 was calculated as 4.04 KHz, indicating a rapid response to 460 nm light signal. According to the law: $f_{-3\text{dB}} = 0.35/\tau_r$,⁶² the response time of PD4 is estimated to be 86.6 μs ,

Table 1 Recent works of broadband PDs

Materials	D* (Jones)	R _t (μs)	Wavelength (nm)	Ref.
PEDOT:PSS / PbS / CsPbCl ₃	5.78 × 10 ¹⁰	–	350–1100	33
CH ₃ NH ₃ PbI ₃ / C8BTBT	2.17 × 10 ¹²	7.1 × 10 ⁴	365–808	67
GeTe / WS ₂	1.67 × 10 ¹¹	3 × 10 ⁴	450–980	68
PbS-SCN / CH ₃ NH ₃ PbI ₃	3.0 × 10 ¹¹	4.2 × 10 ⁴	365–1550	37
PdSe ₂ / FA _{1-x} Cs _x PbI ₃	~ 10 ¹³	3.5/4	200–1550	35
CH ₃ NH ₃ PbI ₃ / PbSe	1.2 × 10 ⁸	3 × 10 ³	300–1500	61
CsPbBr ₃ / PbS QDs	1.13 × 10 ¹⁰	11.5	400–1130	69
GQD-PEDOT: PSS / Si	8 × 10 ¹¹	80/70	300–1100	70
FAPbI ₃	9.4 × 10 ¹¹	6.1 × 10 ⁴	340–700	71
Gd ₃ Fe ₅ O ₁₂ / Gr / Gd ₃ Fe ₅ O ₁₂ / MoS ₂	4.504 × 10 ¹²	2.9 × 10 ⁵ /4.9 × 10 ⁵	300–1500	72
CQDs-halide / CQDs-EDT	2.5 × 10 ¹²	7.79/11.48	400–1400	73
2D Bi ₂ O ₂ Se / CsBi ₃ I ₁₀	1.22 × 10 ¹²	4.1/6.2	365–1500	74
p-WSe ₂ / n-Ge	2.1 × 10 ¹⁰	30	450–1550	75
Bi ₂ Te ₃ -SnSe-Bi ₂ Te ₃	6 × 10 ¹⁰	–	370–808	76
FA _{0.5} MA _{0.45} Cs _{0.05} Pb _{0.5} Sn _{0.5} I ₃	2.21 × 10 ¹¹	0.043	300–1050	6
MoS ₂ / CdTe	6.1 × 10 ¹⁰	43.7/82.1	200–1700	77
FAMAPbI ₃	4.3 × 10 ¹²	6.3 × 10 ⁴	300–800	78
PEDOT: PSS / PbS / CsPbCl ₃	6.77 × 10 ¹²	6.5 × 10 ⁵	405–808	36
CH ₃ NH ₃ PbI ₃	~ 10 ¹¹	4.1/3.6	300–750	79
Cr/Ce/Mn-LC / CsPbI ₃ :Er ³⁺ / BHJ	2.46 × 10 ¹²	350/300	200–1000	23
QC-LC / FTO / SnO ₂ / CsPbI ₃ :Ho ³⁺ -PbS QDs / MoO ₃ / Au	1.05 × 10 ¹³	82/83	200–1700	This work

similar to the response time measured in Fig. 6d. Furthermore, compared to the recent works of broadband PDs (Table 1 and Fig. S36), this broadband PDs shows the higher D* and faster response time from DUV to NIR-II regions. As shown in Fig. S37, the R as a function of light power density (P) can be fitted by the formula: $R \propto P^\alpha$ ⁶³ where α were achieved to be 0.67, 0.56, and 0.66 for PD4 under 260 nm, 460 nm, and 1550 nm, respectively. The α value of the PD4 is not closer to ideal result ($\alpha = 1$), suggesting that defects still exist in the heterojunction interface^{64–66}. Figure 6e, f displays the normalized R variation curves of PD1–PD4 at humidity of 25% and under UV irradiation at room temperature. The R of the PD1 declines to 0% after 100 h storage and 10 h UV irradiation, while the R of the PD4 remained 89% and 99.3% for the original R-value after 100 h storage and 10 h UV irradiation. The enhanced air- and UV- stability of PDs would be attributed to the Ho³⁺ doping, PbS QDs hybridization, and the buffer layer of QC–LC in the devices.

Based on the outstanding DUV–Visible–NIR-II detection performance, the imaging application of this

broadband PD was further explored. As presented in Fig. 6g, the imaging schematic is composed by different light source (DUV of 260 nm, Visible of 460 nm, and NIR-II of 1550 nm), lens, object letters (“U”, “E”, and “H”), broadband PDs and signal collector. We fabricated a 10 × 16 pixel detector array as the each photograph shown in Fig. 6h–j. The thickness of the detectors is 1 mm and the electrode area of each pixel is 1 × 1 mm². It can be seen that the letters were clearly achieved with high light to dark current ratios under different illuminations, highlighting that the excellent performance of broadband detection and imaging capability for the QC–LC / FTO / SnO₂ / CsPbI₃:Ho³⁺-PbS QDs heterojunction / MoO₃ / Au PDs. Moreover, these results strongly indicate that the remarkable adaptability of the PDs and great promising for broadband imaging without low temperature working conditions.

Discussion

In this work, an excellent performance DUV–Visible–NIR-II broadband PD was successfully fabricated based

on QC–LC and CsPbI₃:Ho³⁺–PbS QDs heterojunction, exhibiting the high detectivity of 3.19×10^{12} Jones at 260 nm, 1.05×10^{13} Jones at 460 nm, and 2.23×10^{12} Jones at 1550 nm, respectively. The optimized CsPbI₃:Ho³⁺ PQDs demonstrated low trap density and high charge mobility compared with the undoped CsPbI₃ PQDs, enabling superb responsivity and detectivity of visible region. Then, the hybridization of CsPbI₃:Ho³⁺–PbS QDs heterojunction successfully expand the response of broadband PDs to the NIR-II region, due to the narrow bandgap and large absorption coefficient of PbS QDs. Meanwhile, high efficiency NIR quantum cutting emission (PQLYs ~ 179%) and strong DUV–UV absorption of Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ doped CsPbCl₃ PQDs were embedded to form QC–LC, which can be integrated with the FTO side to improve the responsivity of PDs for DUV–UV light. Our work shows a promising path for fabricated the high performance broadband PDs and imaging capability.

Materials and methods

Materials

Cs₂CO₃ (99.9%), 1-octadecene (ODE, 90%), oleic acid (OA, 85%), oleylamine (OAm, 70%), PbO (99.99%), PbI₂ (99.99%), HoI₃ (99.99%), PbCl₂ (99.9%), CrCl₃ (99.99%), CeCl₃ (99.99%), YbCl₃ (99.99%), ErCl₃ (99.99%), bis(trimethylsilyl) sulfide, toluene, cyclohexane and ethyl acetate (99%) were purchased from Mackline and were used without further purification.

Synthesis of CsPbI₃ PQDs

0.8 g Cs₂CO₃ was added into a mixture of 30 mL of ODE and OA (2.5 mL) and then heated to 150 °C until the white powder was completely dissolved. The mixture was then kept at 120 °C to obtained the Cs-oleate. Then, PbI₂ (0.3 mmol), OAm (1.5 mL), OA (1.5 mL), and ODE (10 mL) were added to a 50-mL 3-neck round-bottomed flask and were evacuated with N₂, by heating the solution to 120 °C for 1 h. The temperature of the solution was then increased to 180 °C for 10 min. Finally, the Cs-oleate (1 mL) was swiftly injected into the solution. After 10 s, the solution was cooled in an ice bath. The CsPbI₃ PQDs were precipitated and then centrifuged, followed by dissolution in toluene.

Synthesis of CsPbI₃:Ho³⁺ PQDs

HoI₃ (x mmol), PbI₂ (0.3 mmol), OAm (1.5 mL), OA (1.5 mL), and ODE (10 mL) were adequately dissolved at 120 °C for 1 h under purging N₂ gas. The following steps were the same with synthesis of CsPbI₃ PQDs.

Synthesis of Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ doped CsPbCl₃ PQDs

For the CsPbCl₃: Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs, PbCl₂ (0.5 mmol), CrCl₃ (0.3 mmol), CeCl₃ (0.2 mmol), YbCl₃

(0.3 mmol), ErCl₃ (0.2 mmol) were loaded into round-bottom flask with ODE (10 mL), OAm (1.5 mL) and OA (1.5 mL). The following steps were the same with the synthesis of the Ho³⁺ doped CsPbI₃ PQDs.

Fabrication of QC–LC

0.8 g PMMA (MW ~ 350000) was dispersed in 5 mL toluene by sonication, where toluene solution (3 mL) of CsPbCl₃: Cr³⁺, Ce³⁺, Yb³⁺, Er³⁺ PQDs were added. The mixture was sealed and stirred overnight to obtain homogenous slurry. The slurry was centrifuged at 2000 rpm and the supernatants were used for LC fabrication. The above supernatants were spin-coating onto borosilicate glass substrates.

Syntheses of PbS QDs

Firstly, PbO (0.36 g), OA (1 mL), and ODE (15 mL) were stirred and heated to 145 °C under nitrogen atmosphere. Then, ODE (4.0 mL) containing bis(trimethylsilyl) sulfide (168 μL) was quickly injected into the reaction flask, and meanwhile the heater was switched off. The hot solution was naturally cooled down, and the formed oil-soluble PbS QDs were precipitated. The purification was carried by isopropyl alcohol and acetone. Finally, the PbS CQDs were dispersed in toluene to produce a 50 mg mL⁻¹ solution.

Preparation of the CsPbI₃:Ho³⁺–PbS QDs heterojunction composite

In a typical procedure, a 200 μL CsPbI₃:Ho³⁺ solution (10 mg mL⁻¹, toluene) was mixed with 2 mL of PbS solution (1 mg mL⁻¹, toluene), and the total volume remained at 5 mL. Under dark conditions, the suspension was ultrasonicated for 10 min and stirred for 0.5 h. Finally, the CsPbI₃:Ho³⁺–PbS CQDs heterojunction composites were collected by centrifuging at 8000 rpm for 5 min.

Device fabrication

FTO coated glass substrates were etched by zinc powder and HCl to define the electrode patterns and washed in deionized water, acetone, and ethanol for 20 min, respectively. The ultraviolet-ozone was used to remove the organic residues of FTO surface. To fabricate the compact SnO₂ layer, the SnO₂ colloid solution by water to the concentration of 2.14 wt% and was spin-coated on FTO substrates at 5000 rpm for 30 s and then annealed at 150 °C for 30 min. The CsPbI₃:Ho³⁺–PbS CQDs heterojunction film was fabricated on the SnO₂ layer by spin-coating at 2000 rpm for 40 s. For broadband PDs, MoO₃ and Au was evaporated on CsPbI₃:Ho³⁺–PbS CQD film layer. Then, the edge surface of QC–LC with the edge size of 1 × 0.4 mm² was attached and fixed to the ITO layer of PD with area of 1 × 1 mm². When UV light radiation on the face of QC–LC, then the emitted 400–1700 nm light is

coupled out of the edge surface into the FTO of PDs. The visible and NIR lights directly pass through the FTO and reach the PD. Because the QC–LC only occupies a part of surface of the FTO layer and has high transparency for photons with the longer wavelength ($>400\text{nm}$), which would not affect the light collection of PDs.

Characterization

UV/vis-NIR absorption spectra were measured with a Shimadzu UV-3600PC scanning spectrophotometer in the range from 200 to 2500 nm. Patterns were recorded in thin film mode on a Bruker AXS D8 diffractometer by Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Atomic Force Microscope was tested using a DI Innova AFM (Bruker) in light tapping mode. The morphology of the products was recorded with a Hitachi H-8100IV transmission electron microscope (TEM) under an acceleration voltage of 200 kV. A Visible-NIR photomultiplier combined with a double-grating monochromator were used for spectral collection. The X-ray photoelectron spectroscopy (XPS) was carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) operated at 150 W with a multichannel plate, and a delay line detector under 1.0×10^{-9} Torr vacuum. Nanosecond fluorescence lifetime experiments were performed by the time correlated single-photon counting system. The Mott–Schottky curves via capacitance-voltage measurements of CsPbI $_3$:Ho $^{3+}$ PQDs were obtained by a Princeton electrochemical workstation. The Xe lamp with the spectral range from 200 nm to 2500 nm equipped with a monochromator was used to generate the monochromatic light to conduct the spectral response measurements. Actually, the intensity of Xe lamp is weak in the region of 200 nm–300 nm, thus we must correct it before the measurement.

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Author contributions

N.D., W.X., and H.L. conceived the idea and initiated the project. Y.J., Z.W. and Y.J. designed the experiments and supervised the project. J.W. and L.S. synthesized the quantum dots and fabricated the devices. G.Z. and Y.J. tested the PDs. N.D. processed the data. H.L. analyzed the experimental results. N.D., W.X., and B.D. wrote the manuscript.

Conflict of interest

The authors declare no competing interest.

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