PbS Nanocrystal Photodetector Technologies

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Abstract

Light detection is the underlying principle of many optoelectronic systems. For decades, semiconductors such as silicon carbide, silicon, indium gallium arsenide and germanium have dominated the photodetector industry. They can exhibit excellent photosensitivity but are limited by one or more aspect, for example high production cost, high temperature processing, flexible substrate incompatibility, limited spectral range or requiring cryogenic cooling for efficient operation. Recently lead sulphide (PbS) nanocrystals have emerged as one of the most promising new materials for photodetector fabrication. They offer several advantages including low cost manufacturing, solution processability, size-tunable spectral sensitivity, flexible substrate compatibility and have achieved figures of merit outperforming conventional photodetectors. We review the underlying concepts, breakthroughs and remaining challenges in PbS nanocrystal based photodetector technologies.

Few other areas of study have uncovered the secrets of the universe like that of the interaction between light and matter, leading to many revolutionary scientific discoveries. The interaction of light, in particular with semiconducting materials, has enabled us to understand the behaviour of various fundamental phenomena and has laid the foundation of the optoelectronic systems that we rely on today. The majority of such systems necessitate the detection of light which is achieved *via* the use of photodetector devices. A photodetector converts incident photons into an electrical signal, which in the solid-state, is assembled together with an application-oriented readout integrated circuit (ROIC). Present-day commercially available photodetectors are typically made from gallium phosphide/silicon carbide (GaP)/(SiC), silicon (Si) and indium gallium arsenide/germanium (InGaAs)/(Ge) for detection in the ultraviolet (UV), visible and near-infrared (IR) regimes of the electromagnetic spectrum, respectively. For mid and far IR, lead sulphide (PbS), lead selenide (PbSe), indium antimonide (InSb), indium arsenide (InAs) and mercury cadmium telluride (HgCdTe) based photodetectors are commonly used. Photodetectors based on a photoemissive principle such as photomultiplier tubes (PMTs) are also widely used for ultrasensitive detection in the UV to near-IR spectral regime and are fabricated using alkali metals having a low workfunction. For applications demanding multispectral detection, '*two-colour*' detectors are often manufactured with a bi-level structure, for example consisting of an IR transmitting Si photodiode mounted over an IR sensitive PbS photoconductor. Such a device structure has drawbacks that include added cost, increased complexity of device fabrication and associated issues in implementation. Furthermore, a significant majority of applications are based upon UV to near-IR light detection where the indirect bandgap of Si, the InGaAs epitaxial growth process, PMT bulkiness and high bias voltage requirement all present challenges and renders their use with flexible platforms impossible. As a result significant research effort continues to be expended on the development of a single-system multispectral photodetector to replace two or more detectors. In the last decade amongst all the candidate materials studied¹ PbS semiconductor nanocrystals (NCs), often referred as '*quantum dots*', have emerged as the most promising material for the fabrication of

this type of photodetector. Such has been the progress in their development that reported PbS NC based photodetectors have already outperformed conventional state-of-the-art photodetectors in many aspects including low-cost room temperature device fabrication *via* solution processing, flexible substrate compatibility, broadband spectral sensitivity along with the figures of merit achieved, Fig 1a.

In this review article, we present an overview of recent developments in PbS NC based photodetectors. We first provide a brief introduction to PbS NCs and their relevant optoelectronic properties and then discuss the various reported PbS NC based photodetector device configurations. We discuss the fundamental operating principles of each class of the photodetector, their individual merits, drawbacks, relative trade-offs and highlight their potential applications. Various terminology and figures of merit that are used in the photodetector industry to evaluate the performance of the photodetector are summerized in Box 1.

PbS Nanocrystals

Bulk crystalline PbS has a 4-fold degenerate (8 including spin) direct bandgap and at four equivalent L-points in the Brillouin zone resulting from its rock-salt crystal structure.² The bulk bandgap of PbS is ~ 0.41 eV and upon excitation of an electron the Coulomb binding between it and the created hole is such that a relatively large average distance of ~ 18 nm exists between them (the exciton Bohr radius). Reducing the PbS crystal dimensions such that they become of similar magnitude to the de Broglie wavelength of these charge carriers (~ 9 nm), approximately equivalent to a PbS crystal size (diameter) of less than twice of the exciton Bohr radius, results in the emergence of PbS NCs with size dependent optoelectronic properties.³ Such reduction in size leads to strong confinement of both the electron and hole wavefunction (as they have similar effective mass of $m_e^* = m_h^* = 0.1m$, m is the free electron mass), giving rise to discrete quantized energy states which may be observed in optical absorption and emission spectra, Fig 1b. The onset of wavefunction confinement at relatively large NC diameters allows bandgap

tuning over a large energy range (0.6-1.6 eV), with optical absorption extending into to the UV.⁴ Additionally, as a direct bandgap semiconductor PbS NCs have a high molar absorption coefficient ($\sim 10^6 \text{ M}^{-1} \text{ cm}^{-1}$ at 400 nm).⁵

PbS NCs can be synthesised *via* a variety of methods that are described in the literature⁴⁻⁸ and may be self-assembled into ordered superlattices, Fig. 1c,d.⁷ The use of surfactant molecules bound to the PbS NC surface, such as oleic acid, enables their dispersion in a variety of solvents and prevents NC aggregation. PbS NCs have well-defined (111) and (001) facets⁹ and can be synthesized with control over size (dispersion <5%), Fig 1 c,d.^{6,7} The similar parabolicity of the PbS valence band (VB) and conduction band (CB) at the L-point bandgap leads to the PbS NCs electron and hole energy levels varying similarly as NC size is changed. The size dependence of NC optical properties has been experimentally studied by various groups.^{10,11} Based on experimental observation, Weidman *et al.* formulated equation 1,⁷ consistent with others¹⁰ that enables the determination of nanocrystal size diameter (d in nm) directly from the spectral position of the first exciton absorption peak ($1S_h$ to $1S_e$ transition, corresponding to bandgap E_g in eV) or vice-versa, Fig. 1b.

$$E_g = 0.41 + \frac{1}{0.0392d^2 + 0.114d} \quad (1)$$

The radiative lifetime in PbS NCs is long (1-5 μs)^{10,12} that may arise due to their peculiar band structure, with a high band-edge degeneracy. PbS NCs have a high dielectric constant (15-20)¹³ close to that of bulk PbS (17) and a low exciton binding energy ($\sim 100 \text{ meV}$).² This is directly reflected in the charge carrier diffusion length in PbS NC films which is found to be as long as 150-250 nm.^{14,15} P-type behaviour is typically observed in PbS NC films due to film oxidation that lowers the Fermi level close to the VB. However, n-type air-stable PbS NCs have been successfully developed *via* bismuth (Bi) doping¹⁶ and passivation with inorganic halide ligands to prevent oxidation.⁸ In addition, ambipolar transport has also been realised in PbS NC based

transistors.¹⁷ PbS NCs also display multiple exciton generation (MEG) by which more than one electron-hole pair can be generated by absorbing a single high energy photon ($>2.7E_g$).¹⁸ Furthermore, the absolute energy of PbS NCs conduction and valence band can be tuned whilst maintaining a constant bandgap *via* capping with different ligands, Fig. 1e.¹⁹ Thus, PbS NC energy levels may be tuned to optimize the energy level alignment with that of commonly used charge extraction materials, for example metal oxides, fullerenes, polymers and graphene. This enables their successful integration with these materials for the fabrication of hybrid photodetector devices.

PbS Nanocrystal Photodetectors

Photodetector devices based on PbS NCs have been fabricated in photoconductor, phototransistor and photodiode device geometries. The device architecture and configuration of a typical device based on each class is shown schematically in Fig. 2. The Sargent group were early pioneers of photodetector devices based on PbS NCs,²⁰⁻²⁵ though earlier to this photovoltaic devices based on PbS NCs had also been the focus of research attention.^{26,27} Following early reports of ultrasensitive PbS NC based photoconductor devices^{21,22} there has been a rapid development of many aspects to understand and improve performance. Progress in PbS NC based photodetector technologies is summarized in Table 1.

PbS NC photoconductor devices. Photoconductor devices work on the principle of measuring a temporary change in resistivity (or conductivity) of the semiconductor upon irradiation with light, Fig. 2a. Commercial photoconductors based on bulk PbS are widely used for IR light detection from 1-3 μm . Over this range they have a typical detectivity of 10^{10} Jones peaking at 10^{11} Jones at 2.2 μm (at 25°C), operating at an applied bias of 100 V with a rise time of 200 μs . The mechanism of photoconductivity in bulk PbS films has been extensively studied.²⁸ Here, we present a brief overview of the dark conductivity and photoconductivity in PbS NC films, the concept of photoconductive gain and the role of trap states in photodetectors.

Film deposition and ligand exchange. PbS NC based photoconductor devices are fabricated by depositing PbS NC films on top of metal electrodes either *via* simple drop-casting, spin coating or dip coating procedures on an insulating substrate such as glass or oxidised Si substrates. The presence of capping ligands has a direct impact on film conductivity. Charge transport occurs *via* ligand assisted NC to NC tunnelling (hopping) and is therefore strongly dependent on the NC to NC separation that is governed by the length of capping ligands. The long length of oleic ligands (~ 2.5 nm)²¹ therefore acts as a tunnelling barrier and results in weak coupling between individual NCs as the wavefunction of charge carriers within each individual NC remains effectively localised within it. Thus the charge transport in dark and photoexcited films of oleic capped PbS NCs is suppressed and displays an insulating behaviour that only breaks down under very high electric fields. To overcome this, insulating ligand-capped PbS NC films may be chemically treated (see Table 1) to replace oleic ligands with shorter ligands to improve the conductivity. This results in an increased coupling of charge carrier wavefunctions between NCs, thus increasing the charge carrier tunnelling rate. Ligand exchange can also be undertaken in the solution phase prior to depositing the PbS NCs films with this procedure enabling smooth film morphologies to be obtained.²⁴ However, in the majority of devices the former method is utilized, referred to as solid-state ligand exchange, often inducing cracks and voids within the PbS NC films. To minimise these, PbS NCs films may be deposited *via* sequential layer-by-layer deposition and treatment (the same method also being employed for phototransistor and photodiode device fabrication).

The concept of gain and role of traps. Photoconductivity in a photodetector principally originates from the generation of a primary photocurrent. Such currents are a direct result of absorption of photons followed by the extraction of photoexcited carriers and governs the external quantum efficiency (EQE) of the device. Photoconductivity may also result from the generation of a secondary photocurrent originating from the injection and transit of charge carriers from the device electrodes and governs the photoconductive gain (G), expressed as given in equation 2:

$$G = \frac{\tau_{lt}}{\tau_{tt}} = \frac{\tau_{lt}\mu V}{l^2} \quad ; \quad \left\{ \tau_{tt} = \frac{l}{\mu F} = \frac{l^2}{\mu V} \right\} \quad (2)$$

where, τ_{lt} is the lifetime of the majority charge carrier, τ_{tt} is the transit time of the majority charge carrier, μ is the mobility of the majority charge carrier, l is the distance between the electrodes and V is the voltage bias used to create electric field $F = (V/l)$. It can be seen that gain ($G > 1$) may be achieved within the device if $\tau_{lt} > \tau_{tt}$. In most practical situations a material's free carrier lifetime is modified by the presence of electron and hole trapping states found within the bandgap. The nature of trap states in semiconducting materials can be classified into two categories: (1) trapping centres – traps which lie close to the band edges and the trapped electron (hole) has a high probability of thermal excitation back into the conduction (valence) band; and (2) recombination centres – traps which lie close to the middle of the bandgap and the trapped charge carriers have high probability of recombining with the opposite carrier.²⁹ Recombination centers can either shorten carrier lifetime (type-I) or can significantly prolong it (type-II or sensitizing centers). It is well established that mid-gap trap states in the PbS NC bandgap are introduced during the solid-state ligand exchange process with a typical energy depth of 0.2-0.5 eV.^{23,30-33} The fundamental origin of these mid-gap states is yet to be fully understood but is often attributed to off-stoichiometry (Pb rich atoms located on the {111} surfaces) or an imbalance between excess Pb atoms and coordinated ligands.^{34,35} These mid-gap trap states can act as sensitizing centers and prolong the carrier lifetime resulting in gain when an adequate electric field is present. The lifetime of a charge carrier in a material with N trap states per unit volume with a capture-cross section area of S can be expressed by equation 3:²⁹

$$\tau_{trap} = \frac{1}{vSN \exp(-\Delta E/kT)} \quad (3)$$

where $v = \sqrt{(3kT/m_e^*)}$ is the thermal velocity of the charge carrier, ΔE is the energy depth of the trap relative to the band edge, k is the Boltzmann constant and T is the temperature. Restricting attention to recombination centers (i.e. $\Delta E \gg kT$) gives $\tau_{trap} = (vSN)^{-1}$. The lifetime of a trapped carrier can be estimated using a thermal velocity $v \sim 10^6$ cm sec⁻¹ and average density of traps $N \sim 10^{14}$ cm⁻³ for PbS NCs as reported in literature.³⁰⁻³² It has been found that for ligand exchanged PbS NCs the electron capture coefficient (vS) is ~ 400 times greater than the hole capture coefficient, therefore electrons are more likely to be trapped.³³ Consequently the electron contribution to the photocurrent is small and the photoconductivity is predominantly due to holes. The capture cross section of the trap depends on the electric field gradient in the neighbourhood of the trap, therefore a trap can be neutral, coulombically attracting or repelling. The value of S for a neutral or uncharged trap is of the order of the atomic dimensions $\sim 10^{-15}$ cm². Charged traps have a large capture cross-section that exerts a coulomb attraction on a free carrier, which is captured if it approaches sufficiently close (i.e. the binding energy due to coulomb attraction becomes $\geq kT$). It is also possible that a trap can exert a coulomb repulsion on a free carrier; such traps have a very small capture cross section.²⁹ Using current-based deep level transient and thermal admittance spectroscopy Bozyigit *et al.* derived the capture cross section area of trap in ethanedithiol treated PbS NCs as being of the order of $\sim (10^{-14}-10^{-16}$ cm²).^{31,32} Using an estimation of the trapped carrier lifetime based on reported values ($v \sim 10^6$ cm sec⁻¹ ; $S \sim 10^{-16}$ cm² ; $N \sim 10^{14}$ cm⁻³), τ_{life} can be as long as ~ 0.1 ms. Thus mid-gap states resulting from ligand exchange process act as sensitizing centers and depending upon the density of traps and their capture cross section area can prolong the carrier lifetime. Under such a condition, at an instantaneous time, the photoconductor is left with a net negative or a positive charge as the majority carriers can be extracted whilst the minority carriers are localised in traps. Thus, in order to maintain the charge neutrality another electron or hole (i.e. a majority charge carrier) is injected from the device electrode leading to flow of secondary photocurrents until the system is brought to equilibrium or electron-hole recombination takes place. The flow of a secondary photocurrent will not necessarily lead to

gain ($G>1$) but may do so. There are several other scenarios independent of recombination centers or traps that may also lead to gain. For example, in lateral bilayer or bulk heterojunction photoconductor devices where one of the photoexcited charge carriers is transferred to a high-mobility charge acceptor material whilst the other carrier remains in the donor material. Likewise, the trapping of a charge carrier in the acceptor material leaving the other charge mobile has the same affect. Under such conditions devices can exhibit gain at high electric fields provided that the electrodes facilitate the replenishment of the extracted carriers. Gain mechanisms have now also been exploited in photodiode devices³⁶⁻³⁹ (where trap rich materials are deliberately introduced in the photoactive region) or by creating heterostructure configurations in order to trap one charge carrier type.

Dark conductivity and photo conductivity. Ligand exchanged PbS NC photoconductor devices display electric field dependent conductivity even under dark conditions, yielding a dark current, and this is a key factor in determining the noise equivalent power (NEP) of the photodetector. The dark current in photoconductors is mainly dependent on the applied electric field, the charge carrier mobility, the choice of ligands, NC dispersity and size distribution, and also on the relative alignment of the metal electrode work function with the conducting band. The dark current density (J_d) can be expressed by equation 4:⁴⁰

$$J_d = \frac{N_h q \mu F}{l} \quad (4)$$

where, N_h is the majority carrier (hole) concentration, q the elementary charge and μ the carrier mobility. The majority of PbS NC photoconductor devices are fabricated with gold (Au) contacts which has a workfunction of $\varphi = -5.1$ eV. As such they can inject holes into the VB of PbS NCs larger than ~ 6 nm (as the Au workfunction matches the VB energy level of PbS NCs). This significantly increases the hole concentration (N_h) inducing p-type transport. Even for smaller diameter NCs there exists only a small potential barrier to hole injection in such cases.^{41,42}

In a study of PbS NC phototransistor devices by Nagpal *et al.* it was observed that the mid-gap trap states that are introduced following the ligand exchange process play a significant role in the dark conductivity of PbS NC films, Fig. 3a.³³ These trap states are moderately delocalized and may form a weakly conductive mid-gap band (MGB) if partially filled, Fig. 3d. In the case of completely filled or vacant mid-gap states their behaviour is insulating. The existence of a high density of trap states in PbS NCs can certainly lead to significant overlap of trap wavefunctions and can facilitate a hopping pathway for charge carriers. Ambiguity still exists as to whether these mid-gap trap states are coupled to the VB or the CB. The dark charge transport in two-dimensional PbS NC arrays has been studied *via* scanning tunnelling and Kelvin probe force microscopy. This provided evidence for charge percolation with pathways for electron and holes being imaged for the first time, Fig. 3e.⁴³ Trap states were found both above the Fermi level and the VB $1S_h$ state. It was observed that under dark conditions electrons can percolate *via* these states as they induce Fermi level pinning whilst holes percolate *via* the intrinsic VB states, Fig. 3f.

Efforts have been made to reduce the dark current in PbS NC photoconductors. It has been shown that the dark conductivity of ligand exchanged devices can be reduced by up to two orders of magnitude *via* blending PbS NCs with an appropriate concentration of silver (Ag) nanoparticles.⁴⁰ Due to the workfunction of Ag ($\phi = -4.3$ eV) the nanoparticles act as an electron donor and fill any shallow electron traps thereby suppressing p-type conductivity. In an another similar study it was shown that under photoexcitation electrons from the CB of PbS NCs can transfer to Ag nanoparticles which act as traps, prolonging the carrier lifetime and increasing the photocurrent by up to three orders of magnitude.⁴⁴

Photoexcitation of a PbS NC film generates electron-hole pairs and the majority of the photocurrent is carried by the holes. The fate of excited electrons can vary; they can be directly excited to mid-gap states ($M1_s$ and M_x) or directly to the CB states ($1S_h$ to $1S_e$), Fig. 3c. Also, the excitation of captured electrons from mid-gap states to CB states is possible, Fig. 3c. Strong

photocurrent features originating from $M1_s$ and M_x transitions, comparable to intrinsic band edge transitions have been observed in wavelength dependent photoconductivity of PbS NC films, Fig. 3b. The transition from mid-gap states to CB states is less observable, as their contribution to the photocurrent is relatively small, but may be found at longer wavelengths depending on the activation energy of the mid-gap states. The responsivity (or the gain) in PbS NC ligand exchanged devices is principally governed by the occupancy of these mid-gap trap states which is strongly dependent on the illumination intensity of the incident light. Under low level illumination, where the density of trap states is higher than the density of photoexcited charge carriers, holes can transit the device whilst electrons can be captured or partially fill the mid gap states resulting in gain. Alternatively, increasing the illumination intensity can fill the trap states, raising the quasi-Fermi level of electrons close to the CB and the device may then lose the gain that was initially governed by the presence of partially filled trap states. Note that the gain expression, equation (2), implies that unlimited gain can be achieved in the device by increasing the applied electric field (assuming that voltage is below device breakdown voltage). However there does exist a fundamental limit as at high electric fields the space charge current set up in the device increases the density of charge carriers filling the traps which leads to fast recombination of charge carriers. The maximum gain in the device will therefore depend on the light level, trap density and distribution, and also on the applied bias. Traps in general can be filled *via* optical excitation, injection of charge carriers, thermal excitation, or *via* introducing a donor to the semiconductor. The current focus of much research remains in deep understanding of trap associated charge transport behaviour in PbS NCs and their role in influencing the device performance.^{30-33,45,46}

As the gain is principally achieved *via* a prolonged carrier lifetime this limits the temporal response of the device that requires a fast recombination and subsequent collection of charge carriers. This sets up a fundamental trade-off between photoconductor gain and the bandwidth. Furthermore, the hole mobility in PbS NC films is very low, typically of the order of 10^{-4} to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and directly influences the transit time thus gain starts to decrease rapidly

with increasing illumination intensity. Although simultaneously with an increase in illumination intensity there is an increase in the device bandwidth due to fast recombination of charge carriers. A promising approach reported to address this challenge induces a bimolecular interfacial recombination process in the device.⁴⁷ Photoconductor devices were fabricated in a bi-level structure by depositing a PCBM film on top of PbS NC film. Upon illumination of the device photoexcited electrons transfer from PbS NCs to PCBM and the transferred electrons then recombine with the hole in the PbS NCs *via* interfacial recombination, thereby terminating the long PbS free carrier lifetime and also avoiding trap assisted recombination. The devices displayed a bandwidth >300 kHz under an illumination intensity of $\sim 57 \text{ mW cm}^{-2}$. Hybrid inorganic-organic photoconductors based on type-II heterojunctions *via* blending PbS NCs with widely used fullerene acceptors, PCBM and C_{60} crystals have also been reported.^{48,49} One advantage of hybrid devices is that they can operate even with oleic acid ligands as the photoexcited charge transport occurs through acceptor materials, although long ligands may suppress the electron transfer process from PbS NCs to the acceptor material. In such hybrid devices both charge carriers may be collected depending upon the charge percolation pathways in the blend film and also the type of NC ligand used. Photoexcited electron transfer from PbS NCs to the fullerene occurs on the sub picosecond scale ($<120 \text{ fs}$).⁵⁰ However charge transfer from PbS NCs to PCBM does not occur above a NC diameter of 4.4 nm due to the higher LUMO level of PCBM relative to PbS NC size dependent bandgap, restricting use of PCBM to wavelengths shorter than $\sim 1400 \text{ nm}$.^{50,51} C_{60} , due to its lower LUMO level ($\sim 4.5 \text{ eV}$), can accept electrons from larger diameter PbS NCs and responsivity at wavelengths up to $\sim 2000 \text{ nm}$ have been demonstrated.⁵² In addition, the use of crystalline C_{60} structures with NCs is beneficial as free charge carriers generated in C_{60} significantly contribute to the overall photoconductivity of the device.⁵³⁻⁵⁷ Charge transfer dynamics in hybrid blends (PbS NC/fullerene and PbS NC/fullerene/polymers) have been investigated in detail in separate studies.^{58,59} Comparative studies on the use of organic and inorganic charge acceptor materials for PbS NCs have also been carried out.⁶⁰⁻⁶² Photoconductor devices fabricated *via* photosensitizing one dimensional

(1D) nanomaterials with PbS NCs, including carbon nanotubes (CNTs)⁶³⁻⁶⁵ and fullerene C₆₀ nanorods,⁵³ benefit from the large donor/acceptor interface and also *via* harnessing plasmonic effects have been demonstrated.^{66,67}

PbS NC phototransistor devices. Phototransistor devices in contrast to photoconductor devices have three electrical contacts. This provides a greater degree of control over the conductivity of the semiconductor *via* the ability to vary the gate voltage in addition to the source to drain voltage and the illumination intensity, Fig. 2b. The application of a negative gate bias for example will induce opposite charge carriers (holes) in a p-type PbS NC film and will therefore increase the conductivity, Fig. 3b.³³ Thus the gate electrode can be used as a switch or an amplifier, and can also control the fermi level position thereby populating or depopulating trap states. As the gain is directly proportional to the mobility of the charge carrier hybrid phototransistors are usually fabricated by integrating PbS NCs with materials having exceptionally high carrier mobilities, for example two dimensional (2D) materials like graphene⁶⁸⁻⁷² and molybdenum disulphide⁷³ (MoS₂). Konstantatos *et al.* reported a hybrid PbS NC:graphene phototransistor, fabricated using mechanically exfoliated single/bilayer graphene flakes from pyrolytic graphite, with a responsivity of $\sim 10^7$ AW⁻¹ and a detectivity $> 10^{13}$ Jones.⁶⁸ Photoexcitation of the hybrid systems leads to hole transfer from the PbS NCs to graphene whilst the electrons remain in the PbS NCs and their associated trap states. The transferred holes transit very fast under the applied electric field due to the high mobility of the graphene. One of the most notable features of the PbS NC:graphene hybrid device is its ability to efficiently detect very low optical powers down to ~ 10 fW. The hybrid device exhibited a slow temporal response with a rise time of ~ 10 ms and a bi-exponential decay of ~ 100 ms and ~ 2 s. In these devices it is demonstrated that the decay time can be shortened (to ~ 10 ms) by applying a voltage pulse at the gate electrode that reduces the potential barrier at PbS NC:graphene interface, keeping electrons trapped in the PbS NCs. Enhancement of the responsivity of the PbS NC:graphene devices has been demonstrated recently *via* capping PbS NCs with shorter ligands with devices displaying an exceptionally high responsivity $\sim 10^9$ AW⁻¹.⁶⁹ Large-area device

fabrication using graphene is challenging, although efforts have been made to realise these *via* chemical vapor deposition (CVD) of graphene on flexible substrates.⁷⁰ PbS NC:MoS₂ phototransistors (operating through electron transfer from PbS NCs to MoS₂) have been reported with improved dark currents relative to the graphene based devices, combined with a comparable responsivity of $\sim 10^6$ AW⁻¹ and a detectivity $> 10^{11}$ Jones.⁷³ A recent significant breakthrough has overcome the fundamental bottleneck of gain-bandwidth trade-off in PbS NCs *via* fabricating a photo-junction field effect transistor (photo-JFET).⁷⁴ The device incorporates a rectifying junction between iodine treated n-type PbS NCs and transparent conducting molybdenum trioxide (MoO₃) deposited on top of a PbS NC film. The device displayed a gain of 10 at modulation frequency of 100 kHz, whilst PbS NC based photoconductor devices typically only display gain below 100 Hz. Hybrid phototransistors fabricated *via* integrating PbS NCs with 2D materials have displayed a gain that is orders of magnitude larger than that of PbS NC only photoconductor devices. In such devices the gain relies more on the short transit time of charge carriers in the 2D material, rather than the long minority charge carrier lifetime of the PbS NCs, although both mechanisms can simultaneously lead to high gain.

PbS NC photodiode devices. Photodiodes can be classified into Schottky-type, heterojunction type, p-n type and p-i-n type, Fig 2c, d, e, f. The operating principle in photodiode devices however is the same, that is to separate and collect the photogenerated electrons and holes by creating a built-in electric field. The photogenerated charge carriers typically need to cross a number of device regions to be collected, therefore the device thickness is critical and lifetime of the carriers must be longer than the transit time of the carriers. The long charge carrier diffusion length in PbS NCs films is therefore beneficial and can significantly enhance the quantum efficiency of the device. In ligand exchanged PbS NC devices the diffusion length of charge carriers is not only governed by their mobility alone as the average spacing among the recombination centers plays significant role in determining the diffusion length.¹⁴ Photodiodes can be operated at zero bias (photovoltaic mode) but are usually used under reverse bias conditions (photoconductive mode) offering high bandwidth and wide linear dynamic range.

The high detectivity in the majority of photodiode devices results from a low noise current rather than a high responsivity.

Schottky-type photodiodes, fabricated by the selection of a suitable metal-semiconductor interface generate an in-built field that may be used to extract the photogenerated holes and electrons. The use of low workfunction metals with PbS NCs typically forms a Schottky barrier that is rectifying in nature. PbS NC photodiode devices based on a Schottky barrier at the interface between PbS NCs and an aluminium (Al) contact, with indium tin oxide (ITO) forming the opposing ohmic contact, were reported with a $3dB$ bandwidth >1 MHz, Fig. 2c.²⁵ Recently, a meniscus-guided direct-writing technology was used to fabricate a hybrid flexible P3HT single nanowire photodetector ($D^* > 10^{12}$ Jones) based on Schottky contacts, sensitized with oleic acid capped PbS NCs.⁷⁵ Heterojunction type photodiodes are based on semiconductor-semiconductor junctions and are usually fabricated *via* employing an organic or inorganic n-type semiconductor for charge extraction in conjunction with PbS NCs and in some cases π -conjugated polymer as well. The energy level alignment of materials used is such that they facilitate both electron and hole collection at the opposite contacts. They can be further classified into planar and bulk-type heterojunction photodiodes. Rauch *et al.* reported hybrid organic-inorganic bulk heterojunction photodiodes fabricated using blend of oleic acid capped PbS NCs, PCBM and P3HT.⁷⁶ The presence of PCBM and P3HT enabled efficient electron and hole transfer from the PbS NCs respectively. The device displayed an *EQE* of 51% with a detectivity of $\sim 10^9$ Jones. Similar devices exhibiting gain with an *EQE* of $\sim 1624\%$ and detectivity $\sim 10^{11}$ were realized by introducing zinc oxide (ZnO) quantum dots into a PbS NC:PCBM:P3HT blend, Fig. 2d.⁷⁷ The gain in these devices arises due to the high density of trap states present in ZnO that traps photoexcited electrons triggering hole injection from the Al contact. PbS NC based p-n photodiode devices utilizing p-type PbS NCs and wide bandgap n-type metal oxides (ZnO/TiO₂) as a charge transport layer have shown reduced dark current upto two orders of magnitude compared to Schottky-type photodiodes, Fig. 2e.⁷⁸ Very recently PbS NC based vertically stacked p-i-n like photodiodes have also been reported, displaying gain

(EQE ~18700%) with a detectivity $>10^{13}$ Jones Fig. 2f.^{79,80} These devices incorporate both electron and hole blocking layers to suppress charge injection from the conducting electrodes. In the case of 1, 3-benzenedithiol (BDT) treated PbS NCs the Fermi level lies close to the middle of the PbS bandgap, therefore these PbS NCs are treated as an intrinsic semiconductor sandwiched between p-type and n-type materials. These reported values of EQE above 100% do not solely originate from measurement of the primary photocurrent alone but include a significant secondary photocurrent contribution.

Summary & Outlook

The emergence of PbS NCs for photodetector device fabrication has been a great success in semiconductor NC research. Over the last decade, PbS NC based photodetectors have shown significant promise, in terms of low-cost ease of device fabrication at room temperature, with flexible platform compatibility and high figures of merit achieved. However, to assist their further development and inform future design rules for commercialisation several challenges still remain outstanding as subjects for further research. These include further control of NC synthesis and subsequent NC stability, an understanding of the dependence of optoelectronic device properties on NC size, optimal ligand choice and treatment, studies of device stability, and a deeper fundamental understanding of charge transport together with the control and engineering of charge carrier traps in PbS NC films.

The development of high quality NCs with uniform size and with high air stability is a key prerequisite to realise high performance devices, and to provide a consistent model of charge transport in NC films. Size disorder and the choice of ligands used plays a significant role in charge extraction and in determining charge carrier mobility within a film.^{81,82} For example, hole mobility in PbS NC films decreases with increasing NC size. A reduction in NC diameter increases charge carrier confinement resulting in increased wavefunction '*leakage*' outside the NC that may then more strongly couple with that of neighbouring NCs.⁸³ Depending upon on

synthesis route employed, NCs may display size dependent air stability with NCs < 4 nm diameter being stable in air whilst their stability decreases with increase in NC size.⁸⁴ The choice of synthesis route may also limit the obtainable range of NC sizes, though one step procedures yielding NCs from 3 nm to 10 nm⁴ exhibiting air stable properties for upto several months have been reported.⁷ Solid-state ligand exchange processes can be employed to improve the mobility of charge carriers in the film, however such a process may result in incomplete ligand exchange and introduce traps. Indeed, such a process is an effective way to intentionally introduce sensitizing centers in order to promote gain in photoconductors,²³ though such centers are detrimental to realising high efficiency high speed photodiodes. Furthermore, the activation energy and the density of the traps are both NC size⁴⁵ and ligand treatment²³ dependent. This directly impacts on device performance and places limitations on the figures of merit that may be achieved. Halide passivation⁸⁵ and hydrazine treatment⁴³ have shown promising way to passivate traps, whilst strategies like amine treatment of NC films that results in ligand removal, rather than ligand exchange have also been proposed⁸⁶

Progress in advanced photodetector design continues with NC photodetectors based on nano-gap^{87,88} and plasmonic flat-lens bull's eye structures,⁸⁹ accompanied by advanced device fabrication methods based on centrifugal casting.⁹⁰ PbS NCs have been integrated with InGaAs⁹¹ and Si⁹² devices enabling them to efficiently detect UV and near-IR light respectively. MEG has also been exploited in PbS photoconductor devices, enhancing the responsivity of the device in the UV regime with an internal gain >100% at 220 nm.²⁶ Improvement in the mobility of the charge carrier may lead to a reduction in the threshold MEG energy towards $2E_g$.⁹³ With both p-type and n-type PbS NC availability along with their tunable bandgap, there remains an interesting opportunity to realise all PbS p-n heterojunction photodiodes.

Photodetectors have already displayed a responsivity of $\sim 10^9$ AW⁻¹, a 3dB bandwidth of ~ 3 MHz, a wide dynamic range of ~ 150 dB, and a detectivity of $\sim 10^{13}$ Jones. Additionally, with a broadband multispectral (UV-Vis-IR) sensitivity they have significant potential to be utilized in

many applications including visible, biomedical and hyperspectral imaging systems, spectroscopy, power meters, opto-couplers, food and pharmaceutical inspection, remote sensing and surveillance. For practical device applications, the lifetime and stability of the devices are major concerns. Typically devices can display a ~20% decrease in performance, in ambient conditions, over a few weeks that is extended if stored in nitrogen environment to a few months.²¹ Photodiode devices fabricated on top of amorphous silicon active matrix (a-Si AM) thin film transistor (TFT) panels, have displayed near-IR imaging and video capability, Fig 4a, b.⁷⁶ These image sensors tested in a climatic chamber have showed minimum lifetime of one year. Air stable devices operating in SWIR regime (2.1-2.4 μm) have also been realised *via* passivating PbS NC films with an Al_2O_3 barrier layer.⁹⁴ PbS NC based focal plane arrays (FPAs) and camera prototype devices have been demonstrated recently with wide range of array and pixel sizes, Fig. 4c,d,e.⁹⁵ These rely on a PbS NC:C₆₀ heterojunction photodiode monolithically integrated with Si ROIC. The arrays display a spectral response from (400 nm - 2000 nm), dynamic range ~ 60 dB, fast rise/fall time ~2 μs with a detectivity ~ 10¹² Jones.^{52,95-97} These PbS NC FPAs display multispectral sensitivity with a detectivity comparable to InGaAs devices that currently dominate the commercial market, and provide infrared performance beyond the capability of Si based technologies, Fig.4f. Photoconductor devices have also been demonstrated as an electronic skin sensor for heart rate detection, displaying an improved performance over commercial heart rate detectors, Fig 4g, h,i.⁶⁴ Interestingly, photoconductor devices can even efficiently detect toxic and hazardous gases including nitrogen dioxide (NO₂) and hydrogen sulfide (H₂S), Fig 4j, k,l.^{98,99} Hence, PbS NCs based detectors show promise for their utilization as a future multipurpose sensor system.

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Competing financial interests

The authors declare no competing financial interests.

Author contributions

R. S. and R. J. C. co-wrote the paper.

Box 1 | Figures of merit for photodetectors

Responsivity ($R(\lambda)$) is defined as the ratio of photocurrent or voltage generated to the incident optical power falling onto the detector at a given wavelength (λ). The spectral response of photodetector is obtained by plotting the responsivity versus wavelength and usually follows the absorption spectrum of the photosensitive semiconductor material used for the fabrication of the detector. The responsivity of a photodetector is given by the expression:

$$R(\lambda) = \frac{I(\lambda)_{ph}}{P(\lambda)_{in}} \quad (A/W)$$

where, $I(\lambda)_{ph}$ is the photocurrent in amperes and $P(\lambda)_{in}$ is the incident optical power in watts. The responsivity of a photodetector is a function of incident wavelength (λ), modulation frequency (f) and applied electric field (F). The responsivity, external quantum efficiency ($EQE(\lambda)$) and photoconductive gain ($G(\lambda)$) are interrelated as:

$$EQE(\lambda) = R(\lambda) \frac{hc}{q\lambda} \cong R(\lambda) \frac{1.24}{\lambda}; \quad \left\{ R(\lambda) = \frac{EQE(\lambda)G(\lambda)}{1} * \frac{q\lambda}{hc} \right\}$$

where, h is Planck's constant, c is the speed of light and q the elementary charge. When using the approximation given for $R(\lambda)$ values of λ in μm should be used. The $EQE(\lambda)$ evaluates the ratio of the number of charge carriers collected to the number of photons absorbed. The expression given (left) is valid for devices operating in photovoltaic mode and in the absence of any secondary photocurrent.

Noise Equivalent Power ($NEP(\lambda)$) is defined as the optical power at which the signal-to-noise ratio (SNR) is unity or the minimum detectable power per square root of bandwidth and is obtained using:

$$NEP(\lambda) = \frac{\sqrt{I_n^2}}{R(\lambda)} \quad (W/\sqrt{Hz})$$

where, I_n is the noise current spectral density. Total noise current in a detector is sum of all the noise sources. These include low frequency flicker noise ($1/f$), thermal noise (I_{th}) and shot noise (I_{sh}). The root-mean-square (r.m.s) value of thermal noise and shot noise current is given by $I_{th} = \sqrt{4kTB/R}$ and $I_{sh} = \sqrt{2qBI_d}$ respectively where, k is Boltzmann's constant, T is absolute temperature, R is the resistive element source contributing to noise, B is the noise bandwidth, and I_d is the dark current. The noise spectrum of a detector is a noise current spectral density versus frequency plot that is used to determine the magnitude of noise at the frequency at which the photodetector operates. Furthermore, in photoconductor devices that involve the trapping of charge carriers, generation-recombination noise (I_{gr}) can be the dominant source of noise and follows:

$$I_{gr} = \sqrt{\frac{4qI(\lambda)G(\lambda)B}{1 + (2\pi f\tau_{it})^2}}$$

where, $I(\lambda)$ is the steady-state output photocurrent. This noise if dominant in the device will typically generate a Lorentzian-type noise spectrum.

Detectivity ($D^*(\lambda)$) is the most important figure of merit for photodetectors as it allows the comparison between photodetector devices having different configurations and area. The detectivity of a photodetector signifies the SNR in an AC signal when an optical power of 1 W is incident on the detector normalized to a noise bandwidth of 1 Hz for a detector area of 1 cm². As the detectivity of a photodetector is directly proportional to the responsivity, it is indirectly a function of wavelength, modulation frequency and applied electric field.

The detectivity of a photodetector is expressed in $cm\sqrt{Hz}/W$ or Jones and is obtained using equation:

$$D^*(\lambda) = \frac{\sqrt{A}}{NEP(\lambda)} \quad (cm\sqrt{Hz}/W) \text{ or Jones}$$

where, A is the active area of the photodetector.

Response time or Time constant (τ) is defined as the time taken by the photodetector output signal to reach $(1 - e^{-1}) \sim 63\%$ of its peak steady-state value in response to an incident optical signal. In photoconductor devices the photocurrent follows the rise and fall of incident modulated light at low frequencies. With increasing modulation frequency the photosensitivity ratio $I(\lambda)_{ph}/I_d$ decreases as the photocurrent does not decay fully within the time $(1/2f)$. The frequency at which the photocurrent is reduced from its peak value (i.e. the dc photocurrent) to $1/\sqrt{2} (\sim 0.707)$ times is defined as the **3dB** bandwidth (f_{3dB}) or the cut-off frequency. The responsivity of photoconductor in the frequency domain is given by the expression:

$$R(\lambda)_f = \frac{R(\lambda)_0}{\sqrt{1 + (2\pi f\tau)^2}}$$

$R(\lambda)_0$ is the DC responsivity where R_f has the maximum value and τ is the response time which related to the cut-off or **3dB** bandwidth of the detector as:

$$f_c = \frac{1}{2\pi\tau}$$

The response time only takes account of the signal rise up to $\sim 63\%$, however it takes ~ 4 more time constants for the signal to reach final steady-state value. Therefore, another set of related parameters: the rise time (t_r) and fall time (t_f) of a photodetector are often used to evaluate the speed of the detector. The rise time and fall time are defined as the time required by the photodetector output signal to rise or fall from 10% to 90% or from 90% to 10% of its final value respectively in response to a light pulse input. These parameters are related to the response time as $t_r = 2.2\tau$ and can also be used to determine the frequency response and **3dB** bandwidth.

$$f_c = \frac{1}{2\pi\tau} ; f_c = \frac{2.2}{2\pi t_r} ; f_c = \frac{0.35}{t_r}$$

Note that t_r and t_f of the detector can be different and should be taken in consideration when determining the bandwidth of the device. Furthermore, the performance of the devices exhibiting gain is often evaluated on the basis of the gain-bandwidth product.

Dynamic Range ($DR(\lambda)$) of a photodetector is defined as the range over which the photocurrent increases with increasing incident optical power. It is this range of optical power over which the detector can be employed to detect the incident signal. Ideally, the responsivity of the device should remain constant with increasing light intensity. The full dynamic range is usually measured from the **NEP** of the photodetector to the optical power at which photocurrent saturates. It is usually reported in decibels (dB). The **DR** can be expressed as:

$$DR(\lambda) = 20 \log \frac{P(\lambda)_{max}}{P(\lambda)_{min}} \quad (dB)$$

where $P(\lambda)_{max}$ is the maximum impinging power above which photocurrent saturation occurs and $P(\lambda)_{min}$ is the minimum detectable optical power or the NEP. The linear Dynamic Range (**LDR**) is the range over which photocurrent increases linearly with increasing optical power.

Table 1 | Progress in PbS NC based photodetector technologies

Photoactive material	Device configuration	Ligand treatment	Active area (mm ²)	Spectral range (nm)	Responsivity (AW ⁻¹)/EQE (%)	Detectivity (Jones)	Dynamic range (dB)	Bandwidth	Year/Ref.
PbS NC	Photoconductor	Butylamine	0.015	800-1500	2700 AW ⁻¹	1.8 x 10 ¹³		18 Hz	2006/21
PbS NC	Photoconductor	Butylamine	0.015	400-900	113 AW ⁻¹	5 x 10 ¹²	150	8 Hz	2007/22
PbS NC	Photoconductor	As ₂ S ₃	0.08	900-1550	200 AW ⁻¹	1.2 x 10 ¹³			2014/100
PbS NC	Photoconductor	OH ⁻ /S ²⁻		2100-2400	50 AW ⁻¹	3.4 x 10 ⁸		40 Hz	2014/94
PbS NC:Ag NC	Photoconductor	MPA	1.5	350-800	4 x 10 ⁻³ AW ⁻¹	7.1 x10 ¹⁰		9.4 Hz	2014/44
PbS NC:Ag NP	Photoconductor	Ethanedithiol	0.015	400-1700	5 AW ⁻¹	2.5 x 10 ¹¹		200 Hz	2015/40
PbS NC:PCBM	Photoconductor	Oleic		700-1400	0.32AW ⁻¹	2.5 x 10 ¹⁰			2009/48
PbS NC:PCBM	Photoconductor	Ethanedithiol	0.59	800-1400	57%	4.4 X 10 ⁷		330 kHz	2010/47
PbS NC:C₆₀ Crystals	Photoconductor	Carboxylate	25	400-1350	7 x 10 ⁻⁴ AW ⁻¹	3.2 x 10 ¹⁰			2013/49
PbS NC:MWCNTs	Photoconductor	MPA		Vis/NIR	0.583 AW ⁻¹	3.2 x 10 ¹²			2014/64
PbS NC:CdS NC	Photoconductor	Ethanedithiol		Vis	0.022 AW ⁻¹	2.1 x 10 ¹⁰			2014/101
PbS NC:C₆₀ NR	Photoconductor	Oleic	25	350-1100	0.125 AW ⁻¹	2.3 x 10 ⁹	100		2014/53
PbS NC:Au NC	Photoconductor	CTAB		350-1000	0.0016AW ⁻¹	1.1 x 10 ¹⁰		61.2 Hz	2014/102
PbS NC:MoO₃	Phototransistor	TABI	0.0075	400-1100	4 AW ⁻¹	2 x 10 ¹⁰			2015/74
PbS NC:Graphene	Phototransistor	Ethanedithiol	9 x 10 ⁻⁷	400-750	3x 10 ³ AW ⁻¹				2012/71
PbS NC:Graphene	Phototransistor	Pyridine	0.2	NIR	10 ⁷ AW ⁻¹				2012/70
PbS NC:Graphene	Phototransistor	Ethanedithiol		600-1600	10 ⁷ AW ⁻¹	7 x 10 ¹³		10 Hz	2012/68
PbS NC:Graphene	Phototransistor	TGL/DTG	6 x 10 ⁻⁷	700-1250	10 ⁹ AW ⁻¹				2015/69
PbS NC:MOS₂	Phototransistor	Ethanedithiol	1.5 x	550-1150	6 x 10 ⁵ AW ⁻¹	5 x 10 ¹¹			2015/73
PbS NC:P3HT:PCBM	Phototransistor	Oleic	5	Vis/NIR	6 x 10 ⁻⁷ AW ⁻¹	1.93 x 10 ⁸			2012/103
PbS NC	Photodiode	Benzenedithiol		400-1800	17 %	1 x 10 ¹²		3 MHz	2008/25
PbS NC:P3HT NW	Photodiode	Oleic	1.25 x	365-940	100 AW ⁻¹	2.1 x 10 ¹²			2015/75
PbS NC:P3HT:PCBM	Photodiode	Oleic	4	1000-1850	0.5 AW ⁻¹	2.3 x 10 ⁹	40	2.5 kHz	2009/76
PbS:P3HT:PCBM:ZnO	Photodiode	Butylamine	6.25	300-1100	1.24 AW ⁻¹	2.2 x 10 ¹¹	70		2014/77
PbS NC:ZnO/TiO₂	Photodiode	Ethanedithiol	9	300-1100	80%	1.45 x 10 ¹²	60		2012/78
PbS NC: TiO₂	Photodiode	MPA		400-1100	0.3 AW ⁻¹	2.4 x 10 ¹³		1.2 MHz	2015/90
PbS NC:C₆₀	Photodiode			400-2000	0.37 AW ⁻¹	1 x 10 ¹²	60		2015/95-97
ZnO:PbS NC:TAPC	Photodiode	Benzenedithiol	4	700-1600	18700%	7 x 10 ¹³			2015/79
NiO:PbS NC:ZnO	Photodiode	Benzenedithiol	4.5	400-1300	0.2 AW ⁻¹	1.1 x 10 ¹²	67	36 kHz	2014/80

PbS - Lead Sulphide; NC - Nanocrystals; Ag - Silver; NP - Nanoparticles; MPA - Mercaptopropionic acid; PCBM - Phenyl-C₆₁-butyric acid methyl ester; MWCNTs - Multi Walled Carbon Nanotubes; CdS - Cadmium Sulfide; NR - Nanorods; Au - Gold; MoO₃ - Molybdenum trioxide; CTAB - Cetyltrimethylammonium bromide; MOS₂ - Molybdenum disulphide; TBAI - Tetrabutylammonium iodide; TGL/DTG - Thioglycerol/Dithioglycerol; NW - Nanowire; P3HT - Poly(3-hexylthiophene); ZnO - Zinc Oxide; TiO₂ - Titanium dioxide; NiO - Nickel oxide; TAPC - 1,1-bis[[di-4-tolylamino] phenyl]cyclohexane.

Figure 1. Tunable optical properties of PbS nanocrystals. **a**, Spectral range of conventional photodetectors operating in different windows of the electromagnetic spectrum compared to the size tunable multispectral sensitivity that can be achieved *via* the use of PbS NCs. The schematic also provides a comparison of the (Typical) figures of merit responsivity and detectivity of standard photodetectors (GaP, Si, InGaAs and Ge photodiodes, and PbS and PbSe bulk photoconductors) operating at room temperatures with those of reported PbS NC based photodetectors. **b**, PbS NCs size dependent optical absorption spectra. The first exciton absorption peak ($1S_h \rightarrow 1S_e$ transition) in the absorption spectra corresponds to the bandgap (E_g) of the PbS NC governed by their size (diameter, d) as formulated in the equation shown in the inset to the figure. With the increase in the PbS NC diameter (as shown in the figure from 4.3 nm to 8.4 nm) the bandgap of the NC decreases, enabling absorption at longer wavelengths. **c**, Transmission electron microscopy (TEM) image of two dimensional self-assembled PbS NC arrays in an hexagonal close-packed arrangement. **d**, TEM image of three dimensional PbS NC

self-assembly achieved *via* simple drop casting of concentrated PbS NCs yielding three-dimensional superlattices approximately 5 NC layers thick. **e**, PbS NC ligand governed band edge energy level tuning. The left of the figure shows a schematic of PbS NC capped with different ligands and the corresponding shift in the CB and VB energy levels is shown on the right. Choosing the appropriate ligand type allows the PbS NCs CB and VB energy levels to be modified to meet a desired requirement. Figures reproduced with permission from: **b**, **c** and **d** (ref. 7), © (2014) American Chemical Society; **e**, (ref. 19), © (2014) American Chemical Society.

Figure 2. Device architecture and configuration of PbS nanocrystal based photodetectors.

a, Schematic depicting a photoconductor device that can be fabricated *via* depositing a PbS NC film between two metal (as shown) or on interdigitated (Au) electrodes (ref. 21). The absorption of photons within the semiconducting material results in the creation of electron-hole pairs that increases the density of charge carriers in conducting bands. The biasing of the electrodes sets up an electric field that may sweep photoexcited charge carriers out of the device, thereby generating a photocurrent in the external circuit. **b**, Schematic depicting a bottom gate phototransistor device with lateral source and drain contacts (Au) (ref. 33). The conductivity of the charge transport material through the channel l can be controlled *via* the application of gate bias (see Fig. 3a,b). **c**, A Schottky-type photodiode can be fabricated *via* sandwiching PbS NC film between two metal electrodes, for example Al and ITO (ref. 25). A depletion region and built-in electric field is created in the PbS NC film as the fermi levels of the semiconductor and the metal are brought to equilibrium. Controlling the PbS NC film thickness is critical in such devices to realise fully depleted devices. In the case of very thick films the

depletion region only occurs over a fraction of the PbS NC layer with the majority of the film remaining quasi-neutral. For a fully depleted device photoexcited electrons and holes created in the depletion region can be collected at the Al and ITO electrode respectively under an applied electric field. **d**, Schematic of a bulk heterojunction photodiode fabricated using a PbS:P3HT:PCBM:ZnO blend film between ITO and Al contacts. A Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer is used as electron blocking/hole transport layer (ref. 77). **e**, Schematic of a p-n junction photodiode fabricated employing p-type PbS NCs and n-type ZnO NPs (ref. 78). Compared to Schottky photodiodes, in these devices fully depleted PbS NC films of thickness ~ 150 nm were observed enabling the efficient separation and collection of photoexcited charge carriers by the built-in electric field. **f**, Device architecture of a vertically stacked p-i-n photodiode device that incorporates intrinsic PbS NCs sandwiched between p-type 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC) and n-type ZnO NCs (ref. 79). Figures adapted with permission from: **c** (ref. 25) © (2006) Nature Publishing Group; **d** (ref. 77) ©(2014) Wiley; **e** (ref. 78) ©(2012) Wiley; **f** (ref. 79) ©(2015) Wiley.

Figure 3. Charge transport in dark and photoexcited films of PbS nanocrystals. **a**, Gate voltage dependent dark conductivity (black line) and photoconductivity as a function of excitation wavelength of a PbS NC phototransistor device. The dark current in the device is significantly increased by the application of negative gate bias due to the injection of holes in the PbS NC film. **b**, The effect of negative gate bias on photoconductivity. Increasing the gate bias yields an increase in the external quantum efficiency across the entire spectral region of operation. Additional spectral features M_{1S} (~ 0.9 eV) and M_X (~ 1.5 eV) are observed. The energy difference ($M_{1S}-M_X$) between these features is ~ 0.6 eV equivalent to half the energy of features observed within the absorption spectrum (inset). This suggests that these features arise due to transitions between the occupied $1S$ and X VB states and the unoccupied mid-gap band (MGB) states, respectively. **c**, PbS NC energy level diagram illustrating optical transitions

between the quantized energy levels and MGB states (solid red arrows)). **d**, Schematic illustration of charge transport under dark conditions and under photoexcitation. Photoconductivity is predominantly due to hole transport *via* the VB, whilst the electron contribution is small *via* MGB states. **e**, Surface potential maps of two-dimensional PbS NC arrays at a gate voltage $V_g = 52$ volts and -52 volts, showing percolation pathways for electrons and holes (under dark conditions). The cyan/blue area represents electron percolation pathways and red/white area represents hole percolation pathways. At a positive gate voltage (i.e. when the electrons are injected) the percolation pathways for electrons are in the form of narrow stripes surrounded by electron-insulating areas (red/white). At negative gate voltage (i.e. when the holes are injected), percolation pathways for holes have larger domains surrounded by hole-insulating areas (blue/cyan). The hole transporting level was observed at ~ -5.0 eV below the vacuum level (PbS NCs VB edge) and electron transport level was observed at ~ -4.8 eV (far below the PbS NCs CB edge ~ -4.1 eV). **f**, Schematic illustrating the observed charge percolation pathways in a PbS NC film. NCs with a high density of MGB or in-bandgap states (IGS) (type-1, shown as violet) provide a conducting path for electrons. NCs with less of these states (type-2, shown as orange) do not enable sufficient wavefunction overlap to provide conducting pathways for electrons. NCs with no such states (type-3, shown as pink) do not facilitate charge transport. Hole transport in NC occurs *via* hopping through VB $1S_h$ states. Figures reproduced with permission from: **a-d** (ref. 33) © (2011) Nature Publishing Group; **e-f** (ref. 43) © (2015) American Chemical Society.

Figure 4. Multipurpose applications of PbS NC based photodetector devices. **a**, Schematic of a near-IR imager fabricated using (PbS NC:P3HT:PCBM) blend with an a-Si active matrix backplane. **b**, Image of a monarch butterfly (inset) taken by the device at ~ 1310 nm. **c**, Schematic showing architecture of PbS NC:C₆₀ heterojunction photodiode fabricated directly onto a readout integrated circuit (ROIC). **d&e**, Images of integrated PbS NC based imaging array on ROICs **f** A relative comparison of PbS NC photodiode devices with commercial InGaAs photodiodes, **g** Left: conventional heart rate detector worn on the middle finger and a PbS NC:MWCNTs detector on the adjacent forefinger. Right: heart rate detection test of the PbS NC based detector under red light. **h**, and **i** show heart rate signals detected using red and infrared light by the PbS NC based photoconductor. The photocurrent as a function of time is measured by the detector corresponding to heart refilling *via* expansion (diastole) following contraction (systole) **j**, A flexible PbS NC photoconductor fabricated on paper substrate with interdigitated Au electrodes for use as a gas sensor. **k** Response curves of the gas sensor to varying concentrations of NO₂ gas. The sensor displays a linear response to changes in NO₂ concentration (inset). **l**, The response of a PbS NC photoconductor gas sensor to different gases

(at a concentration of 50 ppm) at room temperature. Figures reproduced with permission from **a-b**, (ref. 76), © (2009) **c-f**, (ref. 95) © (2015) SPIE, Nature Publishing Group; **g-i** (ref. 64), © (2014) AIP Publishing LLC; **j-h** (ref. 98), © (2014) Wiley.