electronics

Review

Recent Progress of Non-Cadmium and Organic Quantum Dots for Optoelectronic Applications with a Focus on Photodetector Devices

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Abstract: Quantum dots (QDs) are zero-dimensional (0D) nanomaterials with charge confinement in all directions that significantly impact various applications. Metal-free organic quantum dots have fascinating properties such as size-dependent bandgap tunability, good optical absorption coefficient, tunability of absorption and emission wavelength, and low-cost synthesis. Due to the extremely small scale of the materials, these characteristics originated from the quantum confinement of electrons. This review will briefly discuss the use of QDs in solar cells and quantum dots lasers, followed by a more in-depth discussion of QD application in photodetectors. Various types of metallic materials, such as lead sulfide and indium arsenide, as well as nonmetallic materials, such as graphene and carbon nanotubes, will be discussed, along with the detection mechanism.

Keywords: quantum dot; confinement; tunable photoexcitation; solar cell; quantum dot laser; carbon dot; quantum dots photodetector

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Citation: Shabbir, H.; Wojnicki, M. Recent Progress of Non-Cadmium and Organic Quantum Dots for Optoelectronic Applications with a Focus on Photodetector Devices. *Electronics* **2023**, *12*, 1327. https://doi.org/10.3390/electronics12061327

Academic Editor: Lucas Lamata

Received: 30 January 2023
Revised: 3 March 2023
Accepted: 6 March 2023
Published: 10 March 2023

1. Nanomaterials

Nanomaterials have garnered much attention in recent years due to their fascinating and distinctive characteristics that surpass the limitations of bulk materials. Any substance with at least one dimension under 100 nm can be categorized as a nanomaterial [1,2]. Materials with all dimensions larger than nanoscale are called 3D materials or bulk materials, while researchers use a few classifications based on the dimensions of nanomaterials. If two dimensions are larger than the nanoscale, they are called 2D nanomaterials, e.g., quantum wells and nanolayers, a heterostructure composed of two barrier layers sandwiching a single thin well layer. This layer, which contains electrons and holes, is just about 100 Å thick; as a result, the electrons and holes start behaving like waves. In practice, standing waves in a direction perpendicular to the layers correspond to the permissible states in this structure. The system is quantized because only specific waves are standing waves. Many quantum mechanical processes can be observed and controlled in thin quantum well layered semiconductor structures. Modern epitaxial crystal growth techniques can produce them with great precision.

If one dimension of a material is in the nanoscale range and two dimensions are larger than nanoscale, it is categorized as a 1D nanomaterial, e.g., nanorods and nanowires [3,4]. 1D nanomaterials are used in solid-state electronics and as diagnostic tools in medical sciences. They can conduct at the level of one degree of freedom. This enables the utilization of nanowires in applications where electrical conduction is required [5].

If all dimensions of a material are smaller than 10 nm, it is called a 0D material, e.g., nanoparticles and quantum dots (QDs).

As the size limits approach the zero dimension and the region becomes extremely confined, it is also referred to as a dot. QDs are produced when material sizes become smaller and smaller in each dimension, which causes them to behave like groups of atoms and exhibit fascinating features. The electron–hole pair is also produced by some energy input, such as UV radiation, and the pair is kept together by Coulombic forces [6]. QDs' size ranges from 2 to 10 nm, or between 10 and 50 atoms, and they have 100 to 1000 electrons. Almost all material systems, including metal, insulators, and semiconductors, exhibit size-dependent electrical or optical characteristics in the quantum size domain. Due to its fundamental and technological significance, the semiconductor's energy band gap alteration is the most appealing [7]. The materials for the next generation of flat panel displays, photovoltaic, and optoelectronic devices are semiconductors with extensively tunable energy band gaps [8].

Quantum dots (QDs) are tiny semiconductor particles that can be utilized in photodetectors and other applications. They are typically only a few nanometers in size. QDs can be employed as a light-sensitive substance, also referred to as a photoconductive substance, in a photodetector. One example of a photodetector using QDs is a QD infrared photodetector (QDIP) [9,10]. QDIPs use a layer of QDs as the active material, which absorbs the incoming infrared light and generates an electrical current [11]. It has been demonstrated that they have good stability, quick response times, and high sensitivity.

Another example is a QD-based ultraviolet photodetector. The photoactive material employed in the detector is QDs, and it has a high sensitivity and quick response time for detecting UV light [12,13]. Figure 1 shows the different types of materials based on dimensions.

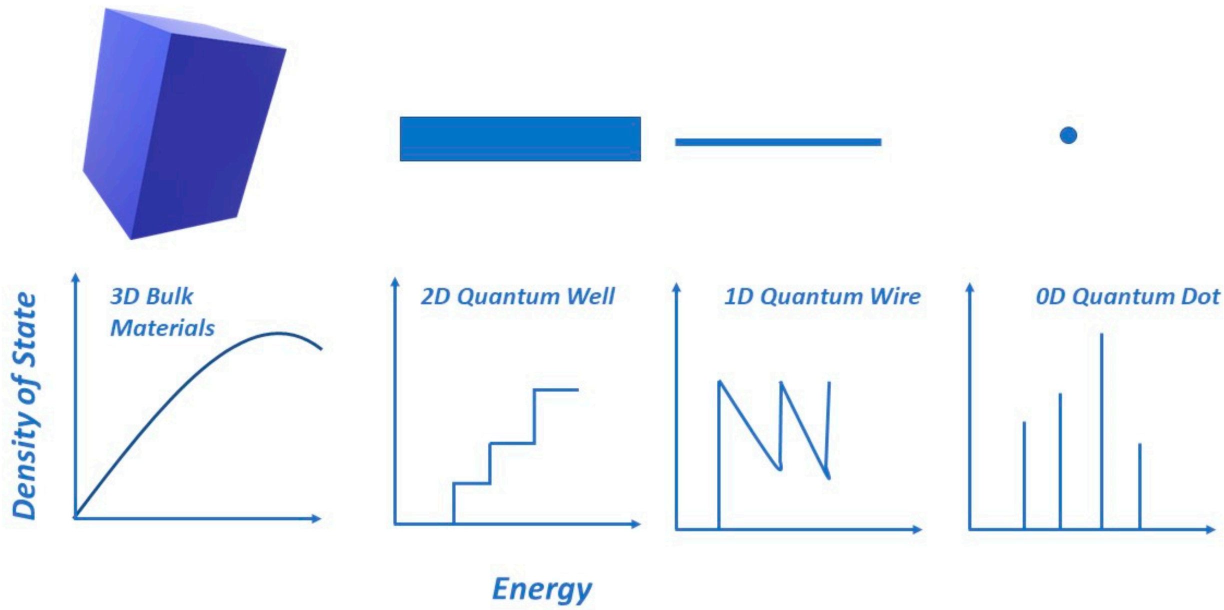

Figure 1. Schematic of nanomaterials based on types.

A third example is a QD-based hybrid photodetector, which combines the benefits of QDs and conventional semiconductor materials, such as silicon [14,15]. These devices combine silicon and QDs to produce a sensitive and effective photodetector. Overall, due to their distinct optical and electrical characteristics and their potential to enhance the performance of these devices, quantum dots are a promising material for use in photodetectors [16].

Although the discovery of QDs is familiar due to the toxic nature of initially observed QDs such as cadmium, their application is limited [17]. The semiconductor quantum dots used to make quantum dots (QDs) photodetectors include cadmium sulfide (CdS), lead sulfide (PbS), indium arsenide (InAs), and organic quantum dots [18]. Due to their distinct optical and electrical characteristics, these QDs have potential applications in photodetector sensors. The most extensively researched QD material for photodetector sensors is cadmium sulfide (CdS) [19]. They can efficiently convert light into an electrical signal due to their high quantum yield and absorption coefficient, allowing them to absorb much light. These characteristics make CdS QDs ideal for ultraviolet and infrared photodetectors [20].

Nevertheless, CdS have many disadvantages. Cadmium is a poisonous heavy metal that can cause serious health issues if inhaled, and proper precautions are needed to dispose of devices made up of cadmium. Quantum dots based on CdS are not biodegradable and can affect the ecosystem [21]. CdS are also more expensive than other quantum dot materials, so researchers are working on different QD materials useful for photodetection applications [22].

The second most commonly used QDs for photodetection applications are lead sulfide (PbS) QDs. They are especially beneficial for infrared photodetectors because they feature a band gap that makes them sensitive to infrared light [23]. Quantum dots made of indium arsenide (InAs), which have a high near-infrared absorption coefficient and are, therefore, particularly effective for near-infrared photodetectors, are another potential material for use in photodetector sensors [24,25]. Overall, the wavelength range of the light that needs to be detected and the specific specifications of the device will determine which QD material is best [26].

This review is focused on non-cadmium nanomaterials for electronic applications. As light-emitting diodes also work with the mechanism of electron–hole recombination, QDs also have potential applications in this area [27]. In terms of applications, quantum dots are used in various fields, including electronics, biomedicine, and renewable energy. For example, quantum dots can be used in electronics to make highly efficient solar cells, LED lights, and other devices. In biomedicine, quantum dots are used as imaging agents to study cells and tissues in the body [28]. In renewable energy technologies, quantum dots are used to produce hydrogen fuel from water using sunlight [29].

2. Optical and Electrical Properties of Quantum Dots

There are different energies for the electrons in quantum dots. When QDs absorb energy above their band gap, an exciton (electron–hole pair) is created. The electron and hole pair is confined if the diameter of the nanomaterial is smaller than its exciton Bohr radius, often known as the average physical distance between the electron and hole [30]. This electron and hole pair confinement is called the quantum confinement effect, which causes a discrete packet of energy and cannot be considered continuous [31,32]. One of the fascinating phenomena that QDs exhibit is photoluminescence. In this phenomenon, QDs absorb higher-energy photons and release low-energy photons. The electron moves into an excited state upon absorption. When it recombines with a pair, it emits lower energy light. This process takes place in femtoseconds [33].

Photoluminescence generally depends not on the type of materials but on the size [34]. As the quantum dot size decreases, the band gap of the quantum dot increases, causing the emission wavelength to shift toward a lower wavelength, and this is known as the blue shift, which is emission in the visible range. However, the emission can also occur in other regions of the electromagnetic spectrum, such as ultraviolet or infrared. QDs have exciting optical properties such as better photostability, high molar extinction, and high quantum yield (ratio of photons emitted vs. photons absorbed). QDs can be observed using confocal microscopy, fluorescence spectroscopy, total internal reflection microscopy, etc. [35,36].

QDs also have fascinating electrical properties, such as when sufficient energy is absorbed by the QD electron excited from the valence band to the conduction band while leaving the hole (empty state) in the valence band. This hole can be considered a positive mobile charge in the valence band. QDs possess a discrete energy state like an electron of a single atom [37]. Typically, a photon can only form one exciton and excite one electron across the band gap of fluorescent materials, with extra energy being lost as heat. However, multiple exciton generation is possible in QDs, which can be produced simultaneously, increasing the efficiency with which the nanocrystals convert energy [38].

Quantum yield measures the efficiency with which a system converts absorbed light into a different form of energy, such as heat or electricity. In the case of quantum dots, it refers to the efficiency with which the dots convert absorbed light into emitted light [39,40].

The equation for quantum yield is typically expressed as the ratio of the number of photons emitted by the quantum dots to the number of photons absorbed by the dots. This ratio can be expressed as follows:

$$\text{Quantum yield} = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}}$$

The quantum yield plays an important role in the properties of QDs. The confinement behaviors produced by QDs' core/shell structures are closely connected to the core and shell materials [41]. For instance, the electron–hole pair is confined within the core when the energy band gap of the shell material is more significant than that of the core material, and when the energy band gap of core materials is more significant, the electron–hole pair is confined in the shell [42]. QDs, like carbon quantum dots, are extremely sensitive to the presence of extra charges, such as electrons or holes, on their surfaces and in their environment, which can change the photoluminescence and absorption wavelength of QDs. The functional group present on the surface of carbon quantum dots can absorb and trap the photon, which can change the emission wavelength of carbon QDs [43]. Due to these fascinating properties, quantum dots are used in many applications, such as solar cells [44], lasers [45], and photodetectors [46].

3. Quantum Dot Lasers

Semiconductor spherical nanocrystals (colloidal quantum dots), monolayers, and nanowires have found usage in the laser industry. CDs offer wide electromagnetic spectrum emissions from infrared to the visible range due to their size tunability, optical transition, and solution processibility. Compared to conventional semiconductors, QD-based semiconductors are easier to manipulate in size and shape [47,48]. Due to the unique absorption and emission properties of QDs, it is possible to produce lasing from a single exciton. A QD laser provides even spacing, low threshold amplification, and continuous wave operation. The shell absorbs the energy and acts as an antenna when the core–shell QDs are excited by photons having energies above the energy band gap. These QD outpace Auger recombination, so the threshold for lasing operation decreases [45].

4. Quantum Dots for Solar Cells

For more than two decades, semiconductor quantum dots (QDs) have attracted much attention due to the optoelectronic properties based on zero dimensions. Through the QD band energy level, colloidal quantum dots and self-assembled quantum dots improve the photogeneration of carriers for photovoltaic applications [49]. By expanding the range of photoexcitation, theoretically, it is possible to achieve maximum thermodynamic efficiency although the mechanism of carrier transport and carrier collection also contribute to its efficiency. Self-assembled and colloidal quantum dots are the two most-used types of QDs in solar cell applications [50]. The growth of solar cell wafers is also crucial for their efficiency, including surface passivation and well-controlled heterointerface [51].

Future risks include rising temperatures caused by global warming, shrinking fossil fuel supplies, and ever-increasing energy needs, which will require scientists and researchers to continuously work on developing efficient and affordable renewable energy alternatives [52]. Sunlight, which is abundantly available worldwide and can be converted into electricity or other forms of energy without polluting the environment, is one of the most commonly used renewable energy sources. Photovoltaic systems are based on converting sunlight into electricity, another valuable form of energy [53]. Photovoltaic device usage to produce electrical energy has increased, but obstacles still need to be overcome before these devices can significantly contribute to satisfying the world's energy needs [54].

Generally, there are three types of solar cells: traditionally, silicon-based monocrystalline and polycrystalline solar cells have been used [55]. The second type is thin-film solar cells, which are less expensive due to the low cost of absorbing material compared to silicon. These include copper gallium indium diselenide, cadmium telluride, and organic solar panels [56]. The third type, perovskite solar cells, uses hybrid organic–inorganic materials as the light-harvesting active layer. Perovskite materials, such as all-inorganic cesium lead halides and methylammonium lead halides, are cheap and straightforward to manufacture. Carrier mobility, doping density, trap density, and diffusion length in films are crucial factors that affect the performance of photovoltaic devices [57].

Junwei Yang et al. [58] reported synthesizing CdTe core QD-based solar cells. They used the aqueous route to synthesize QDs. CdTe core QDs were first synthesized and then deposited on a TiO_2 photoanode. An increase in absorption spectrum is observed for CdTe core QDs compared to CdTe cells. The power conversion efficiency of QD-based solar cells is increased up to 22% compared to CdTe/CdS plain solar cells. The suppressed charge recombination is also confirmed in QD-based solar cells. The authors also reported that thickness plays an important role in quantum efficiency. With optimization of $CdSe_xS_{1-x}$ shell thickness, about 7.24% conversion efficiency can be achieved, while Jun Du reported that Zn–Cu–In–Se alloyed QDs increase the absorption efficiency when deposited on TiO_2 film electrode, and reported conversion efficiency up to 11.66% [44].

5. Nanomaterials for Photodetection

Nanomaterials have properties that are suitable for photodetection, especially two-dimensional nanomaterials Two-dimensional (2D) materials have emerged as promising candidates for photodetectors due to their unique electrical and optical properties. In particular, their ultra-thin structure allows for efficient light absorption and carrier transport, leading to high sensitivity and fast response times. Two examples of 2D materials that are commonly used for photodetectors are:

Graphene is a single layer of carbon atoms arranged in a honeycomb lattice. It has excellent electrical conductivity and high carrier mobility, which makes it an attractive material for photodetectors [59]. When light is absorbed by graphene, it generates electron–hole pairs, which the graphene's high carrier mobility can efficiently collect. Graphene photodetectors have shown high responsivity and fast response times, making them useful for optical communications and imaging applications, while graphene hybrid composite materials with metallic nanomaterials and inorganic nanomaterials can increase photosensitivity [60].

Transition metal dichalcogenides (TMDs): TMDs are a family of 2D materials consisting of a transition metal atom sandwiched between two chalcogen atoms. They have a direct bandgap, which allows for efficient light absorption and emission [61]. TMDs have shown high sensitivity to light in the visible and near-infrared regions, making them useful for applications such as biomedical imaging and environmental monitoring. In addition, TMDs can be easily integrated with other electronic components, making them promising for on-chip optoelectronics [62]. 2D materials have shown great potential for photodetector applications due to their unique electrical and optical properties. Graphene and TMDs are just two examples of 2D materials that are being actively researched for their photodetection capabilities. As research in this area continues, it is likely that even more promising 2D materials will be discovered and developed for photodetector applications.

Infrared light detection is essential for biological sensing, spectroscopy, and in-depth 3D imaging. At the same time, semiconductors such as silicon, Cds, HgCdTe, and HgS are used for photodetectors. However, these materials have a few drawbacks, such as toxicity, low responsivity, and high cost of fabrication. The imaging performance of the quantum well photodetector, which is comparable to that of the mercury cadmium telluride (HgCdTe) detector, has recently attracted a lot of interest [63].

Following progress in the nanomaterials industry, it has been found that they have some advantages for photodetection over conventional materials, and the most-used nanomaterials are quantum well.

Quantum well infrared photodetectors (QWIP) absorb electrons through electronic intersubband polariton in a quantum well [64]. To be used for infrared detection, the energy difference between the first and second quantized states of the quantum well infrared photodetector's quantum wells must match the energy of the incoming infrared photons. III-V direct band gap semiconductor gallium arsenide (GaAs) is usually used to make QWIPs [65].

Therefore, research is also being carried out to create high-performance photodetectors using these nanomaterials. This review article focuses on quantum dot photodetectors [66]. They have been used in applications such as gas sensors and medical images, etc. Quantum well infrared detectors also have some limitations, such as the intersubband transition in the conduction band due to infrared photon polarization not being allowed in quantum wells [67,68]. This limitation can be overcome by using grating. However, they have a few more drawbacks, such as higher dark current, low quantum yield, lower responsivity, and detection level, and require cryogenic temperature to operate, so these limitations can be fulfilled by quantum dot photodetectors that have similar properties to quantum wells and also have some advantages due to the confinement of electrons in three dimensions [69]. QDs have reduced dependence on temperature for carrier transport, and carrier lifetime is also 10–100 times longer, which means that the electron remains excited for a more extended period, which causes a reduction in the dark current and increases sensitivity. QD-based detectors can absorb normal incident light without grating [70].

Similar to a quantum well, a quantum dot exhibits detection through the confinement-induced intraband photoexcitation of electrons. A photocurrent is generated by attracting the electrons in the collector with an electric field generated by the applied bias.

Colloidal QDs are low-cost materials, due to solution-based fabrication into semiconductor wafers and tunable band gap material, that are used as light emitters in flat panel displays. QDs are a cheap alternative to III–V group-based materials for imaging and sensing [71]. Research is being already carried out to make it possible to place QDs in a complementary metal–oxide–semiconductor (CMOS) circuit and increase the responsivity of QDs while decreasing the low noise equivalent power. If QDs can emit electrons across a wide range of the electromagnetic spectrum, they will be more practically efficient [72].

Infrared detectors are mainly categorized based on the material used for detection. Some of these are already extensively used in industry, including direct band gap semiconductor alloys such as HgCdTe and InSb, majority carrier Type-I superlattices, e.g., GaAs/AlGaAs QWIPs, and extrinsic semiconductors, e.g., Si: Ga, Ge: Hg. The fourth type is silicon Schottky barriers such as PtSi, and IrS. At the same time, the other two types include high-temperature superconductors and QD-based photodetectors, e.g., InAs/GaAs-based detectors [73,74]. The QD-based photodetector will be discussed in this review. Examples of quantum dots for photodetection are given below.

6. Lead(II) Sulfide (PbS) Quantum Dots

Lead(II) sulfide (PbS) QDs are special semiconductors with distinctive optoelectronic characteristics. Their strong absorption coefficient and band gap of 0.35 eV make them suitable for photovoltaic, photoconductor, and light-emitting diode applications [75,76]. PbS quantum dots are advantageous for sensing and imaging applications because they also have a high quantum yield and a narrow emission spectrum. Furthermore, their band gap can be modified by varying the quantum dot size, enabling further improvement of their optoelectronic characteristics [60,77].

One of these characteristics is their high absorption coefficient, which enables effective light absorption over a broad range of wavelengths. This is because PbS quantum dots have a significant quantum confinement effect, which confines the electrons to a limited area and causes them to have a high absorption coefficient [78].

The high responsivity of PbS quantum dots is a crucial characteristic that makes them effective as photodetectors which means more transformation of absorbed photons into an electrical signal [59,79]. Due to their high electron–hole recombination rate and rapid electron mobility, PbS quantum dots have a high responsiveness that enables the effective conversion of absorbed photons into electrical current. PbS quantum dots are also ideally suited for applications with high sensitivity and low noise because of their excellent signal-to-noise ratio and low dark current [80,81]. Therefore, lead sulfide (PbS) quantum dots (QDs) are considered potential material options for next-generation light, affordable, and flexible photodetectors due to their wide tunable band gaps, high absorption coefficients, and simple solution synthesis methods.

Alberto Maulu et al. synthesized PbS QDs and then modified their surface properties by using 3-mercaptopropionic acid (MPA) and tetrabutylammonium iodide (TBAI) [82]. It was observed that modification with this ligand significantly alters the properties of QDs. MPA-based QDs showed a decrease in dark current and low noise ratio, which causes the enhancement of detective and photosensitivity compared to TBAI-based QDs. MPA-modified QDs have functional group (Pb–OH bonds), while TBAI has a functional group (Pb–I bond), which is the primary reason for the Pb enhancement properties.

QDs used the trap sensitization method to show photoconductivity, increasing the responsivity but decreasing the response time for low optical power. At medium power incidents, light, when traps are filled with both types of photodetector, shows similar types of properties.

Urvashi Bothra et al. investigated the effect of ligands on PbS properties. They showed that a PbX_2 [X = I, Br])-based photodetector decreases the trap density compared to a PbS-based device, which increases the performance of (PbS) PbX_2-based devices [83].

Jin Beom Kwon et al. fabricated short-wave infrared (SWIR) photodetectors based on PbS QDs [84]. These infrared photodetectors minimize the harmful effect caused by the low wavelength band of SWIR. They fabricated a PbS photodetector with an absorbance peak at 1410 nm and used poly(3-hexylthiophene) (P3HT) as a conductive polymer with PbS QDs. Measurements were made on the properties of the synthesized PbS QDs, and the current–voltage (I–V) features of the PbS SWIR photodetectors. The maximal responsiveness of the PbS SWIR photodetector with P3HT optimization was found to be 2.26 times greater than that of the PbS SWIR photodetector without P3HT. Moreover, the former demonstrated a reduced operating voltage due to the high hole mobility and an adequate highest occupied molecular orbital level of P3HT. Figure 2 shows the I–V characteristics of the PbS-based photodetector.

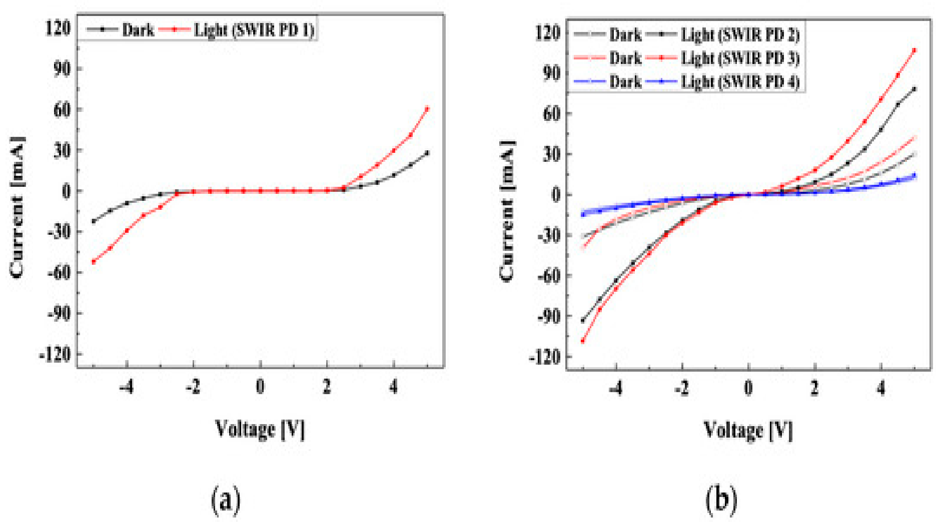

Figure 2. I–V characteristics of (**a**) PbS SWIR photodetector without P3HT polymer and (**b**) PbS SWIR photodetector with P3HT polymer [84].

To compare their performance, they measured the I–V characteristics and responsiveness of the manufactured PbS SWIR photodetectors. The electron–hole pairs produced in the photoactive layer of the PbS SWIR photodetectors were removed from the electrodes by an external electric field when exposed to IR light. When the IR light source was turned off, the dark current was measured, and the light current was measured when the light source was turned on. The output power of the IR light source was 1 W/m^2, and the voltage sweep range was between -5 V and 5 V. The highest current difference between the dark current and light current and responsivity was recorded at -5 V in the case of the PbS SWIR photodetector without a P3HT layer. The largest current difference was 23.72 mA, and when this was divided by the input voltage, the corresponding responsivity was calculated as 2635.6 A/W. The PbS SWIR photodetector with a P3HT layer exhibited the best properties when applying 20 mg/mL of P3HT. The greatest current difference was confirmed to be 5891.1 A/W, which is 2.26 times greater than SWIRs, and the maximum current difference was 53.02 mA at -5V.

The drawbacks of current single-layer PbS-QDs photodetectors include excessive dark currents, slow light responses, and poor on–off ratios. It has been demonstrated that combining high-conducting graphene with organic materials and metal nanoparticles to create hybrid PbS-QDs devices can increase photoresponsivity. However, these hybrid devices bring other problems, and Zhenwei Ren et al. [80] synthesized the bilayer QDs device, which can be easily integrated into a flexible polyimide substrate. It increases the responsivity, signal-to-noise ratio, linear dynamic, and detection.

Moreover, this improvement in the device's properties is attributable to QDs' significant role. For example, the QDs junction accelerates carrier separation when the light is on. When the light is off, the QDs support the recombination of accumulated carriers in two films via the interface. Junction control is more dominant than trap control, which is the main determining factor in single-layer devices. They fabricated the bilayer photodetector using tetrabutylammonium iodide (TBAI)- and 1,2-ethanedithiol (EDT)-treated QDs. They compared it with a single-layer detector and observed that the bilayer photodetector enhanced optoelectronic properties. The bilayer PbS- TBAI/PbS-EDT devices have higher light current and detection efficiency, while the responsivity of PbS- TBAI/PbS-EDT is comparable to PbS-EDT devices due to the very close photocurrent.

It can be concluded that surface functional chemistry and modification of PbS with ligands improve the performance, and hybrid structure with modifications from different ligands can also improve the performance.

7. Indium Arsenide (InAs) Quantum Dots

Indium arsenide (InAs) quantum dots (QDs) are also potential materials for photodetector sensors due to their distinct optical and electrical characteristics. These QDs are especially beneficial for NIR photodetectors due to their high near-infrared (NIR) absorption coefficient [85]. NIR imaging is one possible use for InAs QD-based photodetectors. Due to InAs QDs' band gap, developing highly sensitive NIR imaging systems with them is possible. These gadgets are used in telecommunications for sensing, night vision, and medical imaging [86]. Deep-tissue imaging, optical communication, and covert illumination are just a few of the optoelectronics and biomedical uses for indium arsenide quantum dots, which typically emit in the near-infrared spectrum. Systems with bigger optical band gaps have yet to be produced, despite theory suggesting that further quantum confinement through size reduction could enable visible light emission.

NIR spectroscopy is another use for InAs QD-based photodetectors. Due to the NIR light detection capability, highly sensitive NIR spectroscopy devices can be made [87]. Additionally, the development of optoelectronic devices such as solar cells, LEDs, and lasers has utilized InAs QD-based photodetectors. These devices can increase the efficiency of solar cells and other optoelectronic devices by effectively converting light into electrical energy. Applications for these devices include bio-photonics, environmental monitoring, and chemical sensing [88,89].

Overall, because of their distinct optical and electrical characteristics, as well as their capacity to detect NIR light, InAs QDs have the potential to be utilized in a variety of photodetector applications. They might find use in spectroscopy, optoelectronic devices, and NIR imaging [90]. InAs quantum dots (QDs) might have a different band gap depending on their size and shape. Due to quantum confinement, the band gap of InAs QDs is typically between 0.35 and 0.4 eV, which is lower than that of bulk InAs (0.36 eV) [91], which is shown in Figure 3.

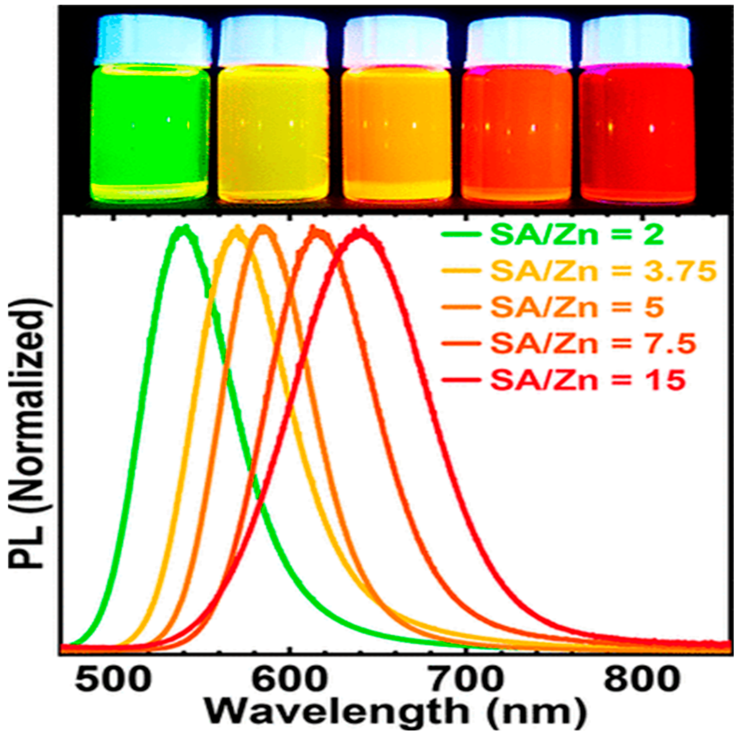

Figure 3. Photoluminescence spectra of In(Zn)As/ZnSe/ZnS QDs synthesized with different amounts of stearic acid (SA) ligand relative to the initial zinc precursor under UV illumination (Reproduced from [92], with permission from ACS Publications).

A low-temperature nanocluster synthesis technique was used by Daryl Darwan et al. to create highly luminous, visible-light-emitting In(Zn)As/ZnSe/ZnS QDs [92]. Each QD has an ultra-confined In(Zn)As nanocluster and emits light with a high photoluminescence quantum efficiency of 58% at tunable wavelengths between 538 and 640 nm. Theoretical calculations support the hypothesis that In(Zn)As nanoclusters are responsible for the infrared to visible spectral shift. This suggests that optical tuning in the visible region is also possible by utilizing confined semiconductor systems with a wide range of applications. The schematic is shown in Figure 4. Using an ultra-confinement technique, they were able to extend the spectrum coverage of InAs-based QDs into the visible range.

8. Organic Materials Based on Quantum Dots

Organic materials, such as polymers or small organic compounds, are used to create organic quantum dots (OQDs), a particular kind of quantum dot. Due to their special optical and electronic characteristics, they could be used in photodetector sensors. Organic photovoltaics is one potential use for OQD-based photodetectors (OPVs) [93,94]. The active layer in OPVs, which transform light into electrical energy, can be made of OQDs. OQDs may absorb various wavelengths, which can enhance the efficiency of OPVs. They could also be used to make solar cells that are less expensive than ordinary inorganic solar cells. OQD-based photodetectors can also be used in flexible and wearable gadgets. OQDs offer thin, bendable, and solution-processable advantages, making them ideal for application in bendable and flexible products such as flexible screens and wearable technology [95].

Devices for sensing and bioimaging have also been created using OQDs. OQDs have the potential to be used in biosensing and biomedical imaging, as well as optical imaging. They are advantageous in these applications because of their high quantum yield, strong stability, and great sensitivity [96]. OQDs are a promising material for photodetector sensors overall because of their distinct optical and electronic characteristics and their potential for usage in a variety of applications, including solar cells, flexible and wearable devices, and bio-imaging and sensing equipment [97].

9. Carbon-Based Materials for Photodetection

Carbon materials, such as carbon nanotubes, graphene, and fullerenes, are used to synthesize carbon-based quantum dots (CQDs), a particular kind of quantum dot. Due to their extraordinary optical and electronic characteristics, they could be used in photodetector sensors [98].

The photodetection of diverse wavelength ranges is one potential use for CQD-based photodetectors. It has been demonstrated that carbon-based quantum dots have a broad absorption spectrum, making them appropriate for use in photodetectors that must detect a variety of wavelengths [99]. They are, therefore, very beneficial for multi-spectral imaging and sensing. High-speed optoelectronics is a further possible use for CQD-based photodetectors. Because of their rapid response times, carbon-based quantum dots can be used in high-speed optoelectronic systems, including optical communications and high-speed data transfer [100]. Devices enabling sensing and bioimaging have also been made with CQDs. The unique optical and electrical characteristics of carbon-based quantum dots make them suitable for biosensing and bioimaging applications, including in vivo imaging. They are helpful in various applications due to their high quantum yield, outstanding stability, and great sensitivity [101]. CQDs are a promising material for photodetector sensors overall because of their distinctive optical and electronic properties and their potential to be employed in a variety of applications, including multi-spectral imaging and sensing, high-speed optoelectronics, and bio-imaging and sensing devices [102].

Both graphene quantum dots (GQD) and carbon dots (CD) are being studied for potential application in photodetector sensors. Small, carbon-based nanoparticles known as CDs have been shown to exhibit robust fluorescence characteristics [103]. On the other hand, GQDs, which are small graphene flakes, have been discovered recently to have fluorescence characteristics similar to those of CDs, with the added advantage of being more stable and simpler to functionalize. CDs and GQDs are promising candidates for photodetector sensors due to their efficiency at absorbing light and transforming it into an electrical signal [104].CDs' performance is negatively influenced by their inefficient near-infrared (NIR-I and NIR-II) excitation and emission. By resolving this, CDs can be utilized for in vivo bioimaging.

10. Graphene Quantum Dots (GQDs)

There may be applications for graphene quantum dots (GQDs), tiny graphene sheets, in photodetector sensors. Their unique electrical and optical features make them suitable for sensing technologies. GQDs have been found to possess strong fluorescence properties, effectively absorbing light and turning it into an electrical signal [105]. GQDs are extremely stable and may be functionalized with various chemical groups, enabling precise control over their optical and electrical characteristics. They are beneficial for sensing applications requiring specificity and sensitivity [106].

Graphene, in particular, is a 2D monolayer of sp^2 hybrid carbon. At the Dirac point, graphene's conduction band meets with its valence band. This causes a linear dispersion relationship, making it a zero-band gap semiconductor with zero density of electronic states and an incredibly high room temperature carrier mobility [107]. The broad spectrum response and quick response of graphene are perfect photoelectric qualities due to its zero-band gap semiconducting nature. Although graphene quantum dots have lesser absorption and responsiveness, researchers are primarily focusing on hybridizing graphene with high-absorption materials to enhance photodetection capability like quantum dots [108].

GQDs are also ideally suited for photodetectors and other optoelectronic devices due to their outstanding charge transfer characteristics. Different photodetector designs, including p–n junction, Schottky, and photoconductive ones, can incorporate GQDs [109]. They are helpful for various sensing applications because they can detect a wide range of wavelengths, from visible to infrared.

Molahalli Vandana et al. fabricated a UV-based photodetector by utilizing graphene QDs with polypyrrole polymer [110]. They used two different amounts of graphene, 20 and 40 mL in polypyrrole, labeled as PGC2 and PGC4, while single graphene QDs (GQDs) were also utilized. The active layer of ITO electrode was illuminated with UV light of 265 and 355 nm for about 200 s. The graphene QDs are an excellent light absorber and electron donor to increase the carrier concentration. Figure 4 compares the photocurrent of GQDs, PGC2, and PGC4.

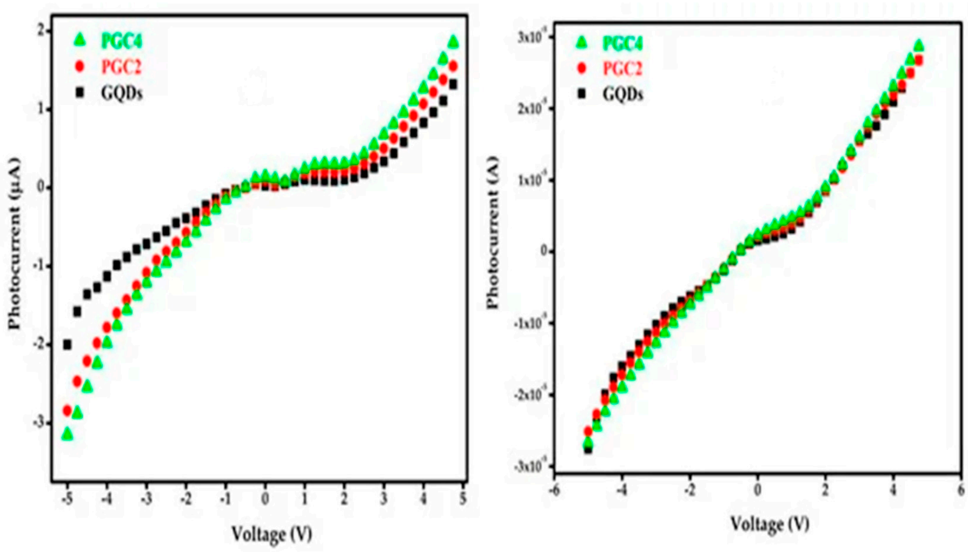

Figure 4. Comparison between the photocurrents of three photodetector devices under illumination [110].

PGC2 and PGC4 show responsivity of about 0.33 μA/W and 0.36 μA/W and corresponding photocurrent of 2.65 μA and 2.9 μA when illuminated at wavelength 265 nm, while a responsivity of 1.93 and 2.33 μA/W and photocurrent of 15.5 μA and 18.7 μA was observed for PGC2 and PGC4 when illuminated with UV light of 355 nm. Based on the results, which show that the PGC4 photodiode had the highest 18.7μA photocurrent, it can be concluded that the quantum dots in the polymer boosted electron mobility due to the high electrical properties of the nanocomposite.

11. Carbon Dots

Carbon QDs are nanomaterials made of carbon, similar to substances such as nanodiamonds, fullerenes, carbon nanotubes, graphene, and graphene oxide. Small, water-soluble carbon nanoparticles known as carbon dots (CDs) have been shown to have potential uses in photodetector sensors [111]. CDs are a desirable material for use in sensing technologies due to their distinctive electrical and optical characteristics. Strong fluorescence qualities have been discovered in them, making them efficient at absorbing light and transforming it into an electrical signal [112]. CDs' high quantum yield and outstanding stability have been found to make them appropriate for use in photodetectors [113]. The precise control of their optical and electrical properties is made possible by their simplicity in synthesis and functionalization. As a result, they are advantageous for sensing applications that demand specificity and sensitivity [114]. CDs' superior charge transport characteristics have also been discovered, making them suitable for photodetectors and other optoelectronic devices. Many photodetector designs, including p–n junction, Schottky, and photoconductive ones, can incorporate CDs [115]. They are helpful for various sensing applications because they can detect a wide range of wavelengths, from visible to infrared. Additionally, CDs are non-toxic and biocompatible, which makes them advantageous in medicinal applications such as cancer therapy and bioimaging. Additionally, CDs can be functionalized with different biomolecules to enable the detection of certain biomolecules and biological activities [116].

They have gained attention due to their environmentally friendliness, chemical stability, and good conductivity, making them useful in various fields such as biomedical and biotechnological research, solar cells, light-emitting devices, imaging, electrochemical studies, and electrochemiluminescence studies [117]. Carbon dots are a class of nanoparticles composed mainly of carbon and oxygen, while some amino and carboxyl functional groups are also present on the surface [118]. These nanodots have unique optical, electrical, and chemical properties that make them highly versatile and helpful in various applications. Some of the critical properties of carbon dots include: Size: Carbon dots are nanoparticles with diameters ranging from 1 to 10 nanometers. Their small size allows them to display unique properties and quantum confinement effects, which are helpful for a number of applications. These properties make carbon dots valuable for various applications, including sensors, catalysts, and energy storage and conversion. Luminescence: Carbon dots can emit light, making them useful for applications such as biosensors and imaging [119]. Chemical stability: Carbon dots are highly stable in many different chemical environments, including basic and acidic conditions. Their stability makes them useful for sensing and imaging applications. Conductivity: Since CDs have excellent electrical conductivity, carbon dots can be used in photovoltaic and energy storage applications [120]. Biocompatibility: Due to their non-toxicity and biocompatibility, carbon dots can be used in biological systems without damaging healthy cells. Surface functionalization: The surface of carbon dots can be modified with different chemical groups, enabling them to be useful for specific purposes [121]. Optical properties: Carbon dots can absorb light in the ultraviolet and near-infrared parts of the spectrum, making them useful for specific applications. For example, their strong absorbance in these spectrum regions can be utilized in solar cells to absorb and convert sunlight into electricity and in LED lighting to provide energy-efficient and long-lasting light sources [122]. CDs can emit light when excited by an external energy source, such as electricity or heat. The emission wavelength, or the specific range of wavelengths that the light emitted by CDs falls within, can be manipulated by changing the size and composition of the CDs. This can be achieved by using different starting materials or synthesis methods while synthesizing CDs. Solubility: Since they are highly soluble in a wide range of solvents, including water, carbon dots are simple to handle and incorporate into different systems [123]. High surface area: The small size of carbon dots results in a high surface area, which makes them ideal for applications such as catalysis and drug delivery [123].

One crucial property of CDs is their ability to emit light when excited by light, also known as photoluminescence. The photophysical responses of CDs, including their light absorption and emission, are influenced by the isolated network of sp^2 carbon bonds in their structure [123]. In contrast, extended networks of carbon bonds, as found in carbon nanotubes, graphite, and graphene, do not interact with light as strongly. This may be due to the rapid recombination of photogenerated electrons and holes without the emission of radiation. CDs typically absorb light over a broad range of wavelengths [124]. They can absorb light over a wide range of wavelengths, but the specific wavelength at which they emit light is determined by the population of a particular energy level or "domain" and the surface properties of the quantum dots. This phenomenon, known as excitation-dependent emission, is a characteristic of CDs arising from these nanomaterials' surface state. Essentially, the surface of the quantum dots plays a crucial role in determining the specific wavelength at which they will emit light when excited by an external energy source [125].

Carbon dots have a high absorption coefficient, which implies they can absorb a lot of light, in addition to their fluorescence and quenching qualities. Due to their ability to transform light into energy that may be utilized to treat a range of medical problems, they are valuable in phototherapy applications [126].

K. Sarkar et al. [127] show the use of carbon dots (CDs) synthesized from Carica Papaya through a facile synthesis method as a potential broadband photodetector in a hybrid (organic–inorganic) heterostructure with a silicon wafer. The engineered CDs' maximum detectivity and responsivity are around 1 A W^{-1} and 2×10^{12} Jones, respectively. The device structure ensures a promising photodetector technology comparable to silicon process technology through a cheap and simple fabrication process. Additional optimization effort and defect engineering can speed up switching.

Sergii Kalytchuk et al. demonstrated the synthesis of purple-emissive CDs utilizing folic acid as the only precursor in a simple and reproducible process [128]. The CDs have a high photoluminescence quantum yield of 54.6% and emit light at a wavelength of 390 nm, which is independent of the excitation wavelength and integrates the emission color spectrum of intensely glowing carbon dots to purple. They employed CDs to increase the silicon photodetector's UV range sensitivity. It was found that the photoresponsivity of the silicon photodetector in the UV range of 0.8 to 2.5 mA/W was enhanced by 203.8% with CDs' integration.

Di Li et al. [129], by modifying the surface of CDs with functional groups of sulfoxide/carbonyl, changed the optical band gap of CDs. They proposed a mechanism for improved NIR emission, which can be seen in Figure 5. The CDs have a layered structure, and the outer layers have bonding sites. The interaction between the S = O/C = O functional group and layers increased surface oxidation, which caused the reduction in the lowest unoccupied orbital (LUMO). As a result, these functional groups disrupt CDs' organized structure. Due to the increased surface oxidation, the LUMO orbitals are lower in the outer layers compared to the inner layers and cause the NIR emission of CDs.

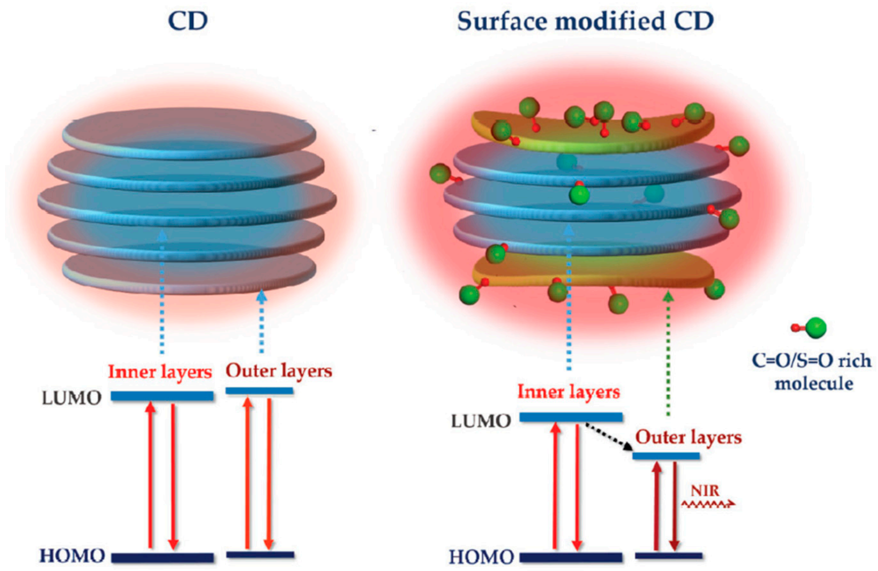

Figure 5. Non-treated CDs (left column) and CDs modified with S = O/C = O rich molecules (right column). The red (oxygen atom) and green double-bonded balls represent the C = O/S = O rich molecule (Reproduced from [129], with permission from John Wiley & Sons, Inc.).

12. Future Prospects and Conclusions

Several optoelectronics applications that have been utilized as a result of advancements in nanomaterial synthesis were covered in this study. Researchers have used QDs in various devices, including solar cells, lasers, and photodetectors. Quantum dots act differently from bulk materials in light emission and absorption due to the quantum confinement effect, which is favorable for laser and solar panel applications. This review briefly discussed different optoelectronic devices based on QDs.

QDs in photodetectors have a bright future, with the possibility of increased performance, reduced costs, and new applications. Future quantum dot photodetectors are expected to have several benefits over current photodetectors. They could, for instance, offer greater sensitivity, faster response times, and lower noise levels. Since they can be tailored to absorb light over a broad range of wavelengths by altering their size and composition, they are also anticipated to be more flexible.

Factors contributing to the usefulness of QDs as compared to a traditional photodetector that is discussed in this review include:

1. Quantum dot-based photodetectors have the potential to provide greater efficiency than conventional detectors, particularly in the infrared spectrum because they can be engineered to have a very narrow absorption spectrum that fits the wavelength of the incident light, whereas organic QDs have a wide surface area, which enables them to efficiently absorb light and produce a large number of excitons (electron–hole pairs) which are useful for photodetectors.
2. Low-cost, solution-based techniques can be used to make quantum dot-based photodetectors. This could make them more affordable than current photodetectors, particularly for applications involving large areas, while organic QDs can be deposited on flexible substrates, which enables the use of wearable electronics, among many other uses.
3. A faster reaction time is possible because of QDs, which can be used to construct photodetectors with quick response times that are suited for high-speed applications.
4. QDs can be combined with other electronic components to build hybrid devices with cutting-edge features. For instance, these could be combined with complementary metal–oxide–semiconductor technology to produce inexpensive, high-performing bio-imaging systems.
5. Since QDs are more flexible in combining organic and inorganic materials, their properties can be easily changed to suit different needs.

PbS quantum dots have a high electron–hole recombination rate and rapid electron mobility, which increases the responsivity and improves the efficiency of the conversion of photons into electric current. PbS quantum dots' properties can also be modified with ligand reactions. Bilayer PbS quantum dots with different modification ligands, tetrabutylammonium iodide (TBAI), and 1,2-ethanedithiol (EDT) devices have higher light currents and detections.

This review study also discusses indium arsenide (InAs) quantum dots (QDs). It was shown that due to their high infrared absorption coefficient, they make good photodetectors in the region of infrared detection. They are helpful for imaging at infrared wavelengths as well.

This review discusses organic quantum dots such as graphene, particularly carbon quantum dots. CDs' particular electrical and optical properties make them desirable materials for sensing technologies. They have been shown to possess strong fluorescence properties, effectively absorbing light and converting it into an electrical signal. Their ease of synthesis and functionalization allows precise control of their optical and electrical properties. They are, therefore, beneficial for photodetectors that require specificity and sensitivity.

Author Contributions: Conceptualization, H.S.; writing—original draft preparation, H.S.; data curation, H.S.; writing—review and editing, H.S. and M.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research received financial support from the AGH University of Science and Technology.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: Not applicable.

Conflicts of Interest: Author declares no conflict of interest.

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