



## Original Research Article

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## Study of PbS Quantum Dots (QDs) and Proposing Pb@PbS-QD@CdSe for New Generation of LEDs

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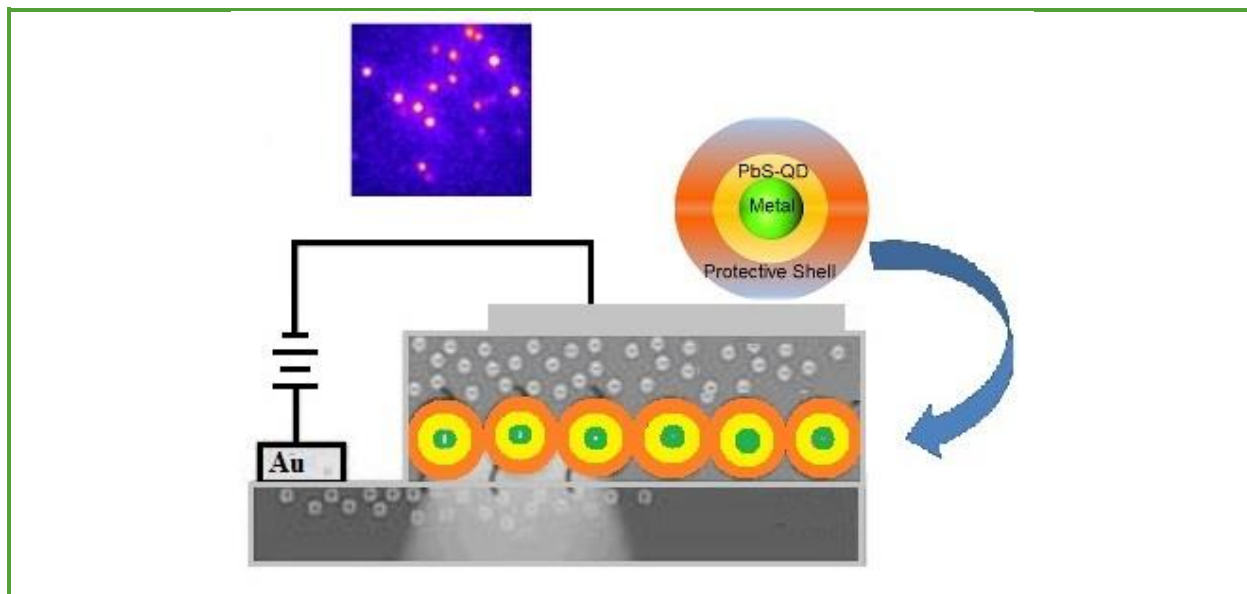
PbS-QDs  
 Blink  
 Protective shell  
 LED  
 Pb  
 CdSe

## ABSTRACT

PbS quantum dots (PbS-QDs) are one of the best candidates in new generation of LEDs. When the PbS-QDs are exposed to light spectrum, the electrons in the valence band (VB) are excited to the conduction band (CB). The excited electrons then return from the CB to the VB and release extra energy by emitting light. The return of electrons to the VB makes it possible to repeat the light absorption-emission circle. If the size of the PbS-QDs is smaller than the Bohr magneton radius (PMR), the probability of the electron return to the VB decreases. This leads to phenomena named quantum dot blinking (QDB) in light-emitting diodes (LEDs), which is not desirable. In this research, a new approach has been proposed in which the addition of a metal substrate for PbS-QDs with a semiconductor shell with a suitable band edge could increase PbS-QDs efficiency in QD-LEDs and overcome the QDB problem.

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## Graphical Abstract



## Introduction

When crystalline and micron semiconductors are converted into amorphous with nanometer dimensions, not only retain their semiconducting property, but also acquire other properties that lead to wide application. Semiconductor nanocrystals are tiny light-emitting particles on the nanometer scale [1]. Researchers have studied these particles and developed them for wide-ranging applications such as solar energy conversion, optoelectronic devices, molecular and cellular imaging, and ultrasensitive detection [2].

The comparison of nanometer semiconductor and micron semiconductor shows that the electron bands in nanometer particles have less density [3]. When the number of atoms reaches 44 in a crystalline particle, the separation begins in electronic levels. Therefore, the CB moves away from the VB and the band gap increases. These changes lead to different behaviors in nanometer semiconductors compared to its micron type [4].

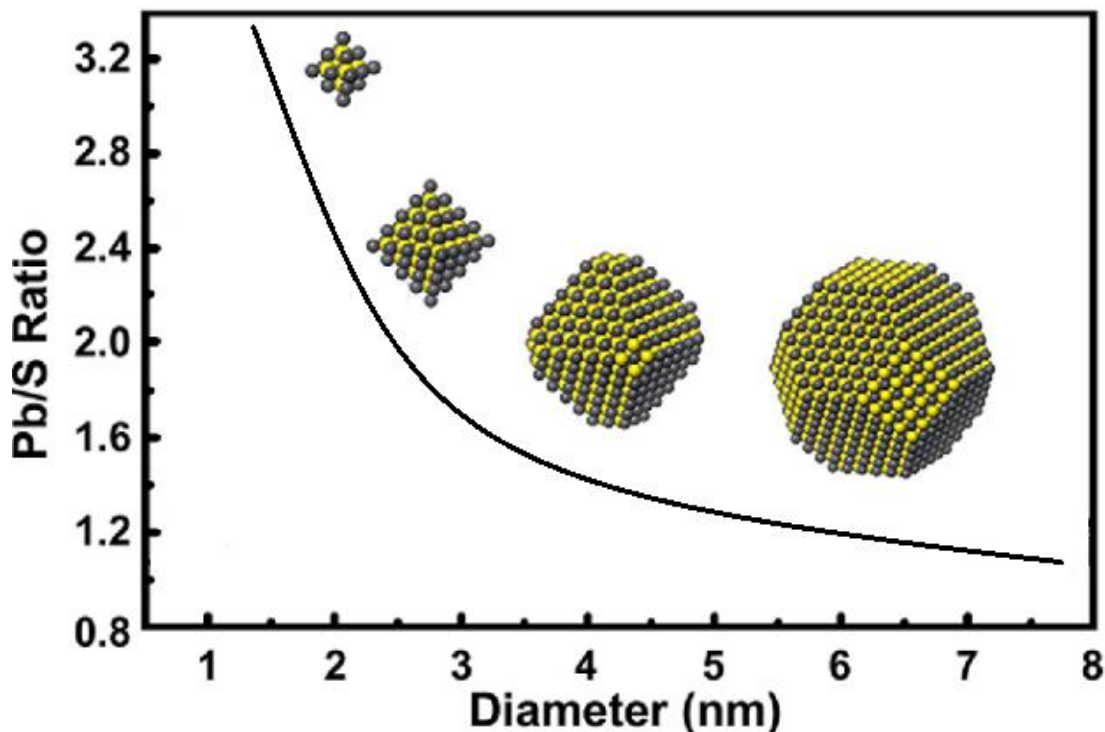
## Size-shape dependence in PbS nanoparticles

The shape, size, and elemental composition of lead sulfide (PbS) depends on the arrangement and density of atoms. In terms of the difference in the ratio of Pb to S (Pb/S), the predicted size is consistent with the measurements reported in the literature, as displayed in Figure 1.

While the surfaces of the smaller particles of PbS (diameter < 2.7 nm) are completely covered with Pb (111) oriented facets, the larger PbS, between 2.7 and 7.5 nm, have a cubic shape with a preferential orientation Pb (100). As the PbS dimensions increase, the Pb/S ratio decreases, although the Pb/S ratio is always higher than one [5].

## PbS quantum dots (PbS-QDs) and BMR

PbS in bulk state (micron) has a bandgap of 0.37 eV. When the PbS size decreases the bandgap increases, so that the PbS size with 10 and 3 nm corresponds to bandgap of 0.6 and 1.3 eV. This results to decrease of absorbed wavelength [6, 7].



**Figure 1.** Relationship between PbS diameter and Pb/S ratio [10]

The bandgap of 0.37 eV is equivalent to an absorption wavelength of 3350 nm in the infrared (IR) range. The bandgap of 0.6 and 1.3 eV is equivalent with 2066 and 953 nm, respectively. This is a blue shift to lower wavelength and higher energy regions, i.e. near-IR. As a theoretical point of view, it is possible to further reduce the size of PbS to reach a band gap of 1.5 eV (826 nm) [8]. In this case, the absorption range of PbS approaches the high energy range in the visible region, which is the intense region, and this can be controversial. When the dimensions of a semiconductor are reduced in all three dimensions and become nanometers, they are called quantum dots (QDs), which are actually zero-dimensional nanoparticles.

In fact, when the size of the semiconductor becomes smaller than the Bohr-magneton radius (BMR), the semiconductor nanoparticle is a QD. The BMR is the equilibrium distance

between electron and hole [9, 10]. When light with sufficient energy meets the semiconductor and the electron is transferred from the VB to the CB, a hole remains in the valence band. The distance between the electron and hole is BMR and different from one to another semiconductor. The BMR is an intrinsic characteristic of a semiconductor [11, 12].

#### *Quantum limitation and problem design*

If the QD size is reduced to such an extent that the electronic levels change from continuous to discrete, and then approach the state of molecular levels and they will show special properties that allow their use in various applications. However, reducing the QD size from the permissible size and less than BMR is associated with quantum limitations such as instability and non-belonging of the excited electron to a QD [13-17].

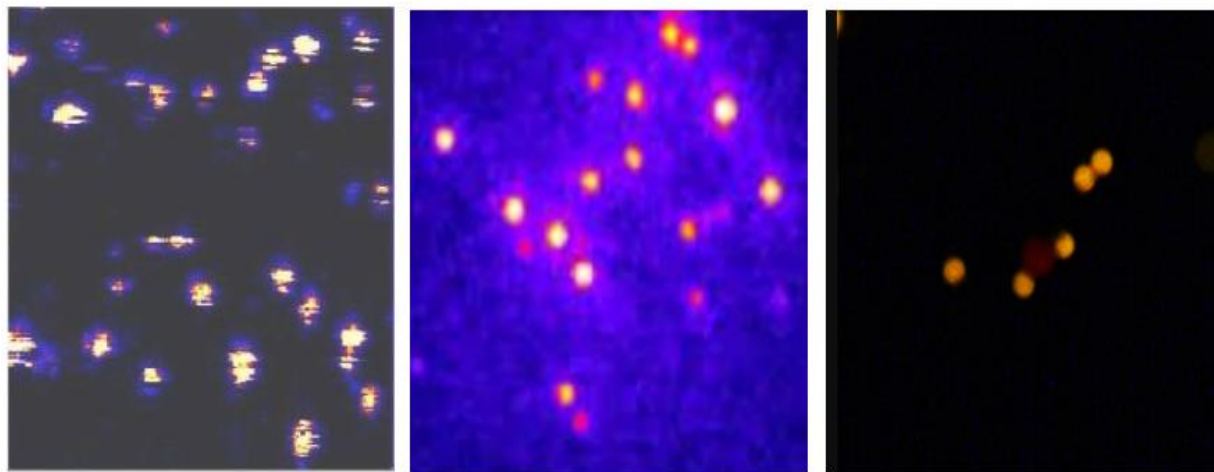
### *Phenomenon of quantum dots blink (QDB)*

The BMR and electron-hole distance for the PbS-QDs is 20 nm. In other words, if the size of PbS crystals becomes less than 20 nm, they become the QDs. The electrons in PbS-QDs are transformed into an excited state by absorbing light corresponding to their bandgap, and then excited electrons return to their original state by emitting light. By this way, they are ready to absorb light again. Because of this property of continuous absorption and emission of light, they emit continuous radiation of light with specific wavelength [13, 14]. If there is no protective shell (PS) around the PbS-QDs, the excited electron can leave the confined space in PbS-QDs domain and would not return to the ground state. This event causes a discontinuity in light emission, which is called the Quantum Dots Blink (QDB), as indicated in Figure 2. The phenomenon of QDB reduces the light radiation efficiency in the QDs [15, 16].

### *Protective shell around PbS-QDs*

Much research has been done on PbS-QDs to solve the size reduction problems. For example, one solution is to create a protective

shell (PS) around it. This is often done to protect the PbS-QDs from instability caused by the QDs dissolution in the solvent. According to Figure 3, by creating a PS around the PbS-QDs, the electrons are trapped inside the PS and cannot escape from the PbS-QDs domain. In this way, the electrons have to return to the ground state and be ready to absorb the light. Thus, the QDB phenomenon is omitted [16]. It has shown that change of the PbS-QDs size results the displacement in VB edge more than the CB edge. Furthermore, the PS can be an insulating or a semiconductor. If the PS is an insulator, it prevents the escape of electrons from the PbS-QDs domain, but if the PS is a semiconductor, the electron exchange may occur between the CB edges of core (PbS-QDs) and the PS. This exchange reduces the PbS-QDs efficiency. In this case, it is very important to choose a suitable semiconductor with a well-defined band edge to minimize the excited electron exchange between the PbS-QDs and PS in the CB edges [18]. A lot of work has been done in this field. Creating a protective semiconductor shell from silica, CdS, CdSe, TiO<sub>2</sub>, and perovskite materials are just a few examples. [19-24].



**Figure 2.** Views of the quantum dots blinking [14, 15]



**Figure 3.** Schematic of a PbS-QD with a PS

#### *Quantum dot light-emitting diodes (QD-LEDs)*

QD-LEDs are made using a QDs film as the emitting layer. When a DC voltage is applied, electrons and holes are injected into the QDs to emit light. In the last two decades, colloidal QD-LEDs as a new generation of LEDs have been upgraded from less than 0.01% to 18%. Its unique feature is high luminescence efficiency and tunable color with specific size of colloidal QDs.

Accordingly, QD-LEDs have a high potential for use in high-quality and energy-efficient thin-film displays [23-26]. If the problem of the QDB is solved, the QD-LEDs are the best replacement of the current LED made from gallium arsenide (GaAs), gallium phosphide (GaP), or gallium arsenide phosphide (GaAsP). The Ga and As are very dangerous for the environment and health [22, 23]. The comparison of Pb with Ga and As, shows that all of them are toxic and dangerous. However, the use of PbS-QDs due to its lower amount and higher efficiency promises that the replacement of PbS-QDs instead of Ga and As are moving in the direction of green chemistry [22].

In addition, there is two ways to increase PbS-QDs efficiency. One is to deposit PbS-QDs on the metal core to increase the capacity of PbS-QDs based on the electrochemical capacity pattern (ECP) of metal [11], and the other is to create a PS on the PbS-QDs to overcome the QDB problem [16]. This type of design of quantum dots with metal substrate is an innovative and new idea. A schematic view of the final product is shown in Figure 4.

#### **Experimental**

The fabrication and electrochemical study of PbS-QDs have all been reported in our previous papers. Likewise, the study of the effect of metal (Pb) substrate on the PbS-QDs capacity has been done by electrochemical method. All electrochemical measurements were carried out in a conventional three electrodes cell powered by a potentiostat/galvanostat (EG&G, model 273 A) that was run by a PC through M 270 and M398 software via a GPIB interface, and a frequency response analyzer (EG&G, model 1025) [11]. In this article, only the theoretical evaluation of the results and its application has been discussed.

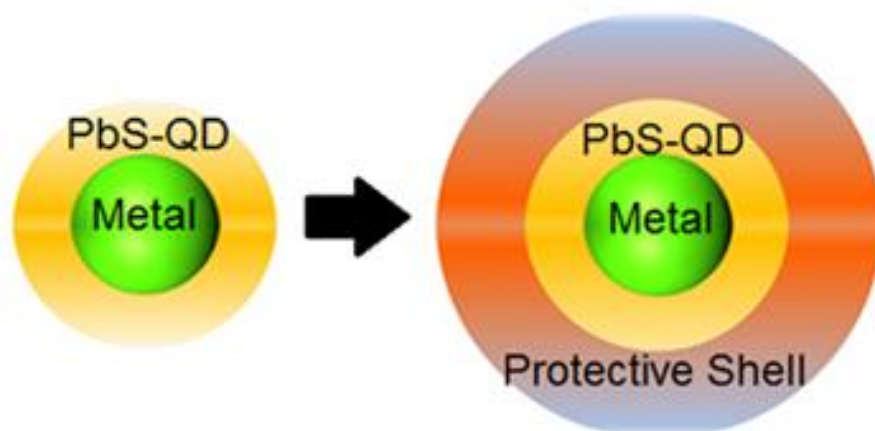
*Theoretical aspect*

The idea followed in this article is that if nanometer particles of the desired metal are already dispersed in the solution where PbS-QDs are formed, and then the PbS-QDs will settle on the surface of the metal particles and Metal@PbS-QD is formed. Finally, a suitable PS is deposited on the Metal@PbS-QD which results Metal@PbS-QD@PS. The procedure is depicted schematically in Figure 5.

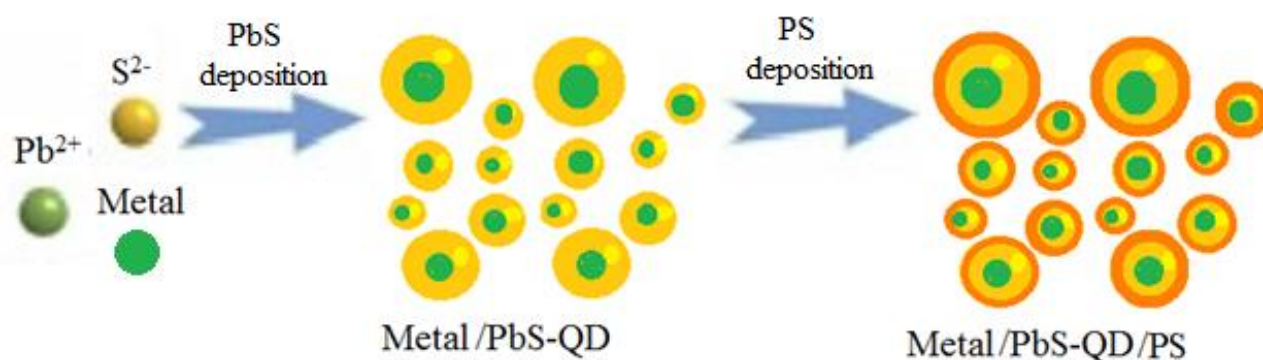
## Results and Discussion

### *Selection of a metal core for PbS-QD*

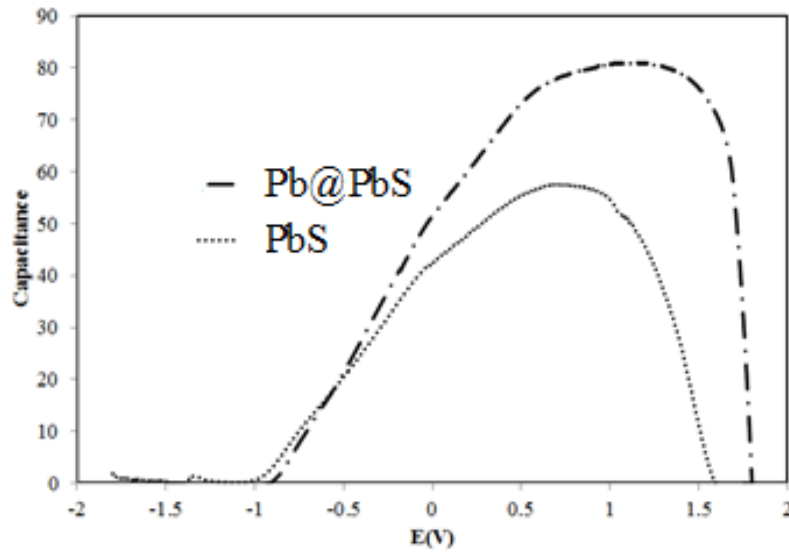
According to previous our research, the formation of Pb substrate for PbS-QD increases the capacity of PbS, which is more noticeable in the potential of -0.3 to 1.5 V, as demonstrated in Figure 6. This potential is very important in red emitting LEDs. Typically, the LED voltage is between 1.8 and 3.3 volts. A red emitting LED works with a potential of 1.7 to 2.0V, but a blue emitting LED requires a potential of about 3 to 3.3V. The Pb@PbS capacity increases by 10 to 50% compared to PbS only in the potential range of -0.3 to 1.5 V. Therefore, Pb@PbS is suitable for use in red emitting LEDs.



**Figure 4.** PbS-QDs deposition on the metal and covered with a PS



**Figure 5.** Preparation of Metal/PbS-QD/PS



**Figure 6.** Capacitance of PbS and Pb/PbS

#### Selection of a semiconducting shell for PbS-QD

When the PS is a semiconductor, its role gets a little complicated. Therefore, when PbS-QD/PS is subjected to a potential difference, both PbS-QD and PS electrons are excited from VB to CB. If the CB edge of PS is higher than that of PbS-QD, the excited electrons are transferred from PS to the PbS-QD. This process enhances the optical activity of PbS-QD because it increases the population of electrons in the CB of PbS-QD. But when the CB edge of PS is not placed in the right position and is lower than that of PbS-QD, the transfer of electrons from PbS-QD to PS will be done. This will interfere with the PbS-QD work process because the population of electrons is reduced in the CB of PbS-QD.

According to Figure 7, the CB edge of cadmium selenide (CdSe) and cadmium sulfide (CdS) is higher than that of PbS. But in the case of titanium dioxide (TiO<sub>2</sub>), the CB edge is lower than that of PbS. Accordingly, in most articles, CdSe and CdS have been used as a PS for PbS-QDs. This selection strengthens the light emitting in PbS-QDs. In addition, the difference

between the CB edge of the PS ( $CB_{PS}$ ) and that of the PbS-QD ( $CB_{PbS-QD}$ ) is presented with  $\Delta CB$ , as indicated in Equation 1. Greater  $\Delta CB$  results show more significant electronegativity difference ( $\chi$ ), i.e.  $\chi \approx \Delta CB$ . Therefore, the excited electrons in PS are more strongly drawn to the CB of PbS-QD. For this reason, the CdSe is the best PS for PbS-QD (PbS-QD@CdSe) with  $\Delta CB=0.24$ , compared with PbS-QD/CdS with  $\Delta CB=0.12$  [27].

$$\Delta CB = CB_{PS} - CB_{PbS-QD} \quad (1)$$

#### Pb@PbS-QD@CdSe application in LEDs

The basis of the LED is a diode, and the semiconductor diode is a crystal piece with a P-N junction, which is connected into two electrical terminals. The N junction is a semiconductor with an additional negative charge, and the P junction is actually a semiconductor with an additional positive charge. The designed structure of Pb@PbS-QD@CdSe can be embedded within the N junction material to strengthen its efficiency, as demonstrated in Figure 8.

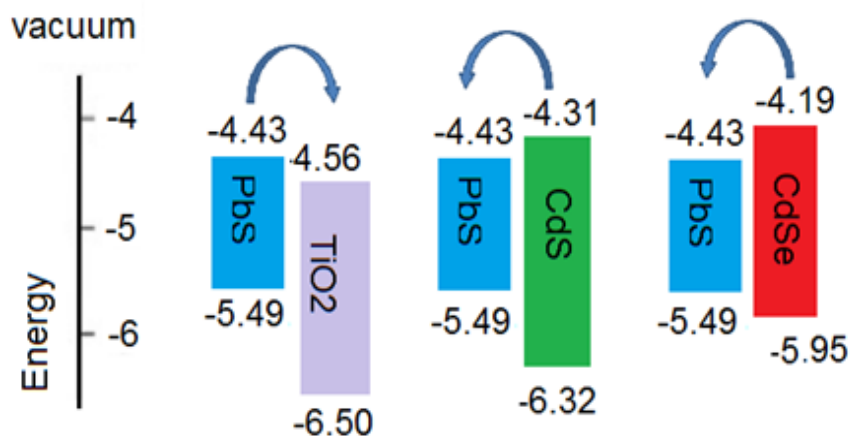


Figure 7. VB and CB edges of CdSe, CdS and TiO<sub>2</sub> with respect to PbS

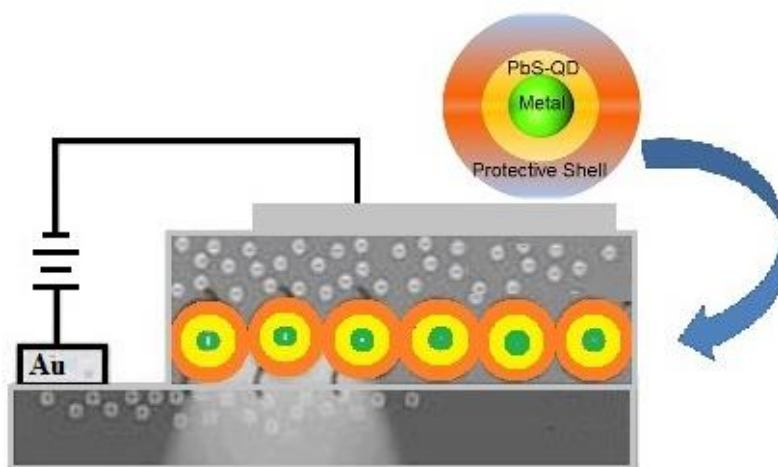


Figure 8. Embedding of Pb@PbS-QDs@CdSe in n junction

## Conclusion

The PbS-QDs are narrow bandgap semiconductors that absorb in the infrared region. By changing the ratio of PbS precursors, the PbS-QDs with desired size and suitable bandgap can be prepared. To stabilize PbS-QDs with dimensions smaller than BMR, it is necessary to create a PS around them. CdSe is a suitable PS for this purpose due to have a CB edge higher than the CB edge of the PbS-QDs. Research has shown that the capacity of Pb@PbS increases by 10 to 50% compared to PbS only in the potential range of -0.3 to 1.5 V.

So the Pb@PbS-QD is suitable for use in red emitting LEDs.

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## Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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