The Role of PbCoS Quantum Dots in Improved Photovoltaic Efficiency

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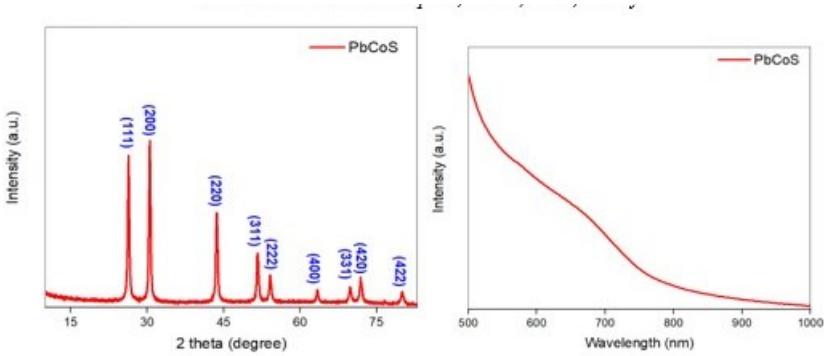
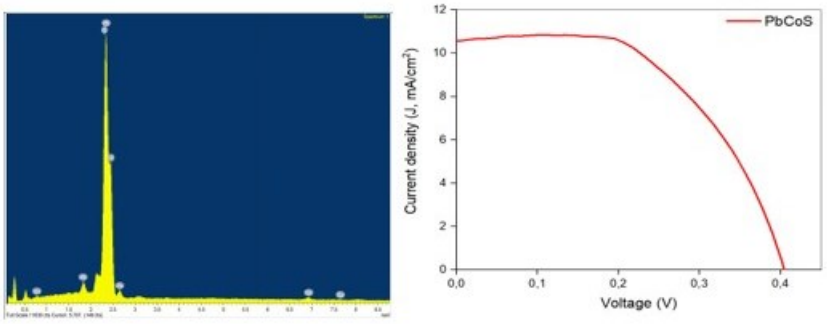
GRAPHICAL ABSTRACT



The XRD patterns of PbCoS

Optical absorption spectra for PbCoS.



The EDX spectra for PbCoS

J-V curve for PbCoS

Abstract

The quest for efficient, sustainable solar energy solutions has propelled the exploration of novel materials with enhanced photovoltaic properties. This study delves into the synthesis, characterization, and photovoltaic application of cobalt-doped lead sulfide (PbCoS) quantum dots (QDs) deposited on titanium dioxide (TiO2) substrates. Employing a hot-injection method, we synthesized PbCoS QDs and characterized their structural, compositional, and optical properties using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and UV-Visible absorption spectroscopy. The QDs demonstrated a cubic crystal structure with an average size of 20.12 nm and exhibited a direct band gap of 1.91 eV, indicative of quantum confinement effects and improved absorption in the visible spectrum. The photovoltaic

performance of quantum dot-sensitized solar cells (QDSSCs) incorporating PbCoS QDs was assessed through current density-voltage (J-V) measurements, revealing a power conversion efficiency (PCE) of 2.17%. This efficiency highlights the potential of PbCoS QDs to enhance the performance of QDSSCs, partly attributed to the impact of cobalt doping on the electronic structure and photovoltaic properties of the material. The study identifies gaps in current research, such as the optimization of cobalt doping levels and the exploration of interface engineering between QDs and substrates, pointing towards future directions for enhancing the efficiency and applicability of PbCoS-based photovoltaic devices.

Keywords: PbCoS Quantum Dots, Quantum Dot Sensitized Solar Cells (QDSSCs), Hot-Injection Synthesis, Photovoltaic Performance, Characterization

1. Introduction

In the quest for sustainable energy solutions, solar energy emerges as a pivotal renewable resource due to its abundant availability and potential for clean electricity generation [1]. Among the various technologies developed to harness solar power, quantum dot sensitized solar cells (QDSSCs) have garnered significant attention. These devices offer a promising avenue for solar energy conversion, combining the advantages of high quantum efficiency, tunable bandgap energies, and the potential for low-cost production [2, 3]. Quantum dots (QDs), with their unique size-dependent optical and electrical properties, enable the absorption of a broader spectrum of sunlight compared to traditional photovoltaic materials, suggesting an avenue to surpass the Shockley-Queisser limit for solar cell efficiency [4-6].

The quest for renewable energy sources has intensified the search for efficient and sustainable solar cell technologies. Quantum dot sensitized solar cells represent a breakthrough, leveraging the quantum confinement effects of nanoscale semiconductor materials to achieve superior light absorption and charge transport properties. Unlike their bulk counterparts, quantum dots can be tuned to absorb a wider spectrum of solar radiation, promising a significant boost in solar cell efficiency [7-10].

Lead-based quantum dots, such as PbS [11-13] and PbSe [14-16], have been extensively studied for their impressive photovoltaic performance. However, the exploration of new materials compositions is crucial for overcoming challenges related to stability, toxicity, and the broadening of absorbance spectra [17-20]. Despite these advancements, the practical

application of PbX quantum dots-based solar cells faces significant challenges [21, 22]. Two major limitations have been consistently identified: (i) the low open-circuit voltage (*Voc*) [23], which is approximately equal to half of the NCs' band gap, and (ii) the low fill factor (FF) [24] of the devices. These issues not only limit the overall efficiency of the solar cells but also underscore the need for material innovation and device architecture optimization. Furthermore, beyond the performance-related challenges, there are environmental and stability concerns associated with lead-based materials. The toxicity of lead compounds poses significant environmental risks, necessitating stringent handling and disposal processes. Additionally, the long-term stability and broadening of the absorbance spectra of lead-based QDs remain critical hurdles for their widespread adoption in commercial photovoltaic applications [25-27].

In this context, the development of PbCoS quantum dots emerges as a novel and intriguing approach. The incorporation of cobalt into lead sulfide quantum dots not only aims to enhance the stability and optical absorption properties but also to mitigate the environmental concerns associated with lead-based materials [6, 28].

This manuscript presents a comprehensive study on the synthesis, characterization, and application of PbCoS quantum dots for quantum dot sensitized solar cells. By integrating PbCoS QDs into the photoanode of QDSSCs, we explore the impact of this unique material composition on the photovoltaic performance of the solar cells. The choice of PbCoS as a sensitizer material is motivated by its potential to offer a synergistic combination of the high electronic quality of lead sulfide and the magnetic properties of cobalt, which could introduce novel pathways for charge separation and transport in QDSSCs.

2. Materials and Method

2.1.Materials

All chemicals were used as received without further purification. Lead(II) acetate trihydrate ($Pb(CH_3COO)_2 \cdot 3H_2O$), cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), thiourea (CH_4N_2S), and other solvents and reagents were purchased from Sigma-Aldrich. Deionized water was used throughout the experiments.

2.2.Synthesis of PbCoS Quantum Dots

The PbCoS quantum dots were synthesized using a hot-injection method. In a typical synthesis, 1M of lead(II) acetate trihydrate and 0.05 M of cobalt(II) chloride hexahydrate were dissolved in 20 mL of oleic acid and 10 mL of oleylamine in a three-neck flask under a nitrogen

atmosphere. The mixture was heated to 120°C to form a clear solution, after which the temperature was increased to 180°C. At this point, 1M of thiourea dissolved in 30 mL of octadecene was swiftly injected into the flask. The reaction mixture was maintained at 180°C for 5 hours before being cooled to room temperature. The quantum dots were precipitated with ethanol, centrifuged, and washed several times with a mixture of ethanol and hexane before being finally dispersed in toluene.

2.3. Characterization of PbCoS Quantum Dots

The synthesized PbCoS quantum dots were characterized by various techniques to determine their size, composition, and optical properties. X-ray diffraction (XRD) analysis was conducted on a Rigaku with Cu Kα radiation to identify the crystalline phases. The composition and elemental ratios were determined by energy-dispersive X-ray spectroscopy (EDX, JEOL JSM 5800). UV-Vis absorption spectra was recorded using a Perkin-Elmer Lambda 2 spectrophotometer.

2.4. Photovoltaic Performance Measurement

The photovoltaic performance of the assembled QDSSCs was evaluated under simulated sunlight with an intensity of 100 mW/cm² (AM 1.5G). Current density-voltage (J-V) characteristics were measured using a PCE-S20 solar simulator and a source meter. The parameters such as open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and power conversion efficiency (PCE) were extracted from the J-V curves.

3. Results and Discussion

Based on the information provided about the XRD patterns of PbCoS quantum dots (Shown in Figure 1) corresponding to specific crystallographic planes, it's clear that the synthesized thin films exhibit a cubic crystal structure. The presence of diffraction peaks at planes (111), (200), (220), (311), (222), (400), (331), (420), and (422) is indicative of the face-centered cubic (fcc) or body-centered cubic (bcc) phases, depending on the material system under study [29]. The sharpness and intensity of the peaks can give insights into the crystallinity and preferred orientation (texture) of the quantum dots. High-intensity peaks, such as those likely observed at the (111) and (200) planes, often indicate well-crystallized materials and might suggest a preferred growth direction if one peak is significantly more intense than others. The calculation of the average crystallite size as 20.12 nm using the XRD data is a crucial parameter for understanding the physical properties of synthesized quantum dots. The crystallite size,

particularly in the nanometer range, can significantly influence the electronic, optical, and mechanical properties of materials, making this information valuable for assessing their suitability for various applications, such as in quantum dot sensitized solar cells. For semiconductor materials, crystallite sizes in the nanometer range, such as the 20.12 nm we have calculated, may result in quantum confinement effects. These effects can lead to changes in the electronic and optical properties of the material, including bandgap widening, which could be beneficial for tuning the absorption properties of quantum dots in solar cells [30].

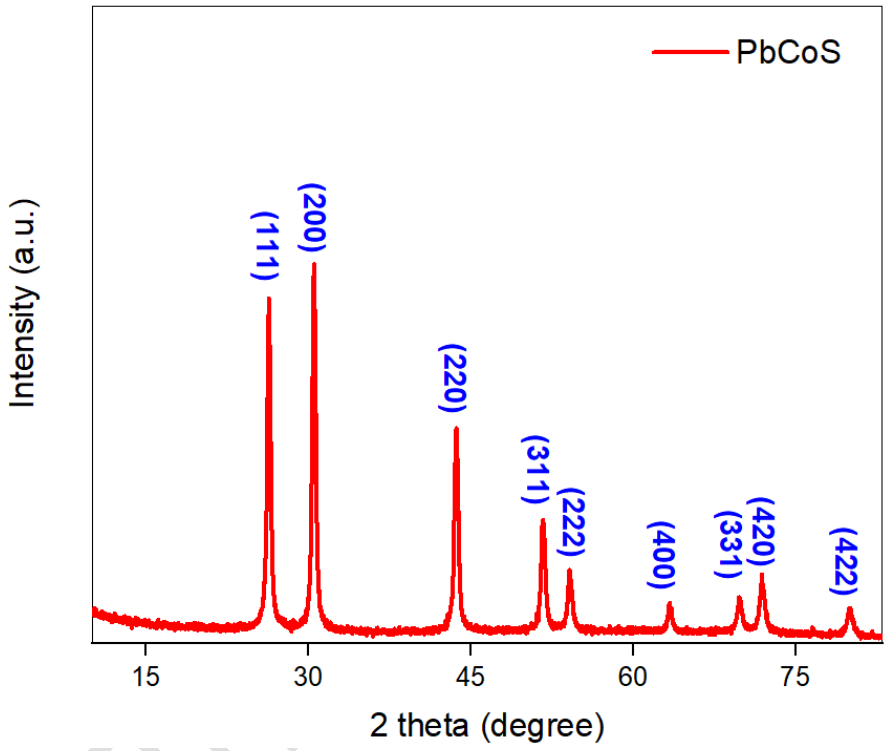


Figure 1. The XRD patterns of PbCoS.

The absorption spectra, as revealed in Figure 2, likely shows the characteristic absorption onset associated with PbCoS. This onset is indicative of the energy required to excite an electron from the valence band to the conduction band, which is directly related to the material's band gap. The curves of $(\alpha hv)^2$ vs. hv (as indicated in Figure 3) are derived from the Tauc relation, which is a method used to estimate the optical band gap of direct band gap semiconductors. The linear portion of these plots, when extrapolated to the hv axis, provides an estimate of the band gap energy. Our finding of a 1.91 eV band gap for PbCoS is a critical parameter, suggesting that PbCoS have a direct band gap. The band gap of 1.91 eV for PbCoS quantum dots being higher than that of bulk PbS is a noteworthy observation. Bulk PbS typically has a band gap of about 0.41 eV at room temperature [31]. The increased band gap in PbCoS indicates quantum

confinement effects, which are pronounced due to the nanoscale size of the quantum dots. This confinement effect leads to the widening of the band gap compared to the bulk material. The band gap of 1.91 eV for PbCoS positions it well within the visible range of the solar spectrum, which is advantageous for solar cell applications. Materials with band gaps in this range can efficiently absorb visible light, potentially leading to higher photocurrents in QDSSCs [32].

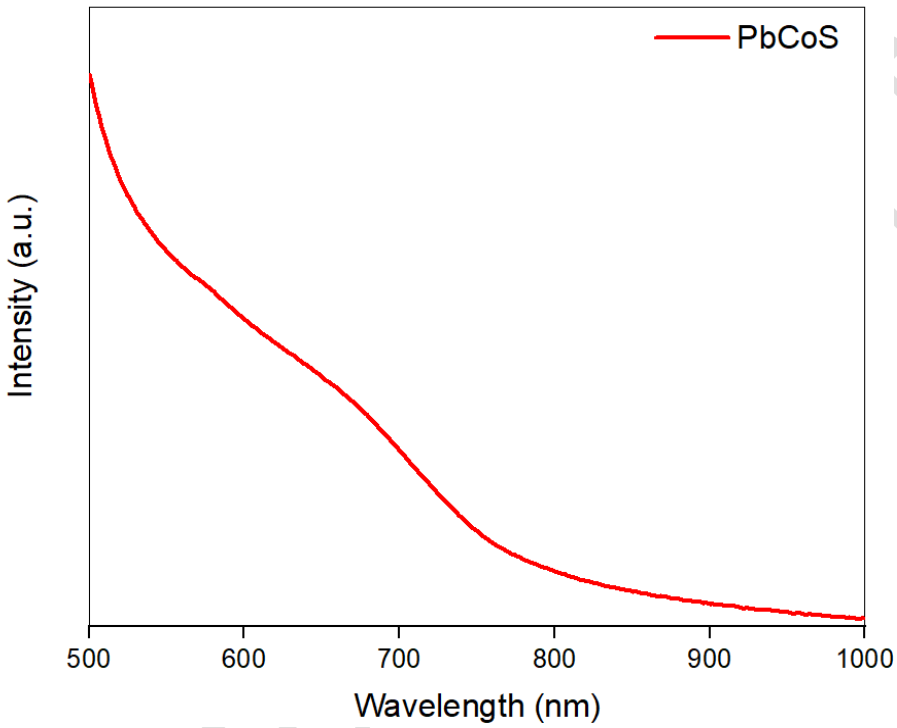


Figure 2. Optical absorption spectra for PbCoS.

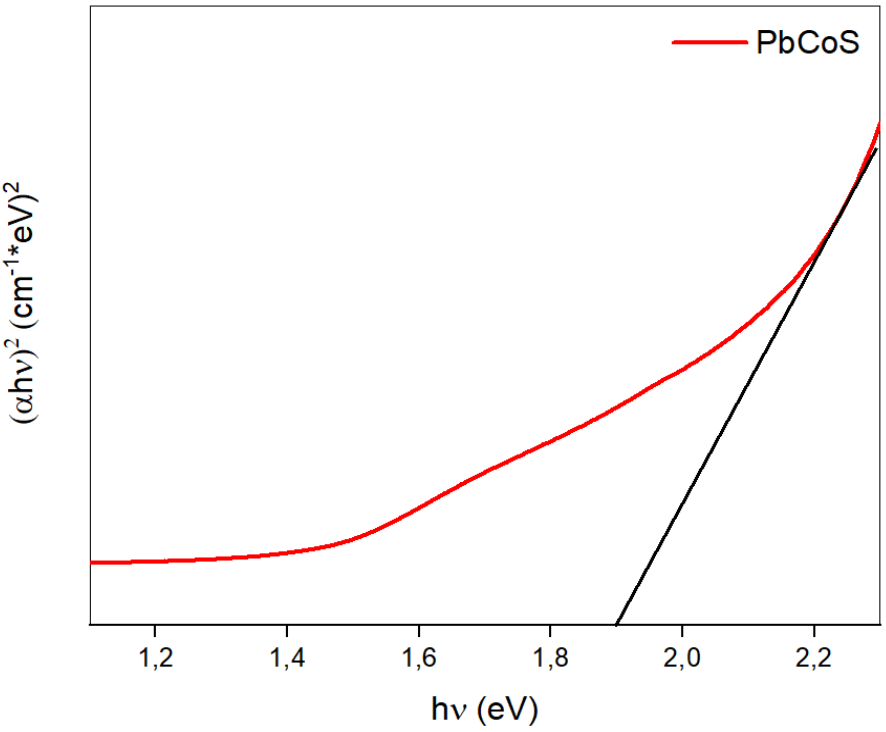


Figure 3. Graphs of $(\alpha h\nu)^2$ versus hν for PbCoS.

The EDX analysis is a crucial step in verifying the composition and purity of synthesized materials, including quantum dots used in solar cell applications. The EDX spectra provide elemental composition data that are essential for understanding the stoichiometry and potential impurities within the sample. Based on the EDX spectra presented in Figure 4, the presence of the Co element in the EDX spectrum was a direct confirmation that cobalt has been successfully incorporated into the PbCoS structure. This observation was critical as it validates the synthesis process, ensuring that the intended material composition was achieved. Determining the real concentration of Co in PbCoS as approximately 4.12% is an important finding. This quantitative analysis allows for a precise understanding of the material's stoichiometry, which is vital for correlating the material's properties with its composition. The presence and concentration of Co in the PbCoS quantum dots could impact the QDSSCs efficiency. The altered electronic structure due to Co doping may enhance charge separation and transport, potentially leading to improved photovoltaic performance. However, the exact impact would depend on the balance between enhanced electronic properties and any potential recombination sites introduced by the Co incorporation.

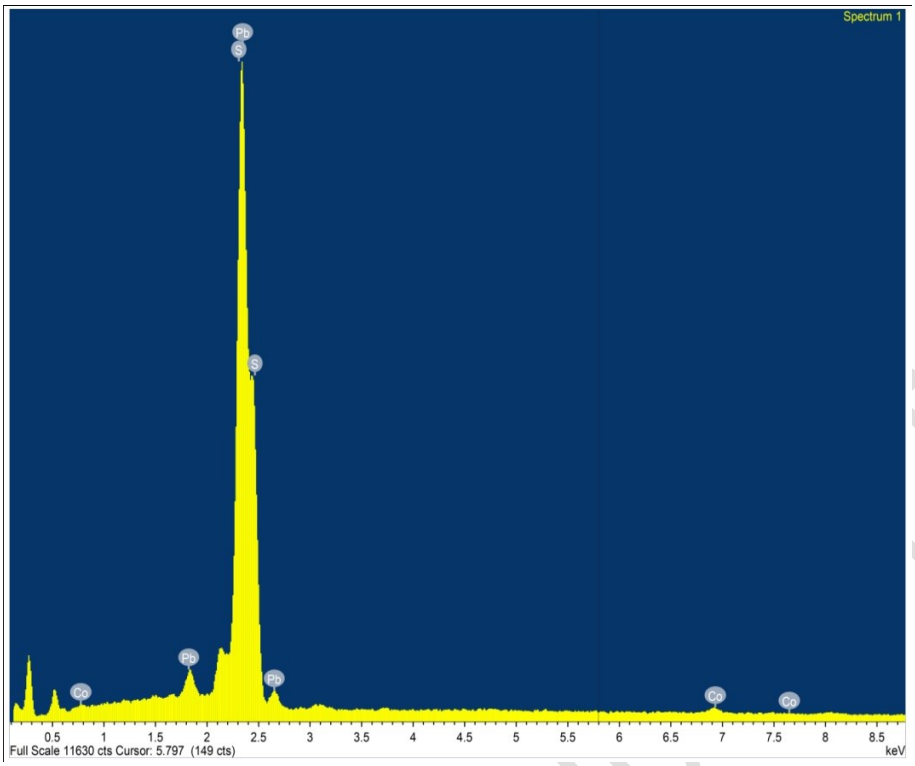


Figure 4. The EDX spectra for PbCoS.

The photovoltaic performance of PbCoS quantum dots grown on a TiO_2 substrate, as characterized by J-V measurements shown in Figure 5 provides essential insights into the efficiency of these materials in converting solar energy into electrical energy. Based on the values provided for the Voc, Jsc, FF, and PCE (η%), here's an analysis of the photovoltaic performance and implications for PbCoS QDSSCs.

The Voc value of 0.42 V indicates the maximum voltage the solar cell can produce under open-circuit conditions, i.e., when there is no external load connected. This value is influenced by the materials' band alignment and the charge carrier separation efficiency. For PbCoS QDSSCs, a Voc of 0.42 V suggests effective charge separation and an adequate band alignment with the TiO_2 substrate.

The Jsc of 10.42 mA/cm² is a measure of the maximum current density the solar cell can generate under short-circuit conditions. This value is primarily determined by the light absorption efficiency of the quantum dots and the charge collection efficiency of the device. A Jsc of 10.42 mA/cm² for PbCoS QDSSCs is indicative of good light absorption and effective charge transport to the electrodes.

The fill factor, given as 0.5 (or 50%), represents the ratio of the actual maximum obtainable power to the theoretical power (Voc × Jsc) of the solar cell. The FF is affected by the series and

shunt resistances in the cell, with higher values indicating lower resistive losses. An FF of 0.5 suggests a moderate level of optimization, with potential room for improvement in minimizing resistive losses and enhancing charge extraction.

The overall PCE of 2.17% quantifies the efficiency with which the solar cell converts sunlight into electrical energy. While this efficiency is a critical step forward for PbCoS quantum dot-based solar cells, it highlights the challenges and opportunities for further enhancement.

Thus, the J-V measurement results for PbCoS quantum dots grown on a TiO_2 substrate provide valuable benchmarks for the current performance of these solar cells. While the efficiency of 2.17% represents a starting point, the detailed analysis of Voc, Jsc, and FF highlights specific areas where targeted research and development efforts could lead to significant improvements in the performance of PbCoS-based QDSSCs.

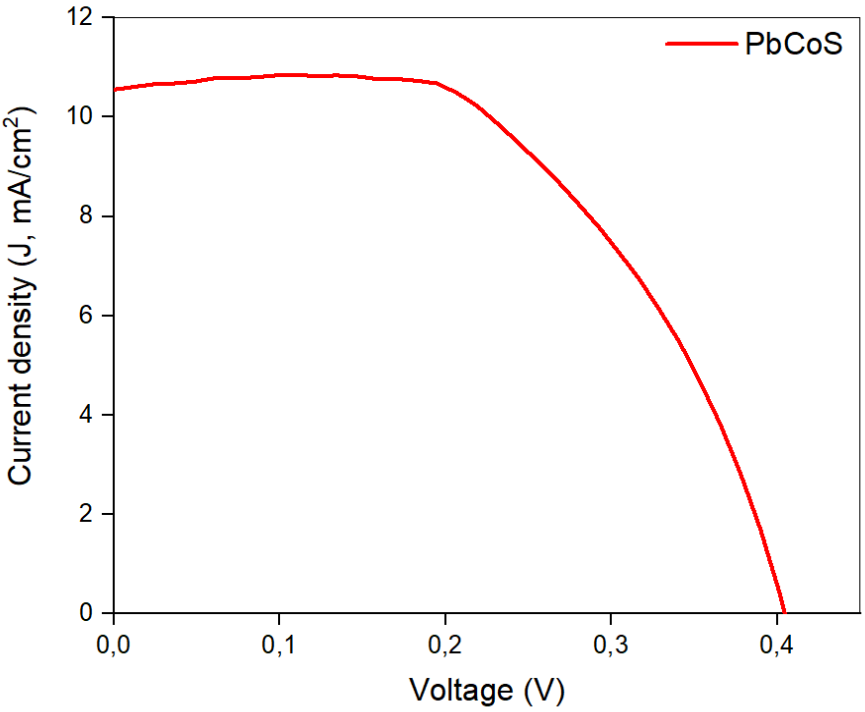


Figure 5. J-V curve for PbCoS.

4. Conclusions

This work presents a comprehensive examination of PbCoS QDs synthesized via a hot-injection method for application in quantum dot sensitized solar cells. The successful incorporation of cobalt into the PbS matrix was confirmed, which not only validated the synthesis process but also introduced a novel avenue for tuning the optical and electronic properties of quantum dots

through doping. The characterized quantum dots showcased a cubic crystal structure, an enhanced band gap due to quantum confinement effects, and a significant absorption in the visible spectrum, which are critical attributes for efficient solar energy conversion. The photovoltaic assessment of the QDSSCs employing PbCoS QDs revealed promising results, with a power conversion efficiency of 2.17%, attributed to effective charge separation and transport mechanisms facilitated by the unique properties of the quantum dots.

Future efforts should focus on optimizing the synthesis and post-synthesis processes to increase the cobalt concentration within the PbCoS QDs, further enhancing their photovoltaic performance. Additionally, exploring the interface engineering between quantum dots and the TiO_2 substrate could provide pathways to reduce recombination losses and improve charge carrier dynamics. This study lays the groundwork for the development of high-efficiency quantum dot sensitized solar cells, highlighting the potential of cobalt-doped PbCoS QDs as a promising material for photovoltaic applications.

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