

Nanostructured metal chalcogenides (SnS and SnSe): Future generation energy storage devices as Photovoltaic applications

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Abstract

Unconventional energy storage and their conversion are likely to play a most important part in the growth of ecological machineries that improve the vitality and conservational challenges that everyone is currently facing. Due to the major problems of human population expansion and environmental degradation, there is an urgent need for clean energy production, novel and innovative nanomaterials (NMs) for the creation of alternative energy storage technologies and the development of unconventional energy foundations. Recently, solar cells (SCs) have received a great deal of attention and play an important role in emerging future clean energy storage devices, mainly owing to their superior energy characteristics (CTs) such as power conversion efficiency (PCE), ecofriendly and long operational life. SCs act as bridges to fulfill the gap between energy consumption and energy usage. The SnS and SnSe termed out to be promising NMs for photovoltaic (PV) absorbers in SCs. Therefore, in this chapter, the PV performance of SnS and SnSe are scrutinized via bulk heterojunction and photocurrent (PC) response.

Keywords: Energy storage devices; SCs; PCE; PV.

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1. Introduction

The energy issue is the most important topic for the last two million years. Excessive use of combustion-based non-renewable fossil fuels brings not only ecology problems but also a severe influence on the global economy and society. There is a big requirement for low cost, environmentally energy storage and conversion devices, varying from portable electronics (e.g., laptops, mobile phones, camcorders) to transportation (e.g., electric vehicles, hybrid electric vehicles). The excess use of non-renewable sources of energy has put severe impact on our environment and their usage may no longer be available. As a consequence, different energy bases are required to meet the energy demands. Owing to the continued availability of solar energy (SE), researchers have recently concentrated on SC. Traditional, direct band gap CdTe and CuIn(Ga)Se₂ (CIGSe) thin film SCs (SCs) are taking the place of conventional crystalline silicon SCs. In CdTe- and CIGSe-based thin film SCs, maximum conversion efficiencies of up to 21.5% and 22.6%, respectively, have been attained [1, 2]. However, given the demand for tetra powder, there are certain challenges with producing CIGSe or CdTe SCs on a big scale. For instance, cadmium is highly poisonous, CdTe-based SCs are not a good choice when it comes to large-scale production. It is challenging to prepare CIGSe absorbers with the appropriate microstructure and composition for CIGSe-based SCs. Another important problem with CIGSe is the dearth of indium (In) and gallium (Ga) deposits. As a substitute, Cu₂ZnSn (SSe)₄ (CZTSSe) SCs are the focus of current research [3], with a extreme transformation efficiency of 12.6% reported thus far in the solution process [4]. Owing to the greater quantity of elements, the quaternary system to which CZTSSe belongs makes it challenging to precisely manage composition and structural transitions. Additionally, having too many components in this absorber may raise the price at which SCs are made. Therefore, the use of both CIGSe and

CZTSe will be restricted in the near future due to mass manufacture at reduced costs. According to this scenario, tin-based binary semiconductors like SnS and SnSe, which are reasonably abundant on Earth, non-toxic, and easily controllable in terms of stoichiometry, are anticipated to play a significant role in replacing the aforementioned technologies in the near future. Tin-based nanoNMs, on the other hand, have also been applied in a number of areas, including photoelectrochemical [5], heat transfer fluids [6], hydrogen generation [7], hydrogen sensing [8], and Li-ion battery electrodes [9]. Additionally, for the effective collection of solar energy, the binary SnS and SnSe NMs have the necessary band gaps (near to the ideal spectral area). These NMs have advantageous CTs such a high absorption coefficient (10^5 cm^{-1}) with p-type conductivity, a reasonable band gap (1.0 eV–1.5 eV), and strong chemical stability [11-14]. Additionally, they have a 33% theoretical maximum efficiency [15]. As a consequence, these NMs have a great chance of replacing the hazardous (CdTe) and element-based (CIGS) PAs.

At eminent conditions and with the space group Pnma, SnS and SnSe preferentially crystallise in the orthorhombic structure; at higher temperatures and with the space group Cmcm, they exhibit cubic crystallisation [16–18]. In addition to the previously stated structures, they also exhibited metastable zinc-blende phases and cubic structures in nano-regime [19–21]. Additionally, NPs have a larger surface energy than bulk NMs, which improves their catalytic properties. Additionally, quantum confinement is a frequently noted feature in methods based on NPs. The electron density of states, which in turn affects the material's physical properties, can be significantly influenced by the quantum confinement phenomenon. Therefore, one may easily adjust the basic CTs of SnSe and SnS by engineering the dimensionality of the NMs using solution growth technology. These NMs can also be recycled to construct devices on lightweight, flexible substrates for commercialisation and technologies like nano-ink printing. As a result,

high-efficiency plastic PVs can therefore be produced and introductory up innovative business opportunities. Therefore, with a significant reduction in load, charge and additional architectural issues, the nanoparticle-based methods of SnSe and SnS absorbers are anticipated to prime in the PVs market. There are excellent articles and book chapters that discuss the CTs of CZTS (tin)-based NCs (NCs) for PV applications, but no one of them extensively concentrated on SnS, SnSe, and SnS(Se) PVA [22-24]. This chapter's emphasis on the development of SnSe and SnS NPs (NPs) develop in solutions and how effectively they function in SCs. The chapter begins by discussing the synthesis circumstances, the impact of ligands on development and the morphological, structural and band gap of these ligands. On the origin of previous findings on SnSe and SnS NPs from the last 16 years, key growths CTs are examined. These NMs are synthesized using a nanoparticle-based technique, and the manufacturing of SCs is also designated.

2. Preparation methods of SnS and SnSe NPs

Presently, the research of well-defined size and shape of the NMs is an main task to the scientific community. A range of techniques have been employed for the construction of SnS and SnSe NMs which depend on the NMs of interest and the size range involved. The basic idea for the preparation of NMs is to yield a huge number of nuclei and to inhibit the growth and collection of grains. Different metals sulfides and their derivatives can be synthesized using several synthetic techniques, which mainly fall under two categories.

- Top-down and
- Bottom-up

The top-down method is produced from the macroscale to the nanoscale. They mostly rely on physical attributes for their processing the arrangement of chemical, electrical or thermal processes. The top-down method includes high energy milling, ion implantation, lithography, laser ablation, sputtering, vapor condensation, etc. In contrast, a bottom-up method is synthesized and processed from the atomic or molecular scale to the nanoscale. The bottom-up method includes sol-gel, precipitation, atomic layer deposition, electrical deposition, cluster assembly/consolidation, self-alignment, chemical vapor deposition, etc. Typically, there are many methods available for synthesization of SnS and SnSe NMs shown in **Fig.1**. Among all these methods, recently, two significant techniques were operated for the construction of SnS and SnSe NMs are Solvo/hydrothermal and chemical precipitation methods.

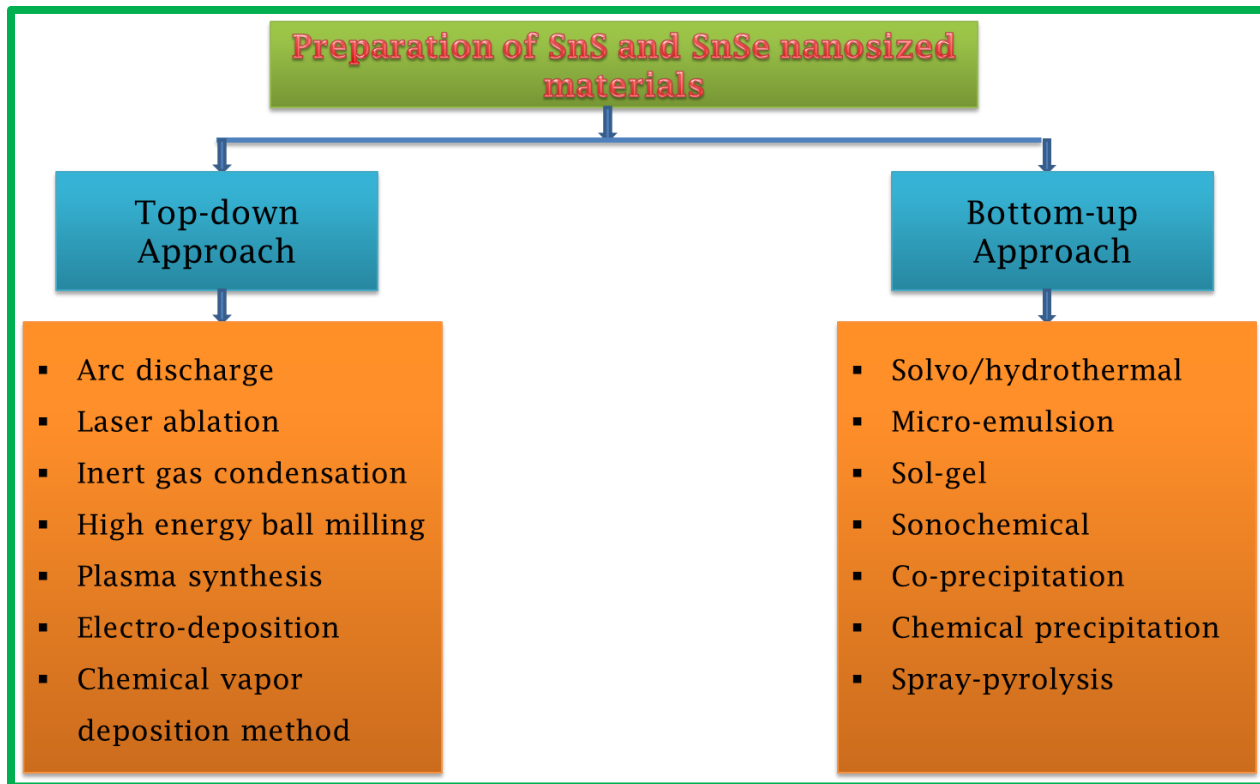


Fig.1: Methods for the preparation of SnS and SnSe nanosized NMs.

2.1. Chemical Precipitation (CP) Method

Certain soluble inorganic NMs can be detached by the accumulation of suitable reagents to convert the soluble impurities into insoluble precipitates. These precipitates can be flocculated and removed by sedimentation. The degree of removal depends on the solubility of the product. This is normally constrained by components like pH and temperature. CP is the utmost conjoint skill used in eliminating liquefied (ionic) precipitates from solutions. The chemical reaction among the solvable metallic complexes and the precipitating agent transforms the ionic precipitates into an unsolvable form. By settling and/or filtration, the particles produced by this reaction are taken out of the solution. The most common type of CP is known as hydroxide precipitation, which produces metal hydroxides by employing NaOH (caustic) or CaOH₂ (lime) as the precipitant. This technique is also called wet precipitation, aqueous precipitation and chemical precipitation. **Fig.2** shows the sample procedure for the construction of NMs using this technique.

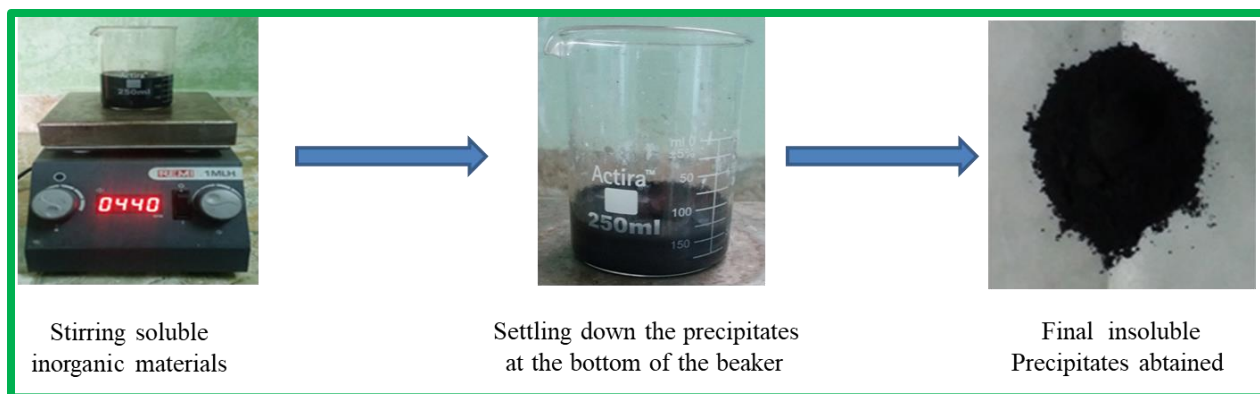


Fig.2: Sample procedure for the construction of NMs.

2.1.1 Advantages of CP method

- By adding counter-ions to decrease their solubility, CP is used to eliminate ionic elements from water.

- It is most commonly utilized to eliminate metal cations, but it can also be utilized to eliminate anions like cyanide, phosphate and fluoride, as well as biological molecules.
- CP practices, in aggregation with numerous physical procedures, have been established for the comprehensive secondary behavior of unprocessed wastewaters, comprising the elimination of both N₂ or P, or both.
- It is one of the most established methods for treating sewage.

2.2. Solvothermal/Hydrothermal method

The solvothermal/hydrothermal method is one of the significant methods for the synthesization of NMs. Hydrothermal (HT) synthesis is a procedure in which NMs can be prepared through chemical reactions in a liquid solution above the boiling point of water. On the other hand, solvothermal synthesis refers to the synthesis of NMs in a non-aqueous solution at a relatively high temperature. Thus the only difference between the two synthesized procedures is of solvent which is utilized in the chemical reaction. This method is the most well-known one, gathering interest for researchers and technologists of various disciplines, especially from the last fifteen years. In the real sense, HT was first evolved with geological origin comprised of two terms; "hydro" signifies water and "thermal" signifies heat. English Geologist, Sir Roderick Murchison (1792 - 1871) was quick to utilize this word, to clarify the activity of water at high temperature and pressure factor in bringing changes in the earth's crust leading to the construction of different rocks and minerals. The solvent plays a key role in the solvothermal synthesis since it can handle the centralization of the substance species in the arrangement, affecting the kinetics in the reaction, modify the coordination of solvated species and induces specific structures. **Fig.3** represents the illustration of a procedure for synthesization of NMs using the HT method.

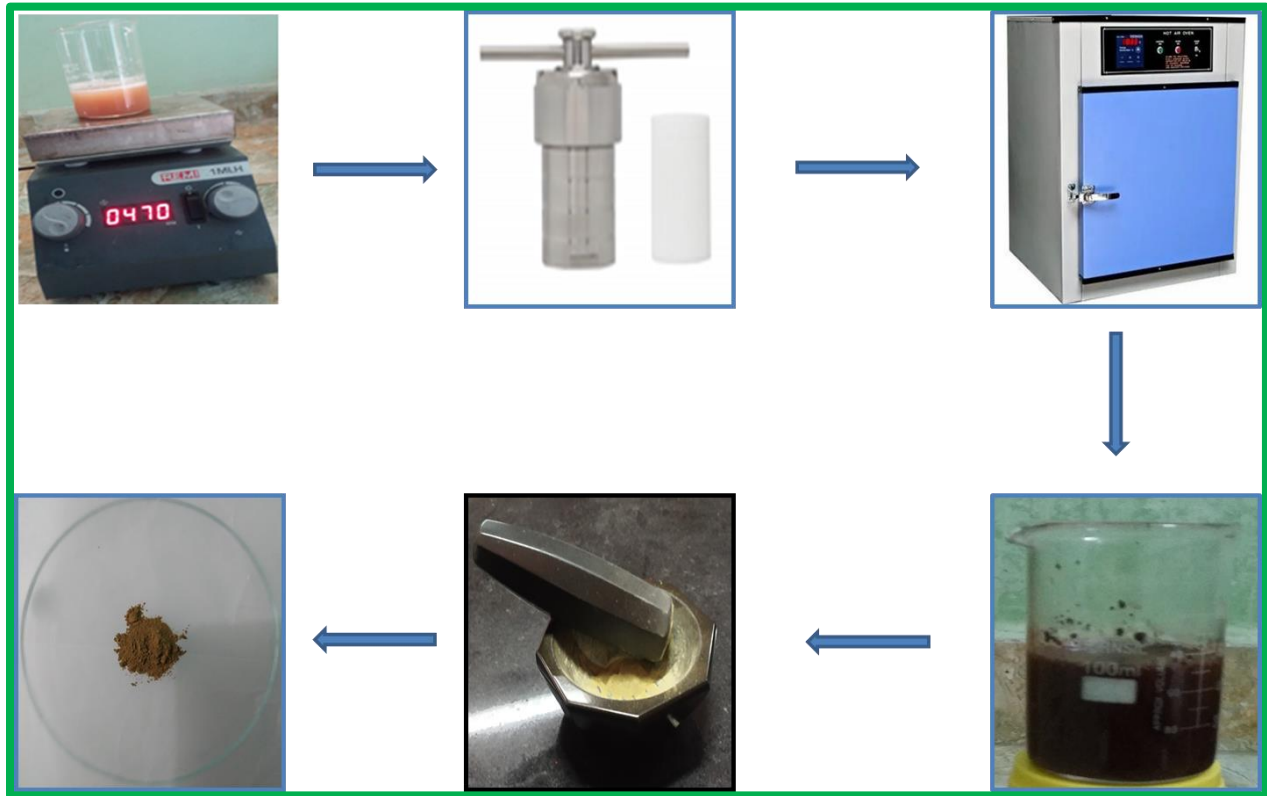


Fig.3: Synthesization of NMs by HT method.

1.5.1. Advantages of Solvothermal/Hydrothermal Processes

HT synthesis offers numerous benefits over conventional and non-conventional synthesis methods since it is environmental friendly, offers significant enhancement to the chemical activities of the reactants and NMs that can not be synthesized with the help of other methods can be easily prepared through this method. Some of the important advantages of this method are given below

- This method is energy efficient because of low-temperature synthesis.
- It can recycle unusual components.

- High purity products can be synthesized.
- Metastable and new phases can be accessed.
- Hydroxylated and hydrated nanoNMs can be made by this process.
- Crystal size, composition and morphology of the synthesized nanoNMs can be easily controlled.
- Substances that are low in melting points and high in vapor pressures and tendency towards pyrolysis will be obtained

3. Tin monosulfide (SnS)

SnS, is one of the well-explored IV–VI group binary compound, shares a similar layered structure like germanium sulfide (GeS) and germanium selenide (GeSe). The layers linked with each other by weak vander walls forces, prominent to the dangling bond free chemically inactive surface [25, 26]. The two phases α -SnS and β -SnS are isolated from each other established on the Sn-S bond length. In β -SnS, the S atoms are attached to the Sn atom with equivalent atomic distances, while in α -SnS, two bonds are slightly longer than the remaining two bonds. Out of several phases, α -SnS is the only stable phase at room temperature, while remaining forms are stable at high temperatures [27]. Including β -SnS, the α -SnS crystallizes in the orthorhombic herzenbergite structure having a rock salt arrangement and the space group of Pnma [28]. This structure illustrates that Sn^{2+} ions coordinate to three S^{2-} ions with active lone pair of electrons [$\text{Sn}^{2+}, 5\text{S}^{2-}$], occupying the last tetrahedral site. This extremely slanted configuration clenches matrix coefficients $\mathbf{a} = 1.1200$ nm, $\mathbf{b} = 0.3987$ nm and $\mathbf{c} = 0.4334$ nm, respectively [29]. SnS shows intense anisotropy as a result of the strong interlayer interaction, unique perspective perspectives, and axial directions. The electrical nature of the SnS compound is significantly influenced by these structural factors. The p-type conductivity of SnS exhibit direct bandgap

energies of 1.2 to 1.5 eV and indirect bandgap energies of 1.1 eV, respectively [30-33]. Thus, SnS is suitable for a range of optoelectronic, PV, and supercapacitor applications due to these distinctive pairings of crystallographic and electrical properties.

4. Tin monoselenide (SnSe)

SnSe belongs to the IV-VI group of layered semiconducting compounds. The phase diagram investigation revealed the existence of three main phases such as SnSe, SnSe₂ and Sn₂Se₃ [34]. Among these three phases, SnSe is the utmost important of these ingredients due to its ideal opto-electronic CTs for PV applications. This substance is also known as stannous selenide and is primarily a grey solid. The orthorhombic structure resides with a slanted NaCl structure, such as the GeS structure. Its arrangement is tightly bonded double layers of Se and Sn atoms along the c-axis. The bonding between the layers is a weak Van der Waals type, resulting in structural anisotropy. At room temperatures, it crystallizes into the Pnma space group, while at high temperatures it exhibits the Cmcm space group [36]. Compared to the transport CTs of SnSe, this phase transition has significant benefits. Additionally, it is p-type with a straight band gap in the range of 0.9 eV - 1.3 eV and has a high absorption coefficient of 10⁵ cm⁻¹ [37, 38]. SnSe is a suitable candidate for a number of applications because of its special properties, such as PV devices, radiation detectors, infrared optoelectronic devices, electrical switches, holographic recording systems, thermoelectric cooling systems and polarity dependent memory switches. [39, 40]. Due to its extensive use in thin film SCs and optoelectronics, NC SnSe has garnered a lot of attention. With the use of the solvothermal approach, Wang et al. [41] published the first report on SnSe NPs in 1999.

5. PV performance of SnSe and SnS NPs

In recent years, tin-based binary and ternary chalcogenides semiconductors, such as SnSe, and SnS have been established as an energetic absorber resources in the PV field due to their optimal band gap, high optical absorption, non-toxic, and earth-abundant nature of the essential elements. In contrast to CdTe, CIGS, and CZTS SCs, very little work has been put towards developing solution synthesised SnSe and SnS-based SCs. For CIGS- and CZTS-based SCs that were solution synthesised, maximum efficiencies of 17.1% and 12.6%, respectively, have been reported [42, 43]. According to hypothetical studies, the device can work superbly for positive conduction band offset CBO values between 0 and 0.4 eV. The short-circuit current (J_{sc}) will abruptly decrease with a CBO greater than 0.4 eV. The fill factor (FF) and open-circuit voltage (V_{oc}) will drop if CBO is negative [44]. On the other hand, the potential of SnSe and SnS as PV absorber NMs has showed an efficiency of about 5% [45-47]. As a result, the PR of SnSe and SnS NPs, which is a clear indicator of PV behaviour, is summarised in the next section. The PR of SnSe and SnS NC gadgets was experienced by a number of authors using the current-voltage (I-V) CTs in the dark and under illumination.

5.1. PR of SnSe NCs

The potential of SnSe NCs in solar applications was estimated by Baumgardner et al. [48]. The SnSe NCs films protecting the interdigitated gold electrodes were tested for their PC. The photoconductivity of these NPs was validated by the transient current-voltage (I-V) CTs in the light and dark. In SnSe NCs films with oleic acid passivation, they also noticed comparable effects. A SnSe nanocolumn was used by Jang et al. [49] to evaluate the opto-electrical CTs. The SnSe nanocolumns showed a 1.5 fold increase in PC during their PC measurements when exposed to visible light (from a Xe lamp with a wavelength > 420 nm) as opposed to when they

were in the dark. Sharma et al. [50] investigated SnSe's PR. Only the films formed at 490 °C showed the PR, according to their observations. Their device's PR demonstrated a quick switching characteristic under illumination and a rise in current of about 20%. I-V CTs of the SnSe NP device were measured by Wang et al. [51] in both low- and high-light conditions. In this experiment, the gadget saw a net rise of 10.0 mA when exposed to radiation with an intensity of 5.6 mWcm⁻² and a bias of 10 V. Li et al. [52] looked at SnSe's PR (NSs or NFs). At an applied voltage of 2 V, they observed dark currents of 2.8 nA for SnSe NSs and 4.8 nA for SnSe NFs. Both SnSe NSs and SnSe NFs showed a 2-fold increase in PC after the light was turned on. Liu et al. [53] explored the PR of the SnSe NC dispersion-fabricated SnSe NC thin film by drop-casting it on top of the electrodes so that the film covered the space between the electrodes. The films they produced displayed a sizable PR, demonstrating the SnSe NCs' potential as an absorber in PV and optoelectronic systems.

5.2. Bulk SnSe SCs

Franzman et al. [54] linked the output power energy of PPV films with SnSe NCs hybrid SCs as a function of the V, and the results showed that the PCE was 100%. SnSe nanowires' optoelectronic CTs were investigated by Liu et al. [55]. In comparison to neat P3HT (PCE 14 0.0038%), the highest PCE was increased by 129% (PCE 14 0.0087% for 1:2 w/w P3HT/short SnSe nanowires). SnSe QDs were created by Ling et al. [56] who also evaluated their prospective PV qualities and achieved a PCE of 0.27%. Recently, Dar et al., [32] synthesized SnSe nanospheres by utilizing precipitation method and attained the PCE of about 9.99%. The above results suggest that the SnSe NCs have a strong PV nature, but further study is needed to enhance the device performance.

5.3. PR of SnS NCs

For the first time, Hickey et al. [57] verified the PC response of the SnS NCs using opto-electrochemical studies. The ITO/SnS working electrode was made into a colloid of SnS NCs on ITO substrates over the course of 3 - 4 hours. The electrode noted that the PC response profile was repeatable over numerous cycles and produced a PC for monolayers and submonolayers in the range of 6 - 8 nAcm⁻². Zhang et al. [58] investigated the photosensitivity of the SnS nanobelt device. They reported that the device had strong PC stability during a 500s period at a 5 V bias, with charging ability of 7%. They credited the device's sandwich form as the reason for its remarkable stability. Patra et al. [59] investigated the PC and I-V properties of the SnS nanoparticle-based (SnS and Au-decorated-SnS) PV devices. They determined the PC gain of the NMs using the I-V plots, which were roughly 3%. Lu et al. [60] determined the PR of the SnS NPs at room temperature in air and vacuum. Their findings demonstrated that the gas environment had a significant effect on the photosensitive CTs of SnS. These findings demonstrate the potential of SnS NPs for use in gas sensors.

5.4. Bulk SnS SCs

Wang et al. [61] combined SnS NPs with a conjugated polymer, and showed the solar cell blended with 86 weight percent SnS in P3HT attained a maximum efficiency of 0.0108%, whereas the MDMO-PPV based solar cell mixed with 67 weight percent SnS displayed a maximum conversion efficiency of 0.0205%. A year later, the same authors created SCs with an active layer made of a mixture of SnS with MDMO-PPV and SnS/SnO with MDMO-PPV And got the same results [62]. Another example is the SnS/PbS NC film heterojunction that was created by Stavrinadis et al. [63], who also investigated the PV CTs of the SnS NCs. The devices were composed of SnS/PbS and PbS 920 nm thick and got PCE of 0.5% and 0.37%, respectively.

Oda et al. [64] used the J-V measurements including V_{oc} , J_{sc} , FF, and PCE to analyse the performance of TiO₂/SnS heterojunction SCs. Due to the excellent band energy alignment, the device used with the SnS QDs synthesised at 90 °C demonstrated the greatest PV performance with an efficiency of 0.01% for the QDSSC. In general, the FF and J_{sc} of bulk or heterostructure SCs determine their efficiency. A high FF and J_{sc} are beneficial and preferred to increase a PCE of SCs. On the other hand, the recounted lesser productivities of metal chalcogenides were mainly due to the lower FF and J_{sc} [65]. To solve this problem, it is essential to exchange the outdated ligands that cover long-chain hydrocarbons with minor restrained inorganic ligands.

6. Conclusion

SnS and SnSe have been recommended to substitute the hazardous (CdTe) and element-based (CIGS) absorbers in PV systems. High PCE using solution-based methods have already been shown to be competitive with vacuum-based methods in CZTSSe NMs. This gives the idea of solution-synthesised SnSe and SnS NCs in solar devices. A new market for a wide range of solar device topologies is also made possible by this kind of technique, including the use of flexible, affordable, and light-weight malleable substrates, which is unthinkable in high-temperature vacuum procedures. The methodologies from earlier papers to engineer the structural and PV performance of the slanted compounds were thus highlighted in the current chapter. The colloidal, solvothermal/hydrothermal and hot injection methods are the most common solution techniques to synthesize these NMs. Because most authors aimed to control the shape, size, and structural properties of SnSe and SnS NCs, very little progress has been made so far in fabricating these PV devices. Therefore, small shift in the efficiency (>10%) of SnSe and SnS based SCs definitely fulfill all future energy demands for the next generation at a lower cost.

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