

RESEARCH ARTICLE

Efficiency Optimization of $\text{TiO}_2/\text{Cu}_2\text{NiSnS}_4$ Heterojunction Solar Cell: A Comparative Study between Experimental Results and SCAPS–1D Simulation Modelling

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ABSTRACT: This study presents a comprehensive investigation of $\text{Cu}_2\text{NiSnS}_4$ (CNTS) thin films deposited on fluorine-doped tin oxide substrates through electrophoretic deposition followed by annealing at 350°C without additional sulfurization. The structural characteristics of the synthesized CNTS powder were thoroughly examined using X-ray diffraction and Raman spectroscopy, which collectively confirmed the formation of a pure cubic phase devoid of secondary impurities. Scanning electron microscopy revealed a uniform, densely packed surface morphology with distinctive nanosphere-like features, while UV-Vis spectroscopy demonstrated absorption coefficients exceeding 10^4 cm^{-1} and a direct optical band gap of approximately 1.7 eV, positioning the material favorably within the visible spectrum for photovoltaic applications. A heterojunction solar cell was subsequently fabricated by combining n-type TiO_2 nanoparticles with the optimized p-type CNTS absorber layer. To gain deeper insights into device behavior, experimental current-voltage characteristics were correlated with theoretical predictions using the SCAPS-1D simulation platform, enabling detailed analysis of band alignment, carrier recombination mechanisms, and performance-limiting factors. The TiO_2 layer effectively reduced surface reflectance, contributing to improved short-circuit current density and overall power conversion efficiency. The close agreement between experimental and simulated parameters, with deviations within 1 %, validates the accuracy of the developed model and highlights the critical role of optical transmission losses in determining device performance. The TiO_2/CNTS material system demonstrates considerable promise for the development of environmentally benign, cost-effective thin-film photovoltaic technologies utilizing earth-abundant constituents.

Keywords: Quaternary chalcogenides, Electrophoretic deposition, Kesterite solar cells, SCAPS-1D simulation, Heterojunction engineering, Optical transmission losses.

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1. INTRODUCTION

The global pursuit of sustainable energy solutions has placed tremendous emphasis on the development of photovoltaic

technologies that can deliver affordable electricity without exacerbating environmental degradation. While silicon-based solar cells continue to dominate the commercial market due to their mature manufacturing infrastructure and respectable efficiencies, the energy-intensive processing requirements and material purity demands have motivated researchers to explore alternative thin-film technologies. These alternative approaches promise reduced material consumption, lower processing temperatures, and compatibility with flexible substrates, though the incorporation of scarce or toxic elements such as cadmium,

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indium, gallium, and tellurium in many high-performance thin-film devices raises legitimate concerns regarding long-term sustainability and environmental safety [1]. Consequently, the search for absorber materials composed exclusively of earth-abundant and non-toxic elements has intensified considerably over the past decade.

Among the emerging candidates, quaternary chalcogenide compounds belonging to the $\text{I}_2\text{-II-IV-VI}_4$ family have attracted substantial research interest due to their favorable optoelectronic properties and compositional flexibility. Copper zinc tin sulfide, commonly referred to as CZTS, has been extensively investigated as a promising absorber material that replaces the toxic and scarce elements found in copper indium gallium selenide devices with more benign and abundant constituents [2]. However, despite significant efforts devoted to CZTS development, persistent challenges related to the formation of secondary phases, narrow phase stability windows, and antisite disorder arising from the similar ionic radii of copper and zinc have limited the achievable device efficiencies [3, 4]. These limitations have prompted researchers to explore chemical substitutions that might circumvent these fundamental materials issues while preserving the desirable optoelectronic characteristics.

The substitution of zinc with nickel in the kesterite lattice yields the quaternary compound copper nickel tin sulfide, $\text{Cu}_2\text{NiSnS}_4$ or CNTS, which has emerged as a particularly intriguing alternative. Nickel incorporation modifies the electronic structure relative to CZTS, potentially offering improved electrical properties and reduced propensity for cation disorder [3, 4]. CNTS intrinsically exhibits p-type conductivity, a direct band gap energy tunable between approximately 1.1 and 1.7 eV depending on synthesis conditions and stoichiometry, and an optical absorption coefficient exceeding 10^4 per centimeter across much of the visible spectrum [3, 5, 6]. These characteristics align remarkably well with the requirements for an ideal solar cell absorber layer, suggesting that CNTS warrants serious consideration for thin-film photovoltaic applications.

The synthesis of CNTS has been pursued through various deposition techniques, with most reported approaches relying on non-vacuum processing methods followed by high-temperature sulfurization treatments. Electrodeposition has been employed by several groups to produce CNTS thin films, typically requiring subsequent annealing in sulfur-containing atmospheres to achieve the desired phase purity and crystallinity [1, 3, 7]. Spray pyrolysis represents another accessible route that has demonstrated reasonable success in depositing CNTS layers, though sulfurization steps remain commonly incorporated [5]. Hydrothermal and solvothermal methods have proven effective for producing CNTS nanoparticles and powders with controlled morphologies, which can subsequently be dispersed and deposited as thin films [8, 9]. Solution-based approaches including dip coating, drop coating, and spin coating have also been explored, offering simplicity and scalability advantages [10, 11]. More sophisticated techniques such as hot injection have enabled the synthesis of monodisperse nanocrystals with well-defined

compositions [12, 13]. The sol-gel method has found particularly widespread application due to its straightforward control over deposition parameters, composition, and doping levels, combined with its suitability for large-area deposition and minimal environmental impact [14, 15].

Titanium dioxide, TiO_2 , has established itself as one of the most extensively studied n-type oxide semiconductors for photovoltaic applications. Its wide band gap of approximately 3.0 to 3.2 eV renders it transparent to most visible light, making it suitable as a window layer or electron transport material in various device architectures. The favorable conduction band alignment with numerous absorber materials, combined with excellent chemical stability, non-toxicity, and abundant availability, has positioned TiO_2 as a preferred choice for dye-sensitized solar cells, perovskite solar cells, and emerging chalcogenide-based heterojunctions. When employed as an electron transport layer in thin-film solar cells, TiO_2 facilitates selective extraction of photogenerated electrons while effectively blocking holes, thereby reducing recombination losses at the front contact interface. Its ability to suppress surface reflectance through appropriate texturing or nanostructuring provides additional optical benefits that can enhance the short-circuit current density of completed devices.

The combination of CNTS as a p-type absorber with TiO_2 as an n-type electron transport layer presents an attractive heterojunction configuration that leverages the respective strengths of both materials. The conduction band offset between these two semiconductors can be engineered to promote efficient charge separation while minimizing interfacial recombination, provided that the band alignment is appropriately characterized and optimized. Despite the apparent promise of this materials pairing, remarkably little research has been dedicated to the experimental realization of TiO_2/CNTS heterojunction solar cells. The existing literature on CNTS-based photovoltaic devices remains relatively sparse, and even fewer studies have attempted to integrate CNTS with TiO_2 in a functional device architecture. Furthermore, the vast majority of CNTS fabrication efforts have relied on post-deposition sulfurization treatments at elevated temperatures, which add complexity, energy consumption, and processing time while potentially introducing safety considerations associated with sulfur vapor or hydrogen sulfide gas.

The novelty of the present work resides in several distinctive aspects that collectively differentiate it from previously reported studies. This investigation demonstrates for the first time the successful preparation of CNTS thin films on TiO_2 -coated substrates using electrophoretic deposition followed by annealing at 350 °C without any sulfurization step, representing a significant simplification of the conventional processing pathway. The electrophoretic deposition method offers particular advantages for depositing nanomaterials onto various substrates, enabling uniform coating thickness and controlled film morphology through adjustment of deposition parameters. Additionally, this work establishes a direct correlation between experimental device

performance and theoretical predictions generated through SCAPS-1D simulation, providing quantitative insights into the factors limiting efficiency and guiding rational approaches to device optimization. The combination of a sulfurization-free fabrication route, the specific TiO_2/CNTS materials pairing, and the integrated experimental-simulation methodology represents an original contribution to the field that addresses gaps in the current understanding of this promising heterojunction system.

In the present work, we report the solvothermal synthesis of CNTS powder followed by comprehensive materials characterization to establish structural, compositional, morphological, and optical properties. The optimized CNTS material is subsequently deposited as thin films onto TiO_2 -coated FTO substrates using electrophoretic deposition, and complete heterojunction devices are fabricated with silver contacts. Experimental current-voltage characteristics are measured under simulated solar illumination and compared directly with SCAPS-1D simulations to validate the device model and identify performance limitations. Through this combined experimental and computational approach, we aim to establish a foundation for the continued development of TiO_2/CNTS heterojunction solar cells and to provide guidance for future efficiency improvements through targeted optimization of material properties and device architecture.

2. EXPERIMENTAL DETAILS

2.1. Chemicals and materials

The synthesis of $\text{Cu}_2\text{NiSnS}_4$ powder was carried out using precursor materials obtained from Sigma-Aldrich, India, and employed without additional purification processes. Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) with stated purity of 99 % served as the copper source, while nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) of identical purity provided the nickel constituent. Tin tetrachloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) with 98 % purity was utilized as the tin precursor, and thiourea (NH_2CSNH_2) with 99 % purity functioned as the sulfur source. Polyvinylpyrrolidone (PVP-K30) was incorporated as a surface capping agent to influence nucleation and growth behavior during synthesis. Ethylene glycol of analytical grade served as the solvent medium for all reactions.

2.2. Synthesis of $\text{Cu}_2\text{NiSnS}_4$ powder

The solvothermal synthesis procedure commenced with the dissolution of copper chloride dihydrate in 60 mL of ethylene glycol under continuous magnetic stirring. A concentration of 0.2 M was established for the copper precursor, and stirring was maintained for approximately 30 min to ensure complete dissolution. Following this initial step, nickel chloride hexahydrate was introduced to achieve a concentration of

0.1M, and stirring continued for another 30 min until the solution became homogeneous. Tin tetrachloride pentahydrate was subsequently added to reach 0.1 M concentration, again followed by 30 min of stirring to ensure complete mixing. Finally, thiourea was incorporated at 0.4 M concentration, and the stirring was maintained for an additional 30 min. The sequential addition approach ensured that each precursor dissolved completely before the next was introduced, promoting molecular-level mixing and minimizing the formation of undesirable intermediate phases.

After all precursors had been dissolved, the resulting mixture, which exhibited a characteristic pale green coloration, was subjected to continued stirring for a period of 5 h to achieve complete homogenization. The homogeneous solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave vessel. The autoclave was sealed tightly to prevent any contamination or solvent loss during the subsequent thermal treatment and placed within a furnace pre-programmed to maintain a temperature of 180°C . The reaction was allowed to proceed under autogenous pressure for 24 h, during which time the solvothermal conditions facilitated the formation of the quaternary chalcogenide phase.

Upon completion of the reaction period, the autoclave was allowed to cool naturally to ambient temperature. The resulting black precipitate was collected and subjected to a rigorous purification procedure involving multiple washing cycles with absolute ethanol. Each washing cycle consisted of dispersion of the precipitate in ethanol followed by filtration to separate the solid product from the liquid phase containing dissolved impurities and reaction byproducts. This process was repeated several times until the filtrate appeared clear and colorless, indicating effective removal of residual organic species and unreacted precursors. The purified precipitate was subsequently transferred to a hot air oven and dried at temperatures ranging between 70 and 80°C for a duration of 5 to 6 hours. The dried powder was labeled as CNTS and stored in desiccators prior to characterization and subsequent thin film deposition.

2.3. Characterization techniques

The crystalline structure of the synthesized CNTS powder was investigated using X-ray diffraction measurements performed on a Bruker D8 Advance diffractometer operating with $\text{Cu-K}\alpha$ radiation at a wavelength of $1.54\text{ \AA}$. Diffraction patterns were recorded across an angular 2θ range of 20 to 80° to capture the primary reflections of the expected phase. Complementary structural analysis was conducted using Raman spectroscopy on a Renishaw In Via microscope equipped with a 532 nm excitation laser source, enabling identification of vibrational modes characteristic of the CNTS phase and detection of potential secondary phases.

Optical properties were evaluated through UV-Vis-NIR spectrophotometry using a JASCO V-670 instrument. Absorption and transmission spectra were recorded across the wavelength range of 200 to 1000 nm , providing data for

subsequent determination of the optical band gap via Tauc plot analysis. Surface morphological features were examined using scanning electron microscopy on a JEOL JSM-6360-LA instrument, while elemental composition and stoichiometry were assessed through energy dispersive X-ray spectroscopy performed in conjunction with the SEM observations.

For device characterization, current density-voltage measurements were conducted on completed solar cells using a solar simulator equipped with a xenon arc lamp providing illumination approximating the AM 1.5G spectrum at an intensity of 100 mW per square centimeter. Electrical data were acquired using a Keithley 2450 source measurement unit, enabling determination of open-circuit voltage, short-circuit current density, fill factor, and power conversion efficiency under both dark and illuminated conditions.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction analysis

The structural characteristics of the synthesized $\text{Cu}_2\text{NiSnS}_4$ powder were investigated through X-ray diffraction measurements, with the recorded pattern presented in Figure 1 across an angular 2θ range of 20 to 80° . The diffraction pattern revealed distinct peaks positioned at 28.47° , 33.02° , 36.98° , 47.35° , and 58.48° , which correspond respectively to the (111), (200), (202), (220), and (311) crystallographic planes of the cubic phase. Systematic comparison with the standard reference data from JCPDS card number 26-0552 confirmed excellent agreement, establishing that the synthesized material crystallizes in the cubic crystal system characterized by the space group $F\bar{4}3m$. This crystallographic assignment carries particular significance because the cubic phase of CNTS is known to exhibit favorable optoelectronic properties for photovoltaic applications.

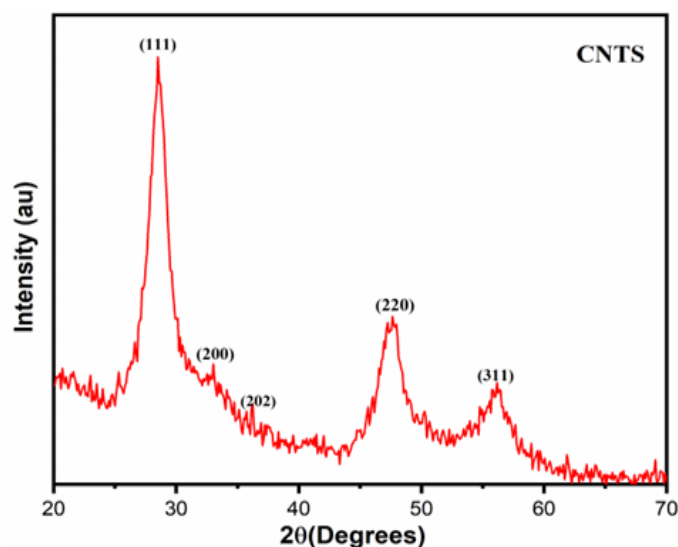


Fig. 1. X-ray diffraction of CNTS powder.

A critical observation from the diffraction pattern concerns the complete absence of reflections attributable to potential impurity phases that commonly plague the synthesis of quaternary chalcogenides. No peaks corresponding to binary sulfides such as NiS, ternary compounds including Cu_2SnS_4 or Cu_2NiS_4 , or related copper tin sulfide phases were detected within the detection limits of the diffractometer. This phase purity represents an important achievement because secondary phases, even when present in relatively small quantities, can introduce deleterious recombination centers and parasitic conduction pathways that severely compromise photovoltaic device performance. The successful avoidance of such impurities underscores the efficacy of the solvothermal synthesis approach combined with the carefully optimized reaction conditions.

The average crystallite size of the synthesized CNTS powder was estimated using the Scherrer formula applied to the full width at half maximum of the most intense diffraction peaks. This calculation yielded an average crystallite dimension of approximately 3.12 nm, indicating that the material is composed of nanocrystalline domains. Such nanoscale crystallinity may have implications for both the optical and electrical properties of the material, potentially influencing carrier transport mechanisms and recombination dynamics within completed devices. The nanocrystalline nature was further corroborated by the moderate broadening observed in the diffraction peaks, which arises from the finite coherence length of the X-ray scattering domains.

Precise determination of the lattice parameters was accomplished through refinement of the peak positions, yielding values of a equals 5.43 Å and c equals 10.77 Å. These experimental values were compared against the standard reference data from JCPDS card 26-0552, which lists an a equal to 5.45 Å and c equal to 10.73 Å. The calculated lattice parameters deviate from the standard values by less than 0.5%, confirming that the synthesized material possesses lattice dimensions very close to those expected for stoichiometric CNTS. The distortion coefficient, defined as the ratio c divided by twice a , was calculated to be 0.99, which compares favorably with the standard value of 0.98 derived from the reference data. This parameter provides insight into the tetragonal distortion of the cubic lattice and its near-unity value suggests minimal deviation from ideal cubic symmetry. The slight discrepancies between experimental and standard lattice parameters can reasonably be attributed to differences in synthesis methodology, with the solvothermal approach employed in this work potentially yielding slight variations in cation ordering or defect chemistry compared to materials produced through alternative routes.

3.2. Raman spectroscopy analysis

While X-ray diffraction provides essential information regarding long-range crystallographic order, Raman spectroscopy offers complementary insights into the local structural environment and vibrational characteristics of the

material, making it particularly valuable for detecting secondary phases that may escape detection by diffraction methods due to nanocrystalline dimensions or low volume fractions. The Raman spectrum of the synthesized CNTS powder, presented in Figure 2, was recorded using an excitation wavelength of 532 nm across the spectral range from 150 to 450 cm^{-1} . The spectrum exhibits a strong band extending across this entire range, with two particularly prominent features observed at approximately 273 cm^{-1} and 312.33 cm^{-1} . This spectral signature aligns remarkably well with previously reported Raman data for CNTS materials [16]. The dominant peak at 312.33 cm^{-1} is assigned to the A_1 vibrational mode, which corresponds to the symmetric breathing vibration of sulfur atoms coordinated by the four metal species copper, nickel, and tin within the crystal lattice [17]. This mode is characteristic of the kesterite-type structure and its presence provides strong confirmation that the intended quaternary phase has indeed formed.

The spectral region between 150 and 450 cm^{-1} encompasses the primary vibrational features expected for CNTS, and the absence of additional peaks outside this region or shoulders on the main bands suggests phase purity. A thorough examination of the spectrum reveals no evidence of Raman features corresponding to common secondary phases that could potentially coexist with CNTS. Specifically, peaks that would indicate the presence of SnS_2 , which exhibits characteristic vibrations at 205 and 312 cm^{-1} , were not observed. Similarly, SnS with its multiple Raman peaks at 94, 160, 185, and 214 cm^{-1} was absent. Copper sulfide phases including Cu_2S , which displays features at 410, 267, and 475 cm^{-1} , and CuS with a peak at 475 cm^{-1} were not detected. Nickel-containing impurities such as NiS with its characteristic peaks at 143, 240, 299, 345, and 371 cm^{-1} , NiO at 472.5 cm^{-1} , elemental nickel at 256 cm^{-1} , and the ternary CuNiSn phase at 580 cm^{-1} were all absent from the recorded spectrum [18].

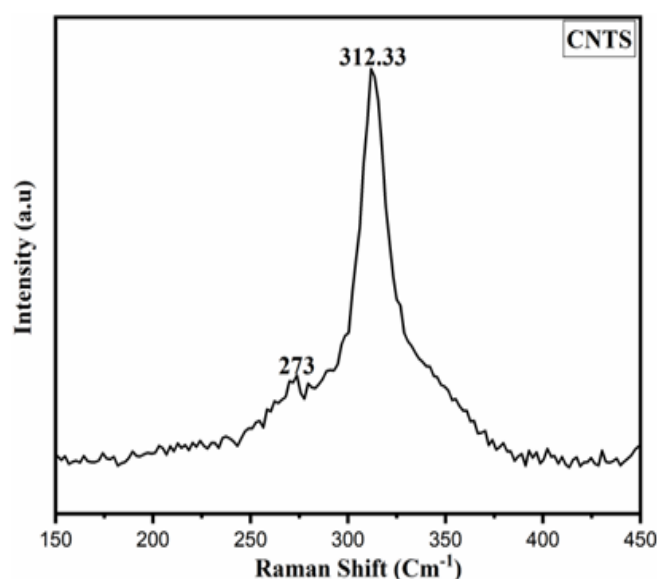


Fig. 2. Raman spectra of CNTS powder.

The absence of Cu_2SnS_3 , which would manifest Raman peaks at 290 and 336 cm^{-1} , is particularly noteworthy given the compositional proximity between this ternary compound and the target quaternary phase. The successful avoidance of Cu_2SnS_3 formation indicates that the reaction conditions, including the precursor ratios, temperature, and duration, were appropriately selected to favor the formation of the desired quaternary phase over competing ternary compounds. The broad nature of the observed Raman peaks is consistent with the nanocrystalline dimensions revealed by X-ray diffraction, as phonon confinement effects in nanoscale crystallites typically produce peak broadening compared to bulk crystalline materials. The combined evidence from X-ray diffraction and Raman spectroscopy provides compelling confirmation that the solvothermal synthesis route yielded phase-pure cubic CNTS without detectable contamination by binary or ternary secondary phases. This establishes a solid foundation for subsequent optical and device characterization, as the observed properties can be attributed confidently to the CNTS phase rather than to unintended impurity contributions.

3.3. Surface morphology and elemental compositions

The morphological characteristics of the synthesized CNTS powder were examined through scanning electron microscopy, with representative images presented in Figure 3. These micrographs reveal that the material exhibits a distinctive nanosphere-like morphology, with spherical assemblies distributed across the imaged area. The observed morphology reflects the influence of polyvinylpyrrolidone incorporated during synthesis as a surface capping agent. PVP molecules adsorb preferentially onto specific crystallographic facets during nucleation and growth, modifying the surface energies and thereby directing the evolution of crystal habit toward the observed spherical morphology.

Each nanosphere assembly appears to comprise multiple constituent flakes or platelets that radiate outward from central nucleation points, creating a hierarchical structure with considerable surface area. Higher magnification imaging reveals that these spheres possess typical dimensions of approximately one to two μm in overall diameter, with individual constituent features exhibiting thicknesses on the order of 50 nm. This morphology may offer advantages for photovoltaic applications, as the nanoscale features could potentially enhance light trapping through scattering effects while the interconnected network of grains could facilitate charge carrier transport if appropriately oriented. The formation of such uniform spherical assemblies can be attributed to the adsorption of PVP molecules on specific surface sites during crystal growth. By occupying these sites, PVP restricts continued growth in directions perpendicular to the adsorbed facets while allowing growth to proceed along unblocked crystallographic directions. This selective passivation mechanism promotes the development of the observed radial morphology rather than the formation of large, featureless crystallites.

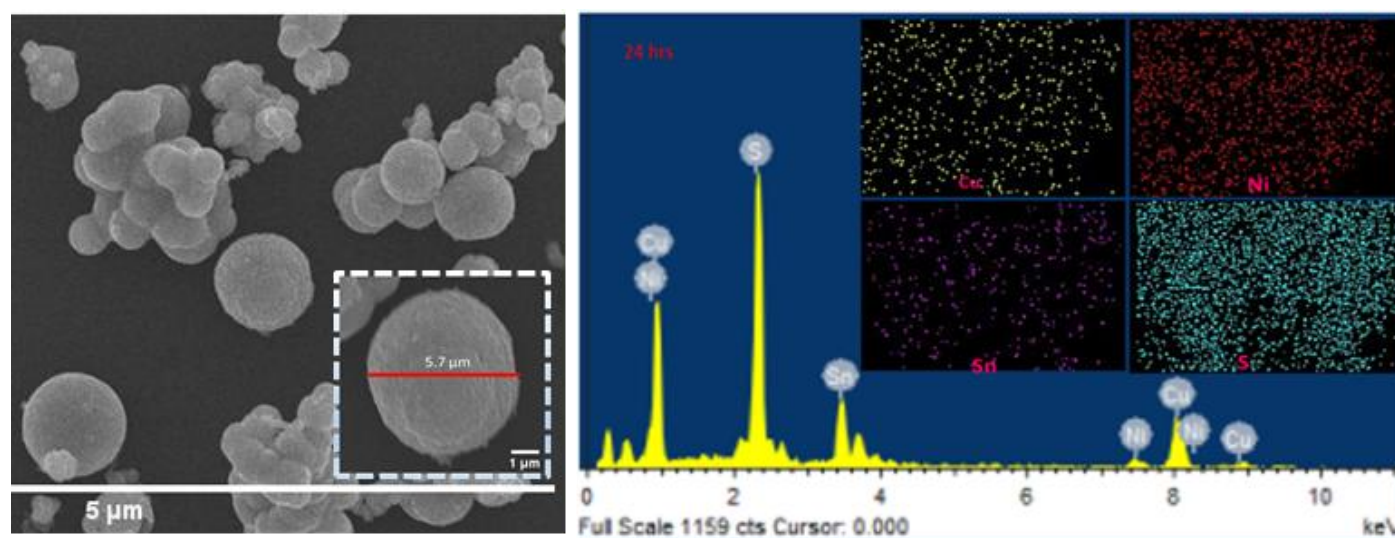


Fig. 3. SEM and EDS images of CNTS powder.

The uniformity of the sphere dimensions suggests that nucleation occurred within a relatively narrow time window followed by controlled growth under consistent conditions throughout the reaction duration.

Energy dispersive X-ray spectroscopy was employed to determine the elemental composition of the synthesized CNTS powder, with the results presented in Figure 3 along with corresponding elemental mapping images. The quantitative analysis yielded atomic percentages of 25.52 % for copper, 12.40 % for nickel, 13.23 % for tin, and 48.84 % for sulfur. These values correspond to elemental ratios normalized to the nickel content, giving copper to nickel ratio of approximately 2.06, Sn to Ni ratio of approximately 1.07, and sulfur to metal ratio of approximately 0.96 when considering the total metal content.

The experimentally determined composition closely approaches the ideal stoichiometric ratio of 2:1:1:4 for copper, nickel, tin, and sulfur respectively. The slight deviation from perfect stoichiometry falls within the typical uncertainty range for EDS quantification and may reflect minor compositional inhomogeneities or surface effects rather than genuine bulk off-stoichiometry. The near-ideal composition confirms that the precursor concentrations and reaction conditions were appropriately selected to achieve the desired product stoichiometry.

Elemental mapping images displayed as insets in Figure 3 reveal the spatial distribution of each constituent element within the imaged region. Copper is represented by yellow coloration, nickel by red, tin by purple, and sulfur by blue. The uniform distribution of all four elements across the mapped area, without evidence of segregation or phase separation, provides additional confirmation of compositional homogeneity. This homogeneous element distribution is essential for achieving consistent optoelectronic properties throughout the absorber layer and minimizing localized variations in band gap or carrier concentration that could adversely affect device performance.

The reaction duration of 24 h proved sufficient to drive the precursor materials to complete conversion while allowing adequate time for nucleation and crystal growth to proceed to the observed morphology. Shorter durations might yield incomplete reaction or poorly crystallized products, while substantially longer durations could promote excessive grain growth or secondary phase formation. The 24 h period thus represents an appropriate balance among these competing considerations.

3.4. Optical analysis

The optical properties of the synthesized CNTS powder were investigated through UV-Vis-NIR absorption spectroscopy, with the recorded absorption spectrum presented in Figure 4 across the wavelength range from 200 to 1000 nm. The spectrum reveals strong optical absorption across the ultraviolet and visible regions, with absorption extending as a tail into the near-infrared portion of the spectrum. This broad absorption characteristic is desirable for photovoltaic absorber materials, as it enables harvesting of a substantial portion of the solar spectrum.

The absorption coefficient was calculated from the measured absorbance and film thickness, yielding values exceeding $10^4/\text{cm}$ across much of the visible range. Such high absorption coefficients are typical of direct band gap semiconductors and indicate that relatively thin absorber layers of approximately one to two μm thickness are sufficient to capture most incident photons with energies above the band gap. This characteristic supports the development of thin-film devices with reduced material consumption and relaxed minority carrier diffusion length requirements compared to indirect band gap materials.

Quantitative determination of the optical band gap was accomplished through construction of a Tauc plot, shown as the inset in Figure 4, in which the quantity $(\alpha h\nu)^2$ is plotted

against photon energy $h\nu$. This representation is appropriate for materials exhibiting direct allowed optical transitions, as predicted for CNTS based on its electronic band structure. The linear region of the Tauc plot was extrapolated to intersect the energy axis, yielding an optical band gap of approximately 1.7 eV. This value falls within the range of 1.4 to 1.82 eV reported in the literature for CNTS materials synthesized through various routes [16, 19–25] and is consistent with the direct band gap nature of the compound.

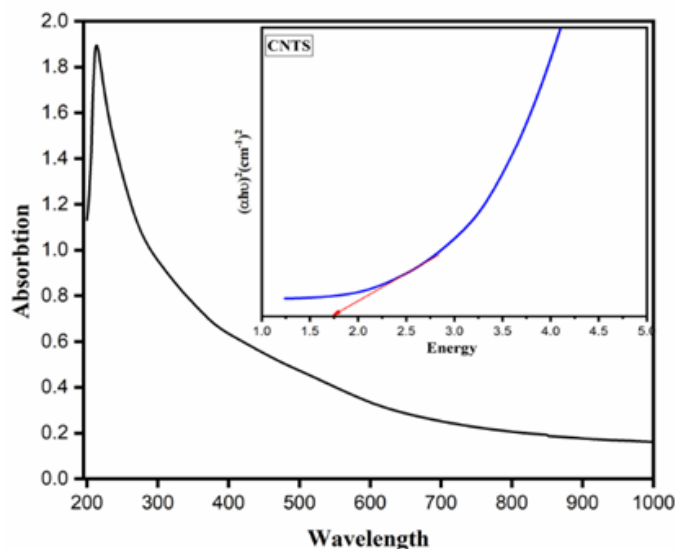


Fig. 4. UV–Vis–Spectra of CNTS Powder.

The band gap energy of 1.7 eV positions CNTS favorably relative to the optimal range for single-junction solar cells under the AM 1.5G spectrum, which theoretical calculations place near 1.4 eV. While slightly above the theoretical optimum, this band gap remains suitable for photovoltaic applications and could be tuned through compositional adjustments or alloying strategies in future work. The direct nature of the band gap ensures strong optical absorption near the band edge, which is advantageous for thin-film device architectures [26–28].

The enhanced visible region absorption observed in the synthesized material can be attributed to its high crystalline volume fraction and the well-defined grain morphology revealed by electron microscopy. Defects and disordered regions typically contribute to sub-band gap absorption without generating photocurrent, so the high crystalline quality implied by the sharp absorption onset and well-defined Tauc plot linear region suggests that such parasitic absorption is minimized.

3.5. Photoelectrochemical analysis

The photovoltaic performance of the fabricated TiO_2/CNTS heterojunction device was evaluated through current density-voltage measurements under both dark and illuminated conditions. The device structure comprised fluorine-doped

tin oxide coated glass as the transparent conductive substrate, a layer of TiO_2 nanoparticles deposited and annealed to form the n-type electron transport layer, a CNTS thin film deposited by electrophoretic deposition as the p-type absorber, and silver contacts applied to complete the device [29–33]. The source region is used to find the J_{sc} , V_{oc} , FF, and PCE of the cell. The fill factor (FF) and efficiency was calculated according to the below equations (Eq. 1 and 2). The FF is calculated using the following equation:

$$FF = \frac{(V_m * J_m)}{(V_{oc} * J_{sc})} \quad (1)$$

The device efficiency is calculated using the following equation:

$$\eta = \frac{V_{oc} * J_{sc} * FF}{P_{in}} * 100\% \quad (2)$$

The illuminated measurements were conducted under simulated AM 1.5G solar irradiation at an intensity of 100 mW/cm^2 .

Figure 5 presents the current density-voltage response comparing dark and illuminated conditions, clearly demonstrating the photovoltaic behavior of the junction. Under illumination, the current density increases substantially compared to the dark condition, confirming that photogenerated carriers are successfully separated and collected by the respective contacts. The rectifying behavior evident in the dark current confirms the formation of a p - n heterojunction between the TiO_2 and CNTS layers [34–36].

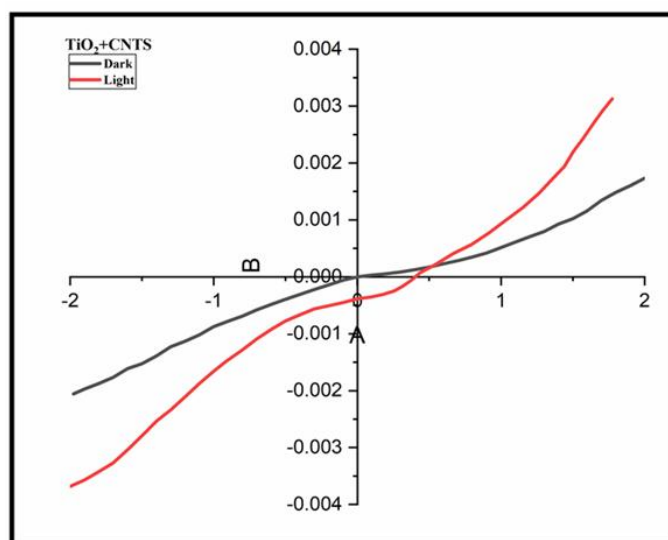


Fig. 5. Current density-voltage response of CNTS.

The fourth quadrant of the illuminated J-V characteristic, magnified and presented in Figure 6(a), provides the parameters necessary for quantitative performance assessment. The short-circuit current density J_{sc} was determined to be 0.387 mA/cm^2 , while the open-circuit voltage V_{oc} reached to 0.401 V.

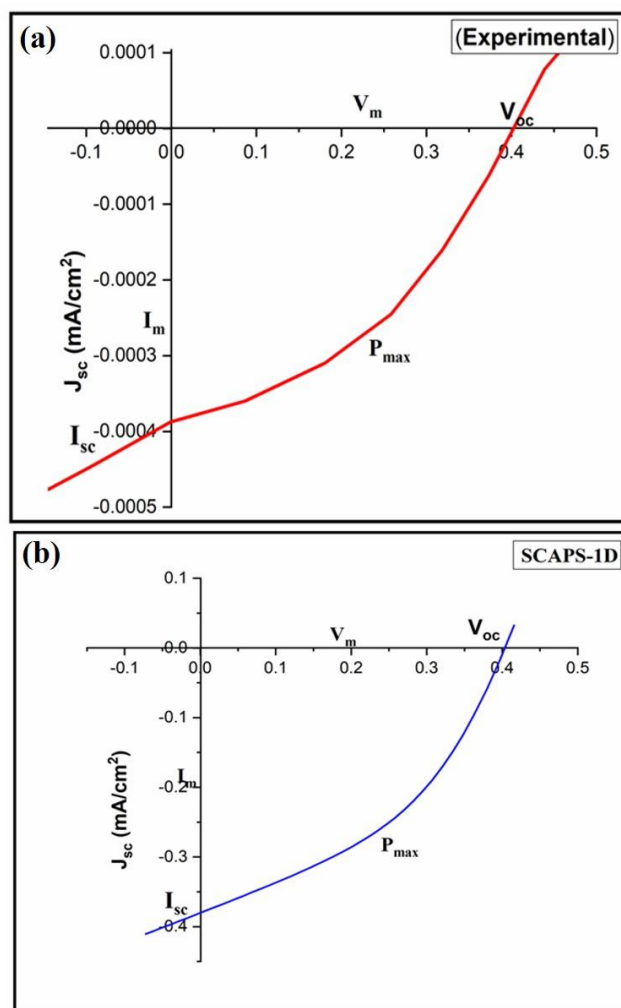


Fig. 6. Current-voltage (J-V) response, (a) Experimental, and (b) SCAPS-1D.

The maximum power point occurred at a voltage V_m of 0.228 V and a current density J_m of 0.271 mA/cm². From these values, the fill factor was calculated using equation (1) as 39.75 %. The power conversion efficiency was then determined using equation (2), yielding a value of 0.061 %.

The modest efficiency reflects the early stage of development for this particular materials combination and device architecture. Several factors likely contribute to the limited performance. The relatively low short-circuit current density suggests incomplete collection of photogenerated carriers, which may arise from recombination losses within the absorber bulk or at the heterojunction interface [37, 38]. The open-circuit voltage, while reasonable for a wide band gap absorber, indicates that interface recombination and possibly unfavorable band alignment limit the achievable voltage. The fill factor, below 40 %, points to series resistance effects and possibly shunting pathways that reduce the squareness of the J-V characteristic.

The SCAPS-1D simulation results, presented in Figure 6(b), were generated using the physical parameters listed in Table 1. These parameters were adopted primarily from experimental measurements where available, supplemented by literature values for properties not directly accessible experimentally. The simulation employed the AM 1.5G spectrum as the illumination source, an operating temperature of 300 K, series resistance of 175 Ω cm², shunt resistance of 3000 Ω cm², and an optical transmission factor of 45 %. Similarly, the changes in series and shunt resistances are optimized with the experimental values of V_{oc} and J_{sc} are given in Table 2. This transmission factor accounts for optical losses including reflectance from the device surface, shadowing by the contact metallization, and parasitic absorption within layers that do not contribute to photocurrent generation.

Table 1. The physical parameters of CNTS and TiO₂.

Parameters	TiO ₂ (n-type)	Cu ₂ NiSnS ₄ (p-type)
Thickness (μ m)	0.010	10
Bandgap (eV)	3.200	1.7
Electron affinity (χ) (eV)	4.260	3.870
Dielectric permittivity (Relative)	10	9
CB effective DOS (1/cm ³)	2.2*10 ¹⁸	2.2*10 ¹⁹
VB effective DOS (cm ⁻³)	1.8*10 ¹⁹	1.8*10 ¹⁸
Electron thermal velocity (cm/s)	1.0*10 ⁷	1.0*10 ⁷
Hole thermal velocity (cm/s)	1.0 x 10 ⁷	1.0 x 10 ⁷
Electron mobility (cm ² /s)	2 x 10 ⁴	1.1 x 10 ¹
Hole mobility cm ²	1 x 10 ³	1.01 x 10 ¹
Donor density (ND) (cm ⁻³)	6 x 10 ¹⁹	0.000
Acceptor density (NA) (cm ⁻³)	0.000	1.00 x 10 ¹⁷
Temp (K)	300	
Series resistances (Ω cm ²)	1.75 x 10 ²	
Shunt Resistance (Ω cm ²)	3 x 10 ³	
Transmission	45%	

Table 2. Cell parameters, experimental and SCAPS-1D values.

Cell parameters	Experimental values	SCAPS-1D values
V_{oc}	0.4029	0.4037
J_{sc}	0.3872	0.3802
V_m	0.2283	0.2572
J_m	0.2707	0.2443

4. CONCLUSIONS

The solvothermal synthesis route employed in this work successfully produced phase-pure $\text{Cu}_2\text{NiSnS}_4$ powder with crystallographic characteristics matching the cubic stannite structure, as confirmed by X-ray diffraction analysis. The absence of detectable impurity peaks in both diffraction patterns and Raman spectra demonstrates that the synthetic approach effectively suppresses the formation of binary and ternary secondary phases that commonly plague quaternary chalcogenide preparation. Polyvinylpyrrolidone incorporation during synthesis proved instrumental in directing nucleation and growth toward an organized nanosphere-like morphology, while energy-dispersive X-ray spectroscopy confirmed elemental composition closely approximating the ideal 2:1:1:4 stoichiometric ratio. Optical characterization established a direct band gap of approximately 1.7 eV with absorption coefficients exceeding $10^4/\text{cm}$ across the visible spectrum, confirming the suitability of CNTS as a photovoltaic absorber material. The fabricated TiO_2/CNTS heterojunction device exhibited clear photovoltaic behavior with measurable open-circuit voltage and short-circuit current density, though the overall power conversion efficiency of 0.061 % remains modest at this early stage of development. SCAPS-1D simulation generated current-voltage characteristics that agreed remarkably closely with experimental measurements, with deviations below 1 % for key performance parameters, thereby validating the accuracy of the physical parameters employed in the device model. The necessity of adjusting the transmission factor to approximately 45% within the simulation to achieve matching between experimental and theoretical maximum power point values revealed that optical losses including surface reflectance, contact shadowing, and parasitic absorption collectively reduce the effective photon flux reaching the absorber to less than half of incident solar radiation. These losses represent substantial opportunities for performance enhancement through antireflection coatings, optimized contact grid design, and improved layer transparency. The TiO_2/CNTS material system, combining non-toxic and earth-abundant constituents, offers a compelling platform for continued development, and the validated simulation model established through this work provides a valuable tool for guiding rational optimization efforts toward meaningful efficiency improvements in subsequent device iterations.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

Availability of data and material

The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

All authors contributed equally to this work.

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