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Enhanced charge separation at the interface of Cu_2O/CuSCN composite thin films synthesized by electrodeposition technique

This study focuses on the synthesis and characterization of hole transport layers (HTLs) for solar cells, particularly copper(I) thiocyanate (CuSCN) and cuprous oxide (Cu_2O), synthesized via electrodeposition techniques. CuSCN and Cu_2O offer promising properties for efficient charge transport in photovoltaic devices. The synthesis processes involve precise control of deposition parameters to achieve desired film morphologies and properties. Characterization techniques including scanning electron microscopy (SEM), atomic force microscopy (AFM), and ultraviolet-visible (UV-Vis) spectroscopy provide insights into film morphology and optical properties. Optimization of synthesis parameters for Cu_2O films is explored to enhance their electrical properties. Photoelectric response measurements indicate improved charge separation at the interface of Cu_2O/CuSCN composite films. These findings can contribute to the advancement of solar cell technology. Furthermore, the study extends its exploration to the fabrication of Cu_2O by electrodeposition at different pH levels. SEM and X-ray diffraction (XRD) analyses reveal the impact of deposition parameters on film morphology and crystal structure, providing valuable insights for tailored synthesis approaches. Overall, this comprehensive study not only advances the understanding of HTL materials synthesis and optimization but also provides valuable guidance for the development of high-efficiency and stable solar cell devices.

Keywords: solar cells; hole transport layers; electrodeposition; copper(I) thiocyanate; cuprous oxide; optimal synthesis conditions; photoelectric response, chare transport.

Introduction

Solar energy stands at the forefront of sustainable energy solutions, offering a clean and renewable alternative to conventional fossil fuels. At the heart of solar energy conversion lie solar cells, devices tasked with harnessing sunlight and converting it into electrical energy. The efficiency and effectiveness of these solar cells hinge on the intricate interplay of various materials within their structures. Among these materials, hole transport layers (HTLs) play a crucial role in facilitating the efficient extraction and transportation of positive charge carriers generated during the photovoltaic process [1].

In recent years, significant research efforts have been dedicated to the development and optimization of HTL materials for solar cell applications. Among the promising candidates in this domain are copper(I) thiocyanate (CuSCN) and cuprous oxide (Cu_2O), both of which exhibit favorable properties for efficient charge transport. CuSCN, a well-known semiconductor for photovoltaic applications, boasts suitable optical properties and native p-type conductivity. Meanwhile, Cu_2O, with its p-type semiconducting properties and direct band gap, presents another attractive option for HTL materials [2, 3].

This study focuses on the synthesis and characterization of CuSCN and Cu_2O thin films as HTLs for solar cells, employing electrodeposition techniques for precise control over their properties. Electrodeposition offers advantages in terms of scalability, cost-effectiveness, and the ability to tailor material properties by adjusting deposition parameters. By meticulously controlling deposition conditions, such as precursor solution composition, deposition potential, and temperature, the study aims to optimize the morphological and electrical properties of the synthesized films.

The experimental part of the study delves into detailed synthesis procedures for CuSCN and Cu_2O films, elucidating the intricacies of electrodeposition techniques employed to achieve desired film morphologies and properties. Characterization techniques, including scanning electron microscopy (SEM), four point probe and photoelectric response (PEC) provide valuable insights into the surface morphology, crystal structure and electrical and charge transfer properties of the synthesized films. Furthermore, the study explores variations in synthesis conditions for Cu_2O films, investigating the influence of parameters such pH on film morphology and electrical properties. Through systematic variation of these parameters, the study aims to elucidate optimal conditions for achieving low resistivity and enhanced charge transport capabilities in Cu_2O films combined with CuSCN films [4].

Methods

To obtain high-quality thin films with minimal impurities, high-purity chemicals purchased from Sigma-Aldrich were utilized. The following high-grade chemicals were employed in this work: Copper(II) sulfate (anhydrous, powder, ≥99.99 % trace metals basis), Ethylenediaminetetraacetic acid (OmniPur® Grade, ≥99.5 %), Potassium thiocyanate (ReagentPlus®, ≥99.0 %), Diethanolamine (BioUltra, ≥99.5 % (GC)), Lactic acid (ACS reagent, ≥85 %), and Sodium hydroxide (ACS reagent, ≥97.0 %, pellets). To prepare the aqueous solutions, deionized water with a resistivity of 18.2 MΩ.cm, purified using a Water Purification System (Drawell Scientific, Smart-Q30UT), was used. The use of these high-grade chemicals helps to minimize impurities in the synthesized thin films, ensuring superior quality.

CuSCN thin films were synthesized by using electrochemical deposition on FTO covered glass substrates. Prior to deposition, FTO substrates were cleaned with ultrasonic in 2 % Hellmanex solution (10 min), deionized water (10 min), 2-propanol (10 min), and dried by a nitrogen flow. Then clean substrates were treated by UV irradiation in order to remove any organic residuals. CuSCN-E is prepared by electrodeposition in aqueous solution containing 12 mM $CuSO_4$ and equivalent amount of EDTA (Ethylenediaminetetraacetic acid) and KSCN (Potassium thiocyanate) whereas CuSCN-D is fabricated in aqueous solution containing 15 mM $CuSO_4$, 67.5 mM DEA (Diethanolamine), and 45 mM KSCN. EDTA and DEA were added before adding KSCN to prevent $Cu(SCN)_2$ precipitate formation. The pH of EDTA-contained precursor solution and DEA-contained precursor solution are 1.6 and 8.2, respectively. A standard three-electrode configuration was used for electrochemical deposition with Pt counter electrode and Ag/AgCl/sat. KCl reference electrode. All films were prepared using chronoamperometry technique with various duration. The deposition potentials of CuSCN-E and CuSCN-D respectively are –0.3 V and −0.45 V versus reference electrode [5, 6].

The electrochemical deposition of Cu_2O films was carried out in an electrolyte solution consisting of 0.4 M cupric sulfate and 3 M lactic acid. By complexing with lactate ion, the copper is stabilized and the pH can be raised to alkaline values. The pH of the bath solution was adjusted in the range of 10–12 by the addition of NaOH. The solution temperature was held constant during deposition by a hot plate with thermoregulator. Deposition temperature was 30 °C. Films were electrochemically deposited onto ITO (indium tin oxide) substrates, which were placed in solution with a Pt counter electrode and a silver chloride reference electrode (SCE). All potentials are reported versus the SCE reference electrode. Electrochemical deposition was controlled by a potentiostat (CS300, Corrtest Instrument).

The surface morphology of thin films was studied by a scanning electron microscopy (MIRA 3 LMU and Carl Zeiss Crossbeam 540 with GEMINI II). The XRD spectra were probed by Rigaku SmartLab X-ray diffractometer. The surface resistivity was measured by Four-Point Probe Unit (Ossila). PEC was measured by potentiostat (CS300, Corrtest Instrument) and chopped light was supported by Ossila Solar Simulator.

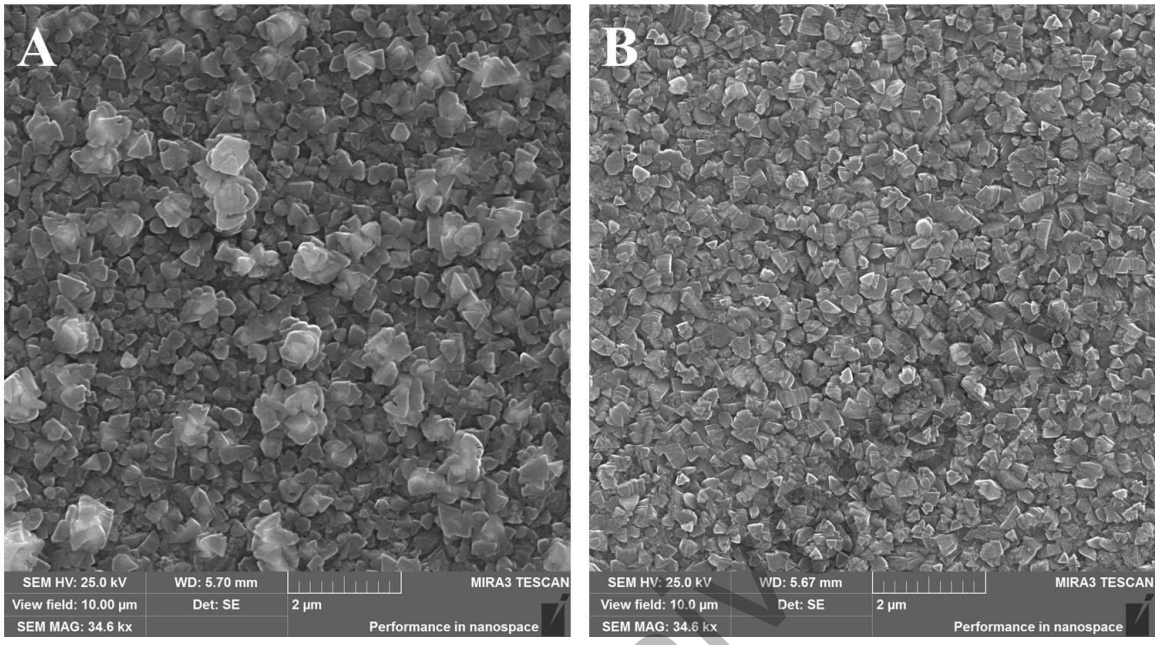
Results and discussion

One of the promising inorganic semiconductors suitable for application in photovoltaics as a hole transport material is copper thiocyanate (CuSCN). CuSCN is a well-known semiconductor for photovoltaic application due to its suitable optical properties and charge transport properties. CuSCN has a high transparency in visible spectrum and have been reported to show native *p*-type conductivity. A benefit of utilizing CuSCN in device applications is that it is non-toxic and its constituents are available in abundance in Earth.

In Figure 1, we present scanning electron microscope (SEM) images depicting the synthesized CuSCN-E and CuSCN-D thin films. Upon examination of these images, a distinct disparity in surface morphology between the two variants becomes evident. Both films exhibit a dense and uniform structure, indicative of a well-controlled synthesis process. However, CuSCN-E demonstrates a notably smoother surface texture, characterized by a relatively even distribution of material across the substrate. The average grain size of the CuSCN-E film, calculated from SEM images, was found to be 2.3 μm. In contrast, CuSCN-D film is not uniform and displays clusters or agglomerates of CuSCN nanocrystals, resulting in a rougher appearance. The average size of the grains in CuSCN-D were estimated to be 4.8 μm. Despite the surface texture differences, analysis reveals that both types of films possess irregular shapes prevalent in the grain structure of each film. This irregularity suggests inherent complexities in the crystallization process, likely influenced by various synthesis parameters.

The observed smoother surface of the CuSCN-E film holds particular significance in the context of its application as a hole transport layer (HTL) in solar cells. The uniformity and smoothness of this film are de-

sirable traits for facilitating efficient charge transport within the device. In contrast, the presence of agglomerates in the CuSCN-D film may introduce discontinuities or barriers to charge flow, potentially compromising device performance. In furthering our study, CuSCN-E films were used as one of the components for fabricating CuSCN/Cu2O composite films.



A — CuSCN-D film and *B* — CuSCN-E film

Figure 1. SEM images of synthesized CuSCN films

Cuprous oxide (Cu_2O) thin films are synthesized by using various techniques, and as a result, the physical and chemical properties are strongly dependent on the synthesis method. Here, we report results of synthesis of Cu_2O by electrodeposition technique (Fig. 2A).

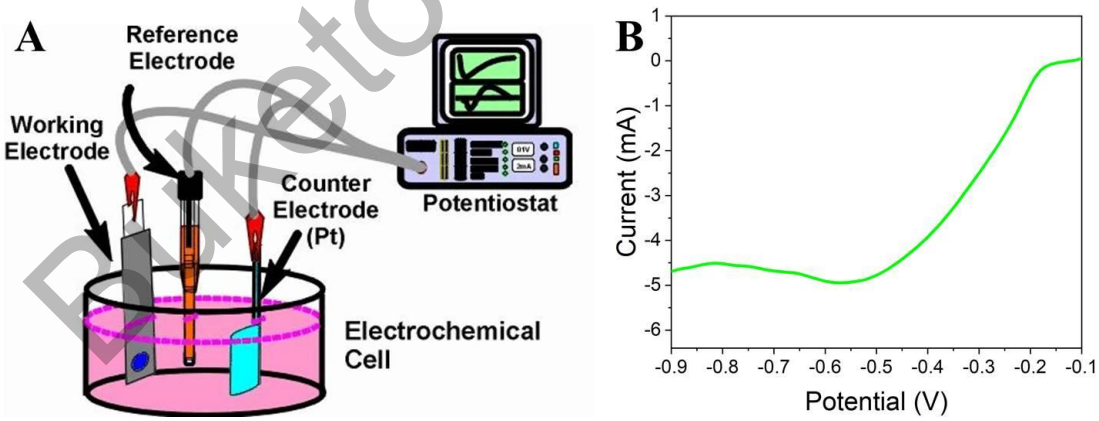


Figure 2. Diagram of the electrodeposition setup (A) and linear sweep voltammetric (LSV) measurement (B). Diagram was adapted from [7]

Electrochemical deposition of films allows precise control of the driving force for the reactions involved in deposition to control the structure and phase composition of the films. The electrochemical deposition of Cu_2O films was carried out in an electrolyte solution consisting of 0.4 M cupric sulfate and 3 M lactic acid. By complexing with lactate ion, the copper is stabilized and the pH can be raised to alkaline values. The pH of the bath solution was adjusted in the range of 10–12 by the addition of NaOH. The solution temperature was hold constant during deposition by a hot plate with thermo-regulator. Deposition temperature was 30 °C. Films were electrochemically deposited onto ITO (indium tin oxide) substrates, which were

placed in solution with a Pt counter electrode and a silver chloride reference electrode (SCE). All potentials are reported versus the SCE reference electrode. Electrochemical deposition was controlled by a potentiostat. The diagram of the electrodeposition is illustrated in Figure 2A.

The electrodeposition potential required for a synthesis in the potentiostatic mode is usually unknown. In this situation, linear sweep voltammetric (LSV) measurements assist to identify oxidation-reduction processes potentially undergone by the system of interest and choose an appropriate potential. Figure 2B shows a cathodic scan performed between –0.9 and –1.2 V at a scan rate of 10 $mV \times s^{-1}$, at temperature of 30 °C and at pH of 11.5. As can be seen from LSV the steady-state currents for the deposition of Cu_2O are in a potential window between –0.35 and –0.55 V. Therefore, electrodeposition of Cu_2O films was performed at working electrode potential of –0.4 V vs SCE.

Synthesis of Cuprous Oxide (Cu_2O) in various modes

In order to study the influence of pH solution on morphology of Cu_2O films the electrodeposition were performed in various pH**.** The plating bath was a 0.2 M $CuSO_4$ and 3 M lactic solution in deionized (DI) water with 0.5 M K_2HPO_4 buffer. pH was adjusted to by adding a controlled amount of 2 M KOH drops. The synthesis was carried out by using potentiostatic mode at 30 ^oC ranging from pH 8 to 12. It should be noted that only the SEM and XRD data of the films deposited at pH 10 and 12 is shown due to there is no any noticeable deference between films deposited at pH 9 and 10 and between pH 11 and 12. In the Figure 3, the morphology and XRD spectra of Cu_2O films electrodeposited at pH 10 and 12 are shown.

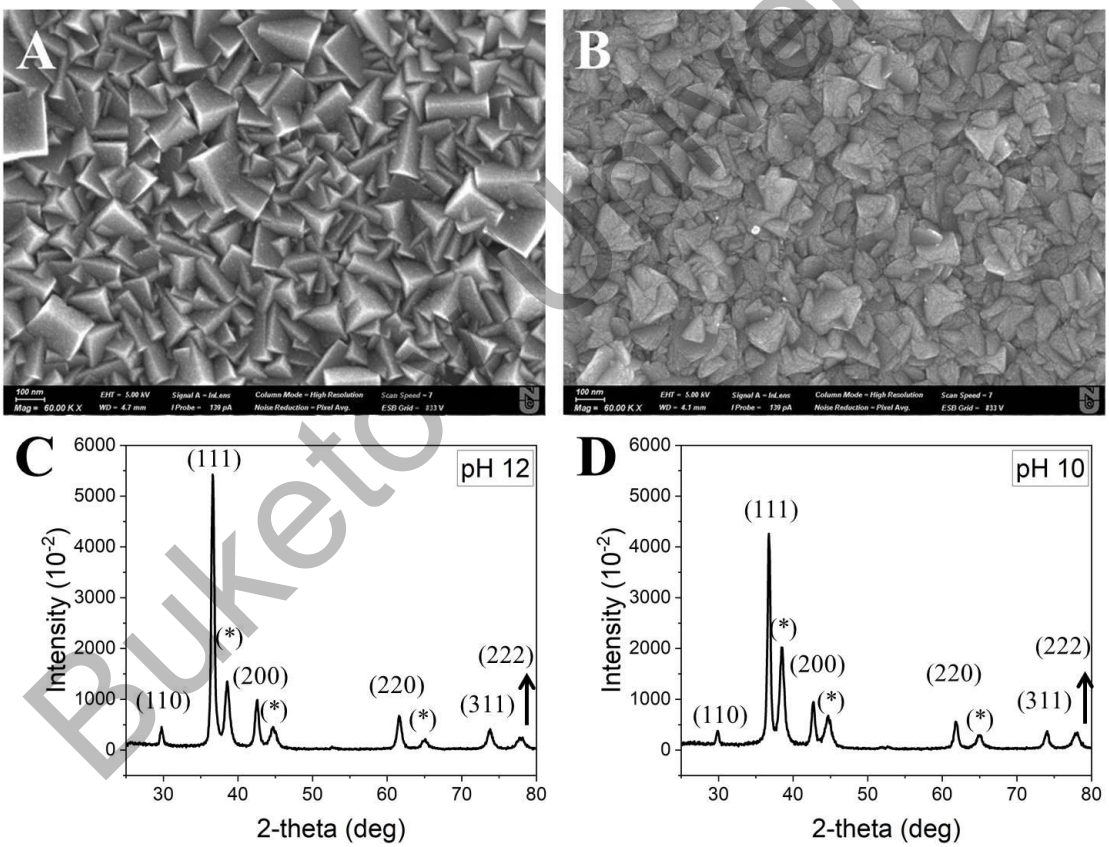


Figure 3. SEM images and XRD spectra of Cu_2O thin films grown by potentiostatic electrochemical deposition at T = 30 ^oC, WE potential –0.4 V and various pH 12 (A, C) and 10 (B, D). Symbol * represents the signals from the substrate

From the SEM image (Fig. 3A), it is seen that the Cu_2O film electrodeposited at pH 12 consists from grains with cubic morphology and oriented along cubic diagonal. Figure 3C shows XRD pattern of this film. XRD confirmed that film is Cu_2O with cubic structure and there is preferential grain orientation, grains mostly grow along the direction perpendicular to the planes. However, SEM image of Cu_2O films grown pH 10 (Fig. 3B) does no reveal any cubical morphology. The morphology of this film is different from the morphology of the film grown at pH 12. Its grains have more irregular shape and their surfaces are rougher.

XRD confirmed the presence of Cu_2O structure and indicate the preferable grain orientation along [7] direction.

Further we investigated the electrical properties of electrodeposited Cu_2O films. In Figure 4, the resistivity of samples is plotted against the pH of the electrolyte used during fabrication. The graph reveals that the resistivity of the film decreases as the pH increases. For instance, the film prepared at pH 9 has a resistivity of approximately $5 \cdot 10^7$ Ω*cm, while the film prepared at pH 13 has a resistivity of about $4 \cdot 10^5$ Ω*cm. Therefore, the lowest resistivity is achieved at pH 13.0, which is two orders of magnitude lower than that of the film prepared at pH 9.0.

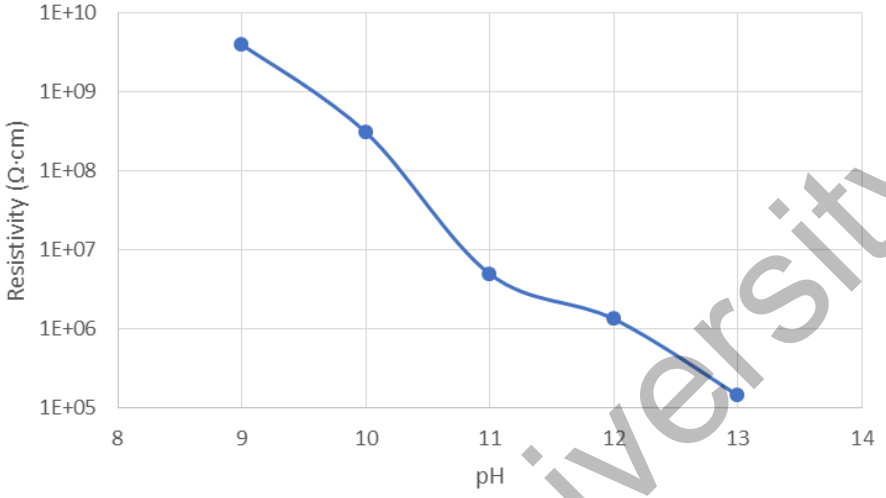


Figure 4. Variation of the resistivity of the films with pH

Finally, we fabricated the composite Cu_2O/CuSCN thin films and studied the efficiency of the charge separation at the Cu_2O/CuSCN interface by a photoelectric responses technique. For it, Cu_2O were deposited on the surface of CuSCN and photoelectric responses (PES) was measured. The Figure 5A represents SEM cross section image of a Cu_2O/CuSCN composite film. The PES responses for bare and Cu_2O/CuSCN composite were measured in order to compare photocurrent response from Cu_2O (Fig. 5B). The PES was measured in a three-electrode configuration. The electrolyte was a 1.0 M Na_2SO_4 solution buffered at pH 4.9 with potassium phosphate (0.1 M). The reference electrode was Ag/AgCl in saturated KCl, and a Pt wire was used as the counter electrode. The photoresponse was measured under chopped irradiation from an Ossila Solar Simulator with a light intensity 100 mW cm^{-2}. The scan rate for the linear sweep voltammetry was 10 mV s^{-1} [8, 9].

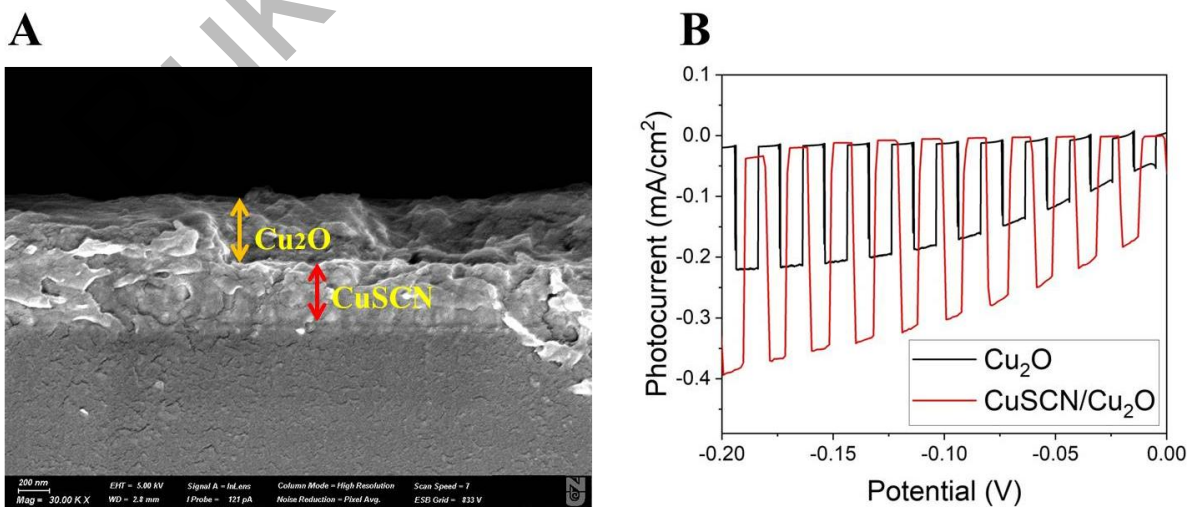


Figure 5. SEM cross-section image Cu_2O/CuSCN thin film (A) and photoelectric responses from a bare Cu_2O and composite Cu_2O/CuSCN films (B)

It seen that Cu_2O/CuSCN HTL has at least two times higher current density in comparison with bare Cu_2O, which indicate on improved charge separation at the Cu_2O/CuSCN. According the work L. Pan et al. a favourable band bending occurs at the CuSCN/Cu_2O interface, which also contributes to the enhanced charge separation, namely, the rapid extraction of holes from Cu_2O [8–10]. In our further study, these fabricated composite Cu_2O/CuSCN thin films will be optimized in order to use as HTL for organic and perovskite solar cells.

Conclusion

In conclusion, this study demonstrates the successful synthesis and characterization of CuSCN and Cu_2O as a potential hole transport layers for solar cells. The electrodeposition techniques utilized allow for precise control over film properties, leading to enhanced charge transport capabilities [11, 12]. Optimization of synthesis parameters, particularly for Cu_2O films, has been investigated to achieve low resistivity, crucial for their application in solar cell devices. Photoelectric response measurements further confirm the effectiveness of Cu_2O/CuSCN composite films in improving charge separation and surface reactivity. These findings provide valuable insights for the development of high-efficiency and stable solar cell devices. Future research may focus on further optimizing synthesis conditions and exploring doping strategies to overcome limitations and advance the practical application of these materials in photovoltaic technology [13–15].

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Электр тұндыру әдісімен синтезделген Cu_2O/CuSCN жұқа композиттік пленкалардың интерфейсіндегі зарядты бөлуді жақсарту

Бұл зерттеу күн батареялары үшін, атап айтқанда электродепозиция әдістерімен синтезделген мыс (I) тиоцианаты (CuSCN) және мыс оксиді (Cu_2O) үшін кемтіктерді тасымалдау қабаттарын (HTLs) синтездеуге және сипаттауға бағытталған. CuSCN және Cu_2O фотоэлектрлік құрылғыларда зарядты тиімді тасымалдау үшін перспективалы қасиеттерді ұсынады. Синтез процестері қажетті пленканың морфологиялары мен қасиеттеріне қол жеткізу үшін тұндыру параметрлерін дәл бақылауды қамтиды. Сипаттама әдістері, соның ішінде сканерлеуші электронды микроскоп (СЭМ), атомды-күштік микроскоп (АКМ) және ультракүлгін (УК) спектроскопия әдістері пленка морфологиясы мен оптикалық қасиеттері туралы түсінік береді. Cu_2O пленкалары үшін синтез параметрлерін оңтайландыру олардың электрлік қасиеттерін жақсарту үшін зерттелуде. Фотоэлектрлік реакцияны өлшеу Cu_2O/CuSCN композиттік пленкаларының интерфейсінде зарядтың бөлінуінің жақсарғанын көрсетеді. Бұл нәтижелер күн батареялары технологиясының дамуына ықпал етуі мүмкін. Сонымен қатар, зерттеу өз зерттеулерін әртүрлі pH деңгейлерінде электродепозициялау арқылы Cu_2O өндіруге дейін кеңейтеді. Сондай-ақ, сканерлеуші электронды микроскоп және рентген құрылымдық талдаулары тұндыру параметрлерінің пленка морфологиясы мен кристалл құрылымына әсерін анықтайды, бұл синтездің жеке тәсілдері туралы құнды түсінік береді. Тұтастай алғанда, бұл жаңжақты зерттеу кемтіктердің тасымалдау қабаттарының материалдарының синтезі мен оңтайландырылуын түсінуді жетілдіріп қана қоймайды, сонымен қатар жоғары тиімді және де тұрақты күн батареялары құрылғыларын жасау бойынша құнды ұсыныстар береді.

Кілт сөздер: күн батареялары, кемтікті тасымалдау қабаты, электр тұндыру, мыс тиоцианаты (I), мыс оксиді, синтездің оңтайлы шарттары, фотоэлектрлік жауап, бөлшектердің тасымалдануы.

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Улучшенное разделение зарядов на границе раздела тонких композитных пленок Cu_2O/CuSCN, синтезированных методом электроосаждения

Это исследование сосредоточено на синтезе и характеристике дырочных транспортных слоев (HTL) для солнечных элементов, в частности тиоцианата меди (I) (CuSCN) и закиси меди (Cu_2O), полученных методами электроосаждения. CuSCN и Cu_2O обладают многообещающими свойствами для эффективного переноса заряда в фотоэлектрических устройствах. Процессы синтеза включают точный контроль параметров осаждения для достижения желаемой морфологии и свойств пленки. Методы определения характеристик, включая сканирующий электронный микроскоп (СЭМ), атомно-силовой микроскоп (АСМ) и ультрафиолетовую (УФ)-спектроскопию, позволяют получить представление о морфологии пленки и оптических свойствах. Изучена возможность оптимизации параметров синтеза пленок Cu_2O для улучшения их электрических свойств. Измерения фотоэлектрического отклика указывают на улучшение разделения зарядов на границе раздела композитных пленок Cu_2O/CuSCN. Эти результаты могут способствовать развитию технологии солнечных элементов. Кроме того, в ходе исследования были определены возможности получения Cu_2O методом электроосаждения при различных уровнях pH. СЭМ- и рентгеноструктурный анализы выявляют влияние параметров осаждения на морфологию пленки и кристаллическую структуру, что дает ценную информацию для разработки индивидуальных подходов к синтезу. В целом, это всестороннее исследование не только углубляет понимание синтеза и оптимизации материалов дырочных транспортных слоев, но и дает ценные рекомендации по разработке высокоэффективных и стабильных устройств на солнечных элементах.

Ключевые слова: солнечные элементы, слои переноса дырок, электроосаждение, тиоцианат меди (I), закись меди, оптимальные условия синтеза, фотоэлектрический отклик, перенос частиц.

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