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Phase transformation and photoelectrochemical characterization of Cu/Bi and Cu/Sb based selenide alloys as promising photoactive electrodes

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ABSTRACT
Two photoactive chalcogenide compounds, copper bismuth selenide (CBSe) and copper antimony selenide (CASe), have successfully been prepared via a robust and facile solvothermal route. The phase transformation characteristics from the triclinic to orthorhombic crystal structure were clearly evinced by replacing Bi$^{3+}$ with Sb$^{3+}$ ions. The changes in the microstructure and electronic composition of each compound have been monitored using field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy characterization techniques. The fabricated CBSe film showed large values of absorption coefficient $>10^5$ cm$^{-1}$, good electrical conductivity, and charge carrier mobilities. The values of optical bandgap energy were estimated to be 0.99 and 1.18 eV for CBSe and CASe alloys, respectively. The electrochemical impedance spectroscopy measurements possessed lower resistance for CBSe electrodes. The photovoltaic performance results for the fabricated CBSe photoelectrochemical cells exhibited the maximum short-circuit current (I$_{sc}$) of 6.22 mA, open-circuit voltage (V$_{oc}$) of 0.492 V, fill factor of 63.9%, and power conversion efficiency of 1.94%. Finally, the as-prepared CBSe and CASe ternary alloys have possessed a good capability for dye sensitized solar cell and superconductor’s applications.

I. INTRODUCTION
Solar energy production is assumed to be one of the most sustainable, clean, and renewable energy resources. Basically, over 90% of the photovoltaic (PV) market is based on silicon technologies whether it is crystalline for Si-wafers or amorphous for thin films. Recently, the development of material types used in the PV thin film technology has extended to include various binary and ternary metallic systems such as CdTe, CuInSe$_2$, and Cu(In,Ga)Se$_2$. The main characteristics of these materials imply a wide range of direct bandgap energy (1–1.5 eV), high light absorption coefficient, and high solar conversion efficiency. Therefore, selenide and telluride based materials were significantly employed in many other electronic applications such as light emitting devices, optoelectronics, and superionic conductors. However, the PV thin film technologies are currently facing many restrictions due to the high cost of In and Ga elements, lower abundance of In and Te elements, as well as the environmental concerns toward Cd metal. Alternatively, the recent experimental studies are shifting toward lower cost, abundant, and environmentally friendly light absorber materials to overcome the previous restrictions.

Upon the technological perspectives, the Shockley–Queisser efficiency limit requires proper values of bandgap energies for each light absorbing material to be more efficient for harvesting a wide range of solar spectrum. Accordingly, huge considerable efforts have been devoted to studying the ternary compounds in
the groups (I-V-VI) including copper bismuth and copper antimony selenides (CBSe and CASe) for improving thin film PV applications. Actually, the application of Cu–Bi–Se thin films revealed a high absorption coefficient of 0.5–1.2 × 10^6 cm⁻¹, an optical bandgap of 1.5 eV, and good photoactivity as a solar absorber material. In addition, the theoretical and practical investigations of CuSbSe₂ compound have shown promising optical and optoelectronic properties. Therefore, wide optical bandgaps (1.5–2.1 eV) and (1.05–1.96 eV) have previously been reported for CBSe and CASe, respectively.\(^7\) Eventually, the indium free light absorber material Cu₃(Sb,Bi) (S,Se)₂ has possessed higher values of absorption coefficient than those of the CuInS₂ and CuInSe₂ materials reaching the double value. Moreover, these compounds have strong optical absorption compared to chalcopyrite CuIn(S,Se)₂, and kesterite Cu₂ZnSn(S,Se)₄.\(^8\)

Plainly, various ternary structures of CBSe or CASe materials have been prepared using different fabrication techniques such as electrodeposition,\(^9\) mechanical alloying from the elemental precursors (solid-state reaction),\(^10\) chemical precipitation,\(^11\) microwave synthesis,\(^12\) solvothermal synthesis, and the fusion method.\(^13\) Obviously, the monocrystalline CuBiSe₂ phase of the cubic structure has been obtained by the vacuum evaporation technique,\(^14\) while polycrystalline Cu₄Bi₈Se₁₄ of the triclinic structure could be easily prepared by the electrodeposition technique.\(^15\) Furthermore, a new orthorhombic structure of formula Cu₄Bi₄Se₇ was also discovered as a naturally formed mineral in the telethelic vein-type deposit with selenides at the El-Dragon mine in Bolivia.\(^16\) Even though the targeted CBSe and CASe materials have successfully been prepared using various wet-chemical processes, scaling-up of these methods for thin film PV industry still suffers from the interference of many binary phases with the targeted ternary phase.\(^11,16\)

In this regard, the present work will apply an affordable solvothermal process to synthesize both CBSe and CASe ternary systems using low cost, environmentally friendly, and earth abundant starting materials that might achieve more feasibility and simplicity. Moreover, the study includes correlation between the physical, structural, and electronic properties for the as-prepared chalcogenide materials. Furthermore, the effect of the structure change on the photovoltaic performance of their dye-sensitized photoelectrochemical cells (DSCs) will be consistently discussed. Finally, the influence of both Bi³⁺ and Sb³⁺ ions on both electronic conductivity and ionic conductivity will be presented.

II. EXPERIMENTAL

A. Material synthesis

Copper bismuth selenide (CBSe) compound was prepared via the solvothermal process with a stoichiometric ratio of 1:1:2 for Cu₄Bi₄Se₁₄. In a typical synthesis, about 0.561 g Cu(NO₃)₂·3H₂O (LOBA Chemie, 99%) and 1.13 g Bi(NO₃)₃·5H₂O (LOBA Chemie, 98%) were dissolved in 130 ml ethylene diamine. Then, about 0.52 g SeO₂ (Chem-lab, 99.5%) was added to the previous mixture followed by the addition of 20 ml hydrazine hydrxide (Research Lab Fine Chem Industries, 99%, NH₄OH) as a reducing agent. A dark brown to black precipitate was formed. The overall mixture was gently stirred on the hot plate at 80 °C for 1 h. Afterward, the homogeneous solution was directly transferred into an autoclave of 200 ml Teflon container closed with a stainless steel cover. The solvothermal reaction vessel was heated in the oven at 200 °C for 24 h. The reaction product was separated by centrifuge and washed many times with a solution of acetone:ethanol (1:1). The obtained black powder was dried at 70 °C for 6 h and ground for further characterizations. On the other hand, copper antimony selenide (CASe) compound was prepared by the same procedure in the same stoichiometric ratio except using SnCl₃ (LOBA Chemie 99%) as an antimony source.

B. Physical characterization

The crystallographic features of each sample were characterized by using a X-ray diffractometer (XRD), Bruker advanced D8 Kristallogfix (Ni-filtered Cu Kα radiation; 1.5406 Å). The surface morphology of the particles was inspected using a Field Emission Scanning Electron Microscope (FESEM, QUANTAFEG 250) operating at 25 kV integrated with an Energy Dispersive X-ray Spectrometer (EDS) coupled with a “Phoenix” detector for compositional analysis. Moreover, X-ray photoelectron emission spectroscopy (XPS) analysis was performed to investigate the oxidation states and composition of the exiting elements in the prepared compounds. The XPS spectra were obtained using the Al Kα X-ray beam as an excitation source with 250 W power. The optical properties for thin films of the photoactive materials coated on glass substrates were characterized using a UV-Vis-NIR spectrophotometer, PerkinElmer Lambda 1050, with an integrated sphere. The spectrophotometer contains deuterium, tungsten, and halogen light sources and a 3-detector module that allows for InGaAs and PbS testing. The Hall effect parameters including charge carrier concentration (density), Hall mobility (µ), resistivity (ρ), conductivity (σ), and Hall coefficient (R) were analyzed by the Nanometrics HL5500 Hall System. The Hall measurement parameters were performed in the temperature range from 298 to 388 K with 10 K interval providing ten different readings. After each 10 K increase, a current range from 1 × 10⁻⁸ to 1.1 × 10⁻⁷ A was applied on the samples with a 2 A interval between each point giving six readings for each reading of temperature.

C. Photoelectrochemical characterization

The working electrodes were fabricated by mixing 0.95 g of photoactive materials (CBSe or CASe) with 0.05 g of binding agent (polyvinylidene fluoride, or PVDF) in the presence of 0.03M N3-Dye solution, e.g., N-methyl pyrrolidone (NMP) as the solvent. Then, the conducting ink was coated on the conducting indium tin oxide (ITO) glass substrate (SPI Company, USA) by a total coated area of about 2.5 cm × 4 cm. The conducting electrolyte of the photoelectrochemical cell was prepared by dissolving 0.5M KI and I₂ in NaOH. The graphite rod was used as the counter electrode. Hence, the dye-sensitized photoelectrochemical cell (DSC) stack configuration was set up as: Glass/ITO/CuBiSe or CuSbSe/N₃-Dye/I⁻/I₂/0.5M KI + I₂ in NaOH/C (graphite). To test the photovoltaic performance, the cell was exposed to a light intensity of 1 sun (100 mW/cm²) using the air mass 1.5 global filter. The solar simulator Scientech SS150W-AAA with a xenon arc lamp of ~150 W power was applied as a light source. The reference detector (SIVT-refl) effective in sensing wavelengths between...
190 and 1100 nm is calibrated with the 1 sun. The current-voltage characteristics were measured using the 2400 Keithley Source Meter SSVT-60WC. The software program was designed to provide the values for various I-V parameters including $V_{oc}$, $I_{sc}$, $P_{max}$, $R_{series}$, $R_{shunt}$, and FF (where $V_{oc}$ is the open circuit potential of the working electrode, $I_{sc}$ is the short circuit current measured at zero voltage, $V_{max}$ and $I_{max}$ are the maximum voltage and current of the I-V relation, power $P_{max} = V_{max} \times I_{max}$, $R_{series}$ is the series resistance, $R_{shunt}$ is the shunt resistance, and FF is the filling factor). The electrochemical impedance spectroscopy (EIS) measurements intended for the cells were measured in the dark using Potentiostat Bio-Logic VMP 300 in the frequency range between 10 mHz and 20 kHz at an amplitude of about 10 mV.

III. RESULTS AND DISCUSSION

A. Phase analysis

Figure 1(a) shows the XRD pattern for CBSe powder produced by the solvothermal reaction. It can be noted that the main diffraction peaks at 20 values 24.38°, 29°, 30.4°, and 43.4° are related to the formation of the triclinic structure $\text{Cu}_{1.8}\text{Bi}_{4.8}\text{Se}_{8}$ as the major phase with space group $P\overline{4}1$. In addition, the corresponding (hkl) reflections to the planes of symmetry are 1 1 2, 1 2 1, −1 1 1, and 2 1 1 showing a good match with JCPDS card No. 01-080-1592. A minor extent of binary phases $\text{Cu}_2\text{Se}$ (JCPDS No. 71-0044) and metallic $\text{Se}$ (JCPDS No. 71-0528) is also detected as associated secondary phases. Meanwhile, Fig. 1(b) reveals the characteristic diffraction peaks of the orthorhombic structure $\text{CuSbSe}_2$ as the pure phase with space group Pmnbc (JCPDS No. 98-041-8754). The corresponding (hkl) reflections are 0 1 3, 2 0 1, 0 1 5, and 3 0 4 at 2θ values 27.8°, 28.5°, 37.1°, and 49°, respectively.

The average crystallite sizes for both samples are calculated by the Scherrer equation,

$$L = \frac{k\lambda}{\beta \cos \theta},$$  

where $k$ is the shape factor (dimensions constant) equal to 0.9, $L$ is the crystallite size (nm), $\lambda$ is the wavelength of the x-ray (1.5406 Å for CuKα), $\beta$ is full width half maximum (FWHM) in radians, and $\theta$ is the calculation diffraction angle. Therefore, it is found that the CBSe sample has smaller crystallite size ~35 nm than CASe ~67 nm. This means that complete replacing of Bi with Sb changes the atom orientation causing significant transformation in the crystal structure. The phase transformation can be explained by studying the dislocation density and microstrain present in the crystal lattice. The dislocation density $\delta$ is calculated using the value of crystallite size $L$ using the following equation:

$$\delta = \frac{1}{L^2},$$  

while the microstrain $\varepsilon$ can be calculated from the following relation:

$$\varepsilon = \frac{\beta \cos \theta}{4}.$$

Table 1 summarizes all the crystallographic parameters of both ternary compounds. It is indicated that the large size of $\text{Bi}^{3+}$ ions leads to the increase in the internal microstrain ($\varepsilon$) and dislocation density ($\delta$), causing lattice defects and oxygen vacancies as well as nonstoichiometric crystallization. Thus, the observed lattice distortion in CBSe compound is also confirmed by the lower crystallinity of detected phases than that of the CASe compound.

B. Microstructure investigation

Figures 2(a), 2(b), 2(d), and 2(e) reveal the surface morphology of CBSe and CASe particles using FESEM imaging. It is observed that the particles of CBSe have a flake like shape. These flakes geometrically grew with hexagonal orientation reaching about 50 nm particle size. It is apparent that a large number of voids are formed due to the packing of flakes in a cross-linking manner, suggesting that the surface exposed area of each flake like particle is very large, due to the packing of flakes in a cross-linking manner, suggesting that the surface exposed area of each flake like particle is very large, which means higher thermal and electrical conductivity. Moreover, the EDS spectrum for the CBSe sample closely reveals the original empirical ratio for $\text{Cu}:\text{Bi}:\text{Se}$ of 1:1:2, which used in the experimental preparation, as depicted in Fig. 2(c). Meanwhile, the particles of CASe show higher degree of agglomeration with the rectangular flake like structure, as indicated in Figs. 2(d) and 2(e). These kinds of flakes are compact and stacked together in a definite shape with an average particle size of about 250 nm. Therefore, the surface area of grain boundaries becomes higher which may lead to lowering of the thermal and electrical conductivities. The elemental composition of the as-prepared CASe sample is found to be consistent with the...
TABLE I. Crystallographic parameters of the as-prepared ternary CBSe and CASe phases.

| Sample | Crystal structure | a (Å)  | b (Å)  | c (Å)  | V (Å³)  | α (deg) | β (deg) | γ (deg) | Crystallite size (L) (nm) | Dislocation density (δ) (nm⁻² × 10⁻⁵) | Lattice strain (ε × 10⁻³) |
|--------|------------------|-------|-------|-------|---------|--------|--------|--------|-------------------------|-------------------------------------|---------------------------|
| CBSe   | Triclinic        | 17.20 | 13.41 | 4.18  | 379.7   | 98.75  | 106.74 | 85.45  | 35                      | 0.86                                | 1.19                       |
| CASe   | Orthorhombic     | 8.79  | 21.05 | 5.42  | 532.2   | 90     | 90     | 90     | 67                      | 0.22                                | 0.84                       |

principle experimental ratio for Cu:Sb:Se ~ 1:1:2, suggesting the efficient crystallization for the ternary compounds without impurities, as illustrated in Fig. 2(f). Obviously, the observed different geometrical orientations (i.e., hexagonal and rectangular) for the flake particles of each sample are in a good agreement with crystal structure investigations.

C. XPS analysis

The XPS analysis can be used to determine the binding energy of the elements, e.g., Cu, Bi, Sb, and Se, for each ternary compound. Thereby, the value of binding energy peaks is relative to the electronic valence of each element, and hence, the empirical formula for the prepared compounds can be confirmed. The XPS survey spectrum for CBSe indicates the presence of the three basic elements (Cu2p, Bi4f, and Se3d) at 935, 162, and 58 eV, respectively, as illustrated in Fig. 3(a). The detected minor peaks at 285, 402, and 433 eV are related to C1s, N1s, and O1s, respectively, as a result of the ethylene diamine residuals which indicate (C–N) bonds. Figure 3(b) displays the XPS scan diagram of copper that consists of two apparent peaks, Cu2p orbital peaks, at 933 and 953 eV, with a peak separation of 20 eV, indicating that the CBSe sample contains Cu¹⁺ (cuprous) electronic state. The additional two peaks are detected at 936.5 and 956 eV for the Cu²⁺ (cupric) electronic state that can be related to the impurity binary phases found in the XRD pattern of the CBSe sample, as mentioned before. Moreover, the XPS scan for bismuth confirms the trivalent cation state as it shows three peaks at 158.1, 160, and 164 eV with an energy difference equal to 5.9 eV related to Bi³⁺, as depicted in Fig. 3(c). Furthermore, the XPS scan for selenium shows a peak at 53.7 eV due to the reduced Se²⁻ electronic state, as shown in Fig. 3(d). The second deconvoluted peak at 55.5 eV indicates the presence of the elemental selenium in the metallic form, which can be interpreted from its reference XPS data. The third peak for selenium is at 95.5 eV, which is attributed to the oxidized form of selenium (Se⁴⁺ in SeO₂). On the other hand, the XPS survey for CASe reveals three basic peaks at 932, 531, and 53 eV for Cu2p, Sb3d, and Se3d, respectively, as shown in Fig. 4(a). Also, the presence of carbon and nitrogen residuals is evinced by the dual reflections at 286.5 and 400 eV. Figure 4(b) indicates that the Cu2p scan in CASe gives three apparent peaks at 931.6, 933, and 952 eV, pointing out the presence of the Cu¹⁺.

FIG. 2. FESEM images with EDS analysis for [(a)–(c)] CBSe sample and [(d)–(f)] CASe.
monovalent state. The Sb3d XPS scan for antimony shows many peaks for two different electronic states. Two peaks at 530.9 and 540.2 eV with the splitting value 9.3 eV stand for Sb$^{+3}$. Two peaks at 532.5 and 538.5 eV are related to the Sb$^{+5}$ electronic state. Another additional peak is found at 529.2 eV that may be assigned to an oxidized form of Sb in Sb$_2$O$_3$.

Similarly, the Se3d XPS scan spectrum shows many peaks for different oxidation states. Two peaks at 53.5 and 54.1 eV with an energy splitting value of 0.6 eV corresponding to the Se$^{2-}$ oxidation form. Meanwhile, the other two peaks at 58.2 and 60.1 eV are related to the oxidized form Se$^{4+}$. Generally, the XRD, EDS, and XPS data results and analysis consistently confirm the formation of the CBSe and CASe ternary phases with a major content.

D. Optical properties

Figure 5(a) illustrates the optical absorbance for both CBSe and CASe samples in the ultraviolet (UV) and visible light range. Generally, the absorbance value decreases with lowering the wavelength and increasing the light energy. Both CBSe and CASe samples possessed the highest absorbance in the range 800–900 nm. Therefore, CBSe and CASe samples showed large values of absorbance coefficient of about $7 \times 10^5$ and $3.9 \times 10^5$ cm$^{-1}$, respectively. Accordingly, the absorbance characteristics of each sample can be determined by applying the following model equation for direct transition bandgap:

$$ahv = A(hv - Eg)^{1/2},$$

where $a$ is the optical absorption coefficient, $h$ is Planck’s constant, $v$ is the photon frequency, $A$ is a constant, and $E_g$ is the energy gap. The energy bandgap is obtained from Tauc’s plot of $(ahv)^2$ vs $hv$ (photon energy) by extrapolation, as illustrated in Fig. 5(b). It is found that the CBSe sample has a lower bandgap of about 0.99 eV than CASe of about 1.18 eV. The estimated values of bandgap energy for both thin film materials are comparable with previously reported experimental results.

E. Electrical conductivity of bulk materials

The Hall measurement results are recorded for the pellets coated with silver paste using the standard four-probe technique at room temperature, as depicted in Table II. The CBSe sample shows higher values of carrier concentration and Hall mobility than CASe. The reason for such an effect could be attributed to the presence of highly conductive phases of Cu$_{1.6}$Se and Se$_8$, which leads to a decrease in the sheet resistance of the CBSe sample by 7.5 times of magnitude than of the CASe sample. Moreover, the CBSe sample possesses an average value of Hall coefficient of $\sim 516$ m$^3$ C$^{-1}$, which means that CBSe behaves as an $n$-type semiconducting material in the majority. Such behavior of superconductivity has previously been exhibited with other Cu–Bi–Se ternary compounds prepared by solid state melting of high purity elements and...
by chemical bath deposition. On the other hand, the CASe sample showed a positive average value of Hall coefficient of ∼3.73 m² C⁻¹, demonstrating the p-type semiconductor behavior of the CASe sample. Similar characteristics of the Hall effect were also envisaged with various CASe compounds prepared by the chemical deposition process.

F. Photoelectrochemical property measurements

1. Diffusion kinetic studies

The electrochemical impedance spectroscopy (EIS) is utilized to investigate the resistance emerged during different underlying chemical reactions between the cell compartments such as
charge transfer, mass transport, phase transitions. Therefore, Fig. 6(a) shows the Nyquist plots of the fabricated CBSe and CASe dye-sensitized photoelectrochemical cells (PECs) in the dark. It is observed that the CBSe cell has a lower total resistance value of ∼29.5 Ω than the CASe cell which is ∼32.5 Ω. Moreover, the extrapolation of the slope line in the low frequency region indicates the diffusion of I⁻ ions into the bulk of the electrode material, or the so-called Warburg diffusion resistance $\sigma_w$. Hence, the plot of the real part of impedance, $Z_{re}$, vs the reciprocal root square of the lower angular frequencies is illustrated in Fig. 6(b). Clearly, the diffusion coefficient values for I⁻ ions diffusion into the bulk electrode materials could be deduced using the following equations:

$$Z_{re} = R_s + R_{ct} + \sigma_w \cdot \omega^{-0.5},$$  \hfill (5)$$D = 0.5 (RT/A F^2 \sigma_w C)^2,$$  \hfill (6)$$Z_{re} = R_s + R_{ct} + 2\sigma_w^2 \cdot C_{dl},$$  \hfill (7)

where $R_s$ is the charge transfer resistance, $R_s$ is the electrolyte resistance, $R_{ct}$ is the angular frequency in the low frequency region, $D$ is the diffusion coefficient, $R$ is the gas constant, $T$ is the absolute temperature, $F$ is Faraday’s constant, $A$ is the area of electrode surface (10 cm²), and $C$ is the molar concentration of I⁻ ions. Meanwhile, the double layer capacitance is given by

$$\omega = 1/R_A \cdot C_{dl}.$$

Table III summarizes all the parameters of the EIS measurements at 298 K. Accordingly, the CBSe cell exhibits a higher value of diffusion coefficient ($D \sim 1.12 \times 10^{-9}$ cm² s⁻¹) than the CASe cell ($D \sim 1.38 \times 10^{-10}$ cm² s⁻¹). This behavior can be explained by calculating the exchange current density that can be given by the following formula:

$$i^o = RT/nF R_A C_{dl},$$

where $n$ is the number of electrons involved in the electrochemical reaction. As a result, it is found that the CBSe cell possessed the lowest charge transfer resistance $R_{ct}$ and the highest double layered capacitance $C_{dl}$ due to the smallest particle size of the CBSe sample, which provides a large surface area for mobility of charge carriers.

**TABLE II.** Hall measurement parameter values at 298 K.

| Sample | Current (A) | Bulk con. (cm⁻³) | Sheet con. (cm⁻²) | Sheet resistance (Ω) | Resistivity (Ω cm) | Conductivity (S cm⁻¹) | Mobility (cm² V⁻¹ s⁻¹) | Avg. Hall (m² C⁻¹) |
|--------|-------------|-----------------|-----------------|---------------------|-------------------|----------------------|----------------------|------------------|
| CBSe   | 6.00 × 10⁻⁴ | -1.75 × 10¹⁵    | -3.50 × 10¹¹    | 1.95 × 10⁴          | 3.90 × 10¹⁰       | 2.56 × 10⁻¹          | 1.66 × 10²           | -5.16 × 10²     |
| CASe   | 6.00 × 10⁻⁴ | -3.96 × 10¹⁹    | -7.93 × 10¹⁵    | 1.46 × 10¹⁰         | 2.93 × 10¹       | 3.41 × 10⁻²          | 1.07 × 10¹           | 3.73 × 10¹⁰     |

**FIG. 6.** (a) Nyquist plots of EIS measurements for the fabricated CBSe and CASe dye-sensitized photoelectrochemical cells in the dark and (b) relationship between real impedance and low angular frequencies for the fabricated CBSe and CASe dye-sensitized photoelectrochemical cells in the dark.

**TABLE III.** Electrochemical impedance spectroscopy parameters of the fabricated solar cells at 298 K.

| Sample | $R_s$ (Ω) | $R_{ct}$ (Ω) | $\sigma$ (S cm⁻¹) | $\sigma_w$ (Ω⁻⁰·⁵) | D (cm²/s) | $i^o$ (mA/cm²) | C_{dl} (F) |
|--------|-----------|-------------|-----------------|-----------------|----------|----------------|----------|
| CBSe   | 26.77     | 1.41        | 7.11 × 10⁻⁴     | 1.12 × 10⁻¹     | 1.12 × 10⁻⁹ | 1.83 × 10⁻²     | 6.91 × 10⁻² |
| CASe   | 29.51     | 2.97        | 3.37 × 10⁻⁴     | 3.20 × 10⁻¹     | 1.38 × 10⁻ⁱ | 8.66 × 10⁻³     | 4.17 × 10⁻⁵ |
where \( A = 10 \text{ cm}^2 \) denotes the area of the working electrode and \( I_{sc} \) is the incident intensity of the light (100 mW cm\(^{-2}\) = 1 sun). The measured photovoltaic specific parameters and efficiencies are given in Table IV. It is noticed that the CBSe cell possessed the maximum values for power conversion efficiency and fill factor of about 1.94\% and 63.9\%, respectively. The reason for high power efficiency of the CBSe cell is attributed to the high ionic conductivity about 1.94\% and 63.9\%, respectively. The reason for high power efficiency of the CBSe cell is attributed to the high ionic conductivity of \( \sim 0.7 \text{ S cm}^{-1} \), which is promoted by the largest mobility value of electrons in CBSe. The CBSe compound enhances the electron-hole pair transition between the valence and conduction bands. The measured I-V results for the prepared ternary CBSe and CASe samples are consistently comparable to the previously investigated Cu–Sb–Se systems mentioned in previous reported work were deposited using advanced and highly costive RF and DC sputtering processes of binary components. Also for the cell reported with PCE 3\%, the synthesized alloy was put in a photovoltaic device containing CASe/CdS as the heterojunction absorber layer, ZnO/IZO as the front contact layer, and Mo as the back contact, which resulted in increasing the value of PCE. For CBSe, no reports were mentioned about its PCE. On the other hand, the energy band diagrams for the dye-sensitized photoelectrochemical CBSe and CASe cells are shown in Figs. 8(a) and 8(b). Typically, the absorption of photons generates excited electronic states in the illuminated semiconductor film (S) such as CBSe or CASe. These excited states have lifetime of limited duration. Therefore, the intrinsic energy of each excited state tends to be lost through the relaxation process without separation of charges in the dark, as explained in the following equations:

Light absorption:

\[
\text{hv} + S_l \rightarrow h^+ \text{S}_l + e^- \text{S}_l. \tag{12}
\]

Recombination:

\[
h^+ \text{S}_l + e^- \text{S}_l \rightarrow \text{heat}. \tag{13}
\]

Meanwhile, the mechanism of charge separation has been considered in designing efficient photoelectrochemical systems. As a result of illuminating semiconductor/liquid interfaces, an electric field induces continuous current with charge/ion redistribution (charge separation) at the interface. Upon photogeneration of electron/hole pairs, this electric field impedes recombination processes by oppositely accelerating and separating these charges, resulting in minority carrier injection into the electrolytic redox couple according to the following equations:

Charge separation:

\[
e^- \text{S}_l \rightarrow e^- \text{bulk}, \tag{14}
\]

\[
h^+ \text{S}_l \rightarrow h^+ \text{surf}. \tag{15}
\]

The electrolyte has the following ions:

\[
\text{KI} + I_2 \rightarrow I_3^- + K^+. \tag{16}
\]

This concept of carrier generation is illustrated in Figs. 8(a) and 8(b) for n-type CBSe and p-type CASe vs graphite as counter and reference electrodes. The theoretical approach for the N3-dye loaded CBSe or CASe semiconductor/I\(_3^- /3I^-\) redox couples can be expressed by the following interfacial reactions:

\[
2e^- \text{surf} + I_3^- (\text{Ox}) \rightarrow 3I^- (\text{Red}), \tag{17}
\]

\[
2h^+ \text{surf} + 3I^- (\text{Red}) \rightarrow I_3^- (\text{Ox}). \tag{18}
\]

![FIG. 7. Current-voltage output plots for the solar irradiated CBSe and CASe dye-sensitized photoelectrochemical cells.](image-url)

### Table IV. Photovoltaic characteristic parameters of fabricated solar cells at 298 K.

| Sample | \( V_{oc} \) (mV) | \( I_{sc} \) (mA) | \( P_{max} \) (W) | FF (\%) | \( R_{series} \) (\( \Omega \)) | \( R_{shunt} \) (\( \Omega \)) | \( \eta \) (\%) |
|--------|-----------------|-----------------|-----------------|--------|-------------------------------|-------------------------------|--------|
| CBSe   | 492             | 6.22            | \( 1.94 \times 10^{-1} \) | 63.9   | 13.519                        | 2.47 \times 10^2              | 1.941  |
| CASe   | 482             | 5.13            | \( 1.58 \times 10^{-1} \) | 63.7   | 15.824                        | 2.23 \times 10^2              | 1.58   |
IV. CONCLUSION

An affordable solvothermal process was successfully utilized to prepare Cu–Bi and Cu–Sb based selenide alloys. The major phase of the triclinic structure has been detected for the CBSe alloy, while pure orthorhombic phases were only characterized for the CA-Se sample. The FESEM investigations confirmed the change in morphology of flakelike particles from hexagonal to rectangular geometry with a noticeable increase in the particle size by replacing Bi with the Sb atom. The Hall effect measurements demonstrated n-type semiconducting behavior for the CBSe sample and p-type semiconducting behavior for the CA-Se sample. The EIS studies indicated a higher diffusion coefficient of $\sim 1.12 \times 10^{-9}$ cm$^2$ s$^{-1}$ and a lower value of total resistance of $\sim 29.5$ $\Omega$ for the fabricated CBSe photoanode, resulting in fast electrochemical reaction kinetics and improved photovoltaic performance. Hence, the fabricated CBSe sample displayed the maximum power conversion efficiency of about 1.94%.

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