Copper indium selenide water splitting photoanodes with artificially designed heterophasic blended structure and their high photoelectrochemical performances

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ABSTRACT

Conventional $p$-CuInSe$_2$ absorbers for solar cells have been homogenously synthesized using multi-step process despite a narrow crystal phase region in the phase diagram and the existence of various secondary phases. In contrast, here we propose artificially-designed heterophasic blended copper indium selenide compounds for water splitting photoanodes using a simple one-step annealing synthetic process where the electrodeposited metal precursors were directly annealed with Se vapor injection and without additional intermediate steps. The resultant product is revealed to possess a novel “phase-blended structure” comprising two phases of $p$-type CuInSe$_2$ and $n$-type CuIn$_3$Se$_5$ crystals. The CuInSe$_2$ nanoparticles with a higher Cu fraction are three-dimensionally (3D) embedded in the CuIn$_3$Se$_5$ matrix, which has been verified by various analysis methods such as X-ray diffraction, transmission electron microscopy, and capacitance-voltage curve. The average diameter of the CuInSe$_2$ nanoparticles is 66.8 nm and the interval between the nanoparticles in the CuIn$_3$Se$_5$ matrix is 67.6 nm. Consequently, the phase-blended structure photoabsorber exhibits a remarkably enhanced anodic photocurrent gain of the phase-blended structure photoanode is attributed to the excellent charge separation facilitated by the built-in potential generated from the 3D $p$-$n$ junction.

1. Introduction

Typical copper-based chalcogenide thin films such as CuInSe$_2$ (CIS) and Cu(In,Ga)$_2$S$_2$ (CIGS) are one of the most promising inorganic absorber layers for photovoltaic cells due to their high absorption coefficient and appropriate band gap that have accorded energy conversion efficiency up to 22.6% \cite{1}. Recently, the interest in photovoltaic devices has shifted to their applications in photoelectrochemical water splitting system since hydrogen generation from solar energy is widely known as one of the clean routes \cite{2}. Conventional absorber materials for solar cells, active semiconductors for efficient water splitting should have a preferentially suitable band position: a negatively higher conduction band minimum than the proton reduction potential or a positively higher valence band maximum than the water oxidation potential \cite{3}. Since the discovery of photoelectrolysis, TiO$_2$ photoanode has been actively studied due to its suitable band position for water oxidation, and electrochemical stability in aqueous systems \cite{4,5}. Alternative photoactive materials such as WO$_3$, ZnO, BiVO$_4$, and Fe$_2$O$_3$ have also been researched \cite{6–9}. However, these materials intrinsically have large band gaps (2.4–3.2 eV) or low electrical conductivity, which cannot sufficiently absorb visible light for photogeneration or transfer photocarriers to the electrolyte or substrate. Thus, various strategies for band gap engineering such as doping, defect engineering, and electron beam modification have been introduced to

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enhance the light absorption efficiency [10–12]. In addition, type II heterojunction using bilayer structure was suggested to induce the built-in electric field for photogenerated electron/hole separation, and hydrogen/oxygen evolution catalysts were loaded to facilitate the charge injection to the electrolyte [13,14]. Specifically, it was empirically proved in organic photovoltaic solar cells that the effective exciton charge separation can be realized by the formation of bulk heterojunction structure with three-dimensional (3D) p-n junction by inducing large area internal built-in electric field [15,16]. However, to our best knowledge, there are no meaningful experimental approaches to synthesis phase blended inorganic photoactive materials due to the difficulty in intentionally producing multi-crystalline phases without photovoltaic degradation.

When considering the synthesis of multi-crystalline phases, copper based chalcogenides, ABC (A = Cu; B = In, Ga; C = S, Se, and Te), can be considered as one of strong candidates for high performance photoelectrodes owing to their excellent absorption property and the existence of complex multi-phase crystals. The photo-absorption CuInSe2 layer with a Cu:In atomic ratio of 1:1 is a well-known p-type semiconductor, which shows an α-phase in the phase diagram of the Cu2Se-In2Se3 complex [17]. On the contrary, the relatively obscure CuIn6Se8 and CuIn5Se8 compounds that are obtained from Cu-poor conditions are typically n-type semiconductors, referred to as the β-phase and γ-phase, respectively [18,19]. Besides, the Cu-In-Se compounds can form many kinds of phases depending on the atomic ratio of Cu/In. Thus, one of the most important technical barriers for CIGS thin film photovoltaic applications is to produce homogeneous p-CIGS compounds with a highly crystalline structure and a designed atomic ratio. Interestingly, the existence of the so-called ordered vacancy compounds, such as CuIn5Se8 and CuIn6Se8, with n-type characteristics on the surface of the CIGS absorbers is generally accepted for high efficiency solar cells [20]. In addition, some solar cells fabricated with β-phase compounds have been reported despite their relatively reduced cell efficiency.

In contrast, for photoelectrochemical cell (PEC) applications, Zhao et al. synthesized p-type CuIn6S6 with a high cathodic photocurrent of 13.0 mA/cm² at 0 V versus the reversible hydrogen electrode (RHE) by modifying the thin films with additional thin layers of GdS and TiO₂ [21]. However, the p-type CuIn6S6 revealed severe corrosion problem in cathodic aqueous solutions. Gannouni et al. controlled the molar ratio of [Cu]/[In] to confirm the optimal condition for producing high quality n-type CuIn₅S₈ photoanodes with minimized electron-hole recombination rate [22]. Nevertheless, until now, most of the studies on copper based chalcogenides have concentrated on the p-type CuInSe₂ films, while some research groups demonstrated the results of p-type Cu₃ZnSnS₄ revealing the low photocurrent and stability of the bare absorber films [23,24]. Similar to those of solar cell applications, the few studies on the development of n-type CuIn₅Se₈ films for photoanodes unfortunately showed a low current density as compared that of the p-type CuIn₅Se₈ films [25].

To our best knowledge, no previous investigations for the CIS based photoelectrodes with p-n-CIS heterojunction structure have been reported, even though the generation of the built-in potential is wise approach [26,27]. Here, we invented an artificially controlled synthetic procedure for an inorganic phase-blended structure with n-CuIn5Se8 matrix and p-CuInSe₂ nanoparticles. This phase-blended structure which induces a three-dimensional (3D) p-n junction for high performance photoelectrode, was conveniently obtained by simplifying the annealing process and depositing with a suitable Cu/In atomic ratio and selenium vapor flow [28–30]. Interestingly, it will be shown that this structure considerably enhances the photoelectrochemical performances of the n-type CuIn5Se8 photoanode, i.e., a significantly enhanced photocurrent from the p-n phase-blended structure and re-inforced photoelectrochemical stability with an Al2O₃ film.

2. Methods

2.1. Preparation of metal precursors using a multi-bath electrodeposition method

For the preparation of metal precursors, a conventional electrodeposition method with a three-electrode system was employed with an Ag/AgCl reference electrode and a Pt plate counter electrode. Glass substrates coated with an 800 nm-thick Mo layer were used as the working electrode. Prior to the electrodeposition process, the substrates were cleaned via ultrasonication in acetone, ethanol, and deionized water for 10 min each, and finally dried under nitrogen gas. The Cu/In double metal layers were deposited with a Cu/In coulomb ratio of 0.4. Here, an aqueous solution containing 0.1 M copper sulfate (CuSO₄), 0.1 M sodium sulfite (Na₂SO₃), 0.2 M indium chloride (InCl₃), and 0.1 M sodium chloride (NaCl) was used as the electrolyte to deposit Cu and In, respectively. The pH of the solution was adjusted to 1.0 by the drop-wise addition of H₂SO₄. Electrodeposition of the Cu layer was carried out with two potential steps. In the first step, −1.2 V was applied for 0.1 s to generate sufficient nuclei to improve the adhesion between Mo substrate and Cu layer. In the second step, −0.4 V was continuously applied until the total charge reached to 8.0 C/cm². In contrast, the In electrodeposition was carried out at −0.68 V until the total charge was 19.9 C/cm². The relation between the Cu/In thickness ratio in the metal precursors (or coulomb ratio) and the final Cu/In composition ratio is shown in Fig. 1a.

2.2. One-step thermal annealing in selenium vapor

A thermal evaporation system was used to synthesize the Cu-In-Se compounds from the prepared Cu/In bilayer precursors. To protect the precursor layers and provide plentiful Se vapor, 1 μm-thick Se layers were preferentially deposited on the precursors before the annealing process. The temperature was then raised from 293 K to 823 K (550 °C) for 27 min under an excess Se vapor supply of 20 Å/s. After raising the temperature, the synthesis was continued under the same Se supply rate for 20–70 min. Hereafter, the samples prepared at a fixed Se vapor flux of 20 Å/s for 20, 30, 40, and 70 min at 550 °C will be referred to as 20-CIS, 30-CIS, 40-CIS, and 70-CIS, respectively, in the text. Consequently, this process for CIS synthesis utilizes “one-step annealing” without additional intermediate steps, unlike the conventional CIS synthesis processes. To optimize the synthesis condition and control the phase of the final CIS compounds, only the key factor, i.e., the Se supply time, was varied (20–70 min) at 550 °C, as shown in Fig. 1b. For surface passivation, 5 nm-thick Al₂O₃ layers were deposited by atomic layer deposition at 200 °C, and the samples were additionally annealed in air at 350 °C for 1 h in a furnace.

2.3. Characterization of CIS compounds and their photoelectrochemical performances

The surface morphology, thickness, and chemical composition of the CIS compounds were analyzed using a field emission scanning electron microscope (FE-SEM, JSM-7600F) equipped with an energy dispersive spectroscopy (EDS, JSM-7600F). Their structural properties were characterized by high-resolution X-ray diffraction (HRXRD, Bruker D8 Advance) using a Cu-Kα radiation source with triple-axis coupled ω–2θ scans and glancing angle modes. The nanoscale images and chemical compositions of the nanoparticle and matrix were analyzed using transmission electron microscopy (TEM, JEM-2100F HR) and the EDX (JEM-2100F HR) attachment of a scanning TEM (STEM). The average atomic distribution of Cu, In, and Se in the final CIS (Se supplied for 30 min) compounds was obtained with Auger electron spectroscopy (AES, SAM 4300).

All the photoelectrochemical tests were performed at pH = 8 with 0.1 M KOH solution and 1 M Na₂SO₄ background solution at room
temperature. A solar simulator (Yamashita-Denso YSS-50A, 150 W Xenon lamp) was used as a beam source to produce an AM 1.5 G spectrum, where the light intensity of 100 mW/cm² was calibrated with a standard silicon photodetector. Linear scan voltammetry (LSV) was performed in photo- and dark-current (on/off pulse: 2 s) at a voltage sweep of 0.13–1.23 V vs RHE. Capacitance-voltage (C-V) analysis was obtained in dark at a voltage sweep of −0.4–1.4 V vs RHE. The cyclic voltammetry sweep curves were measured in electrolyte under illumination and dark conditions to illustrate the occurrence of photoelectrochemical and electrochemical corrosion. Nyquist plots (electrochemical impedance spectroscopy, EIS) with a frequency sweep from 100 kHz to 1 Hz were obtained from bare 30-CIS and Al₂O₃ coated 30-CIS to analyze the capacitive behavior.

3. Results and discussion

For the multi-bath electrodeposition method, we first stacked the Cu and In precursor layers on a soda-lime glass/Mo substrate, which is an easy approach for controlling the precursor ratios and the designed thickness. We controlled the amount of total accumulated charge and optimized the Cu/In ratio in the CIS compounds. As a result, we deduced the relationship between the Cu/In precursor coulomb ratio and the actual Cu/In ratio in the final products, as shown in Fig. 1a. The experimental results revealed that by adjusting the Cu/In precursor coulomb ratio, we could artificially synthesize CIS compounds under the Cu-poor condition of Cu/In = 0.4 to obtain abnormal n-type CIS compounds. Typically, the CIS compounds were synthesized via a three-step procedure when selenization process was introduced [30]. In the first step, Cu-In binary metal alloys (Cu₁₁In₉ + CuIn₂) are synthesized and distributed at relatively low temperatures. This is followed by the formation of binary Cu₂Se and In₂Se₃ phases at intermediate temperatures in the second step. Lastly, the final phase of the CIS compounds are produced from the designed ratios of the Cu₂Se and In₂Se₃ phases and a crystal growth process that yields large grains, resulting in the production of highly crystalline high-efficiency CuInSe₂ and Cu(In,Ga)Se₂. This complex fabrication procedure is designed for high uniformity and crystallinity of the p-type CuInSe₂ and Cu(In,Ga)Se₂ compounds with a narrow stable region in the phase diagram. In contrast, we suggested a simple synthetic process of “one-step annealing” without additional intermediate steps for the synthesis of unusual CIS compounds, as shown in Fig. 1b. In this procedure, sufficient time and temperature were not provided for the formation of Cu-In binary alloys and pure binary compounds. Thus, the one-step annealing process involving direct temperature ramp-up does not follow the general synthesis equation for homogeneous CuInSe₂ compounds because it did not experience the intermediate Cu₂Se and In₂Se₃ phases. Alternatively, we injected plentiful Se vapor during temperature increase (27 min) and initial crystallization annealing (different times) for selenization, as shown by the sky-blue-colored region in Fig. 1b. Finally, Se vapor supply was stopped and the samples were continuously annealed for 6 h at 550 °C to allow the formation of large grains. Then, we analyzed the atomic distribution of Cu, In, and Se in the final CIS product prepared with 30 min of Se vapor flow by AES (Fig. 1c). An atomic ratio of around 13:36:51 corresponds to α, β, or γ phases. Nevertheless, the CIS film exhibited highly uniform and extremely large grains, as shown in Fig. 1d.

Fig. 2a shows the photoelectrochemical and photocurrent performances of the produced CIS compounds using LSV analysis, where the designated times indicate the duration of Se vapor injection at 550 °C, as indicated by the colored region in Fig. 1b. Firstly, it is revealed that all the prepared samples have primary n-type semiconductor photoabsorption performances, regardless of the duration of Se vapor injection and contrary to the typical p-type CuInSe₂ photoabsorbers; this indicates that the photoanodic n-type CIS compounds can be synthesized under Cu-poor conditions. Among the various CIS photoanode samples, 30-CIS and 40-CIS showed a very low dark-current and a high photocurrent. In contrast, 20-CIS showed a low photocurrent of about 150 μA/cm² at RHE vs. 1.23 V and a large dark-current, which might be
attributed to the formation of incomplete CIS compounds owing to a short Se supply time. In addition, 70-CIS, with an excess of Se supply, generated unnoticeable dark-current despite considerable photocurrent (about 5.1 mA/cm² at RHE vs. 1.23 V). An excess of Se supply deposits Se residues on the surface of the CIS products, resulting in the generation of dark current from the electrochemical corrosion of Se, which can be confirmed from the theoretical Pourbaix diagram of Se. Based on these results, the optimum Se supply time was found to be 30 min owing to the highest photocurrent (5.8 mA/cm² at RHE vs. 1.23 V) and lowest dark current obtained for the corresponding sample. Generally, the surface of the as-deposited CuInSe₂ and Cu(In,Ga)Se₂ photoabsorber films have randomly distributed Cu₂Se by-products leading to a large leakage current. Thus, chemical etching using KCN is generally performed to etch the unwanted by-product phases. Our photoanodic CIS compounds also exhibited a relatively Cu-rich near surface and we suspect the formation of Cu₂Se by-products. To investigate the influence of the by-products present on the surface, we measured the I-V characteristics, horizontally and laterally, of the as-deposited n-CIS thin films (Fig. S1) and observed the degraded electrical properties and the existence of a Schottky barrier (black graph). We selectively etched the surface of the 30-CIS sample with 0.5 M potassium cyanide (KCN) etchant for 3 min to eliminate the secondary phase Cu₂Se [31]. The significantly improved electrical characteristics (red and blue curves) revealed the effectiveness of the KCN etching treatment. Subsequently, KCN treated 30-CIS sample exhibited a remarkably enhanced photocurrent of 12.7 mA/cm² at RHE vs. 1.23 V, but still showed a low dark current level, as shown in Fig. 2b. To our knowledge, this is the highest photocurrent ever measured for an n-CIS based photoanode for water splitting under an AM 1.5 illumination without any photocatalyst [22,25]. The photoanode PEC performances reached around 10 mA/cm² when buffer layers, passivation layers, and various catalysts were combined with the photoanode films to enhance their photoabsorption performances [32]. Therefore, we believe that our CIS compounds showing high photoanodic performances without additional coatings would have a great impact on the water splitting system. Interestingly, the 30-CIS sample with high photoanodic current also showed meaningful cathodic photocurrents with clear on/off characteristics, as shown in Fig. 2c.

Next, we investigated their microcrystalline structures to understand the improvement mechanism because our process was unusual and the products showed n-type behavior with slightly dual photovoltaic properties. As shown in Fig. 3a, we identified the exact crystal phases of the 30-CIS sample (black graph) using HR-XRD, where the typical p-type Cu₃InSe₅ (red graph) used in photovoltaic cells was taken as a reference. The XRD peaks of the Cu₃InSe₅ crystal lie very close to the peaks of the CuInSe₂ crystal, according to ICDD #89–5646 (Cu₃InSe₅) and #51–1221 (CuInSe₂). Because these compounds have the same tetragonal structure (α = b = c, α = β = γ = 90°) and similar lattice parameters, the diffractions occurred at similar degrees, and thus, it is not easy to distinguish between Cu₃InSe₅ and CuInSe₂. Fortunately, they have different Bravais lattices; Cu₃InSe₅ has a body-centered tetragonal lattice with two lattice points and CuInSe₂ has a primitive tetragonal lattice with one lattice point. Due to the difference in lattice constants, the reflections at specific planes could be observed. The primitive lattice showed all the reflections, while the body-centered lattice showed few reflections, except that the summated results of h + k + l were odd. As shown in Fig. 3a, the peaks whose h + k + l sums are even are indicated with circles (O) and those with odd h + k + l sums are shown with stars (★). We undoubtedly identified that the main phase was Cu₃InSe₅ because star peaks were detected in the HR-XRD result of the fabricated CIS film. The most interesting thing is that the peak indicated by circles (O) in the 30-CIS sample have asymmetric shapes, while those indicated by stars (★) have relatively symmetric shapes, as shown in Fig. 3b, which displays one of the asymmetric (O) peaks. The asymmetric XRD peaks can originate from sample strain, doping, or overlapping of more than two peaks. In our case, however, the presence of overlapping peaks is possible, and we could reasonably propose that the CuInSe₂ and Cu₃InSe₅ peaks overlapped because only the peaks whose h + k + l sums are even are asymmetric [indicated by circles (O)]. Based on ICDD standards, the CuInSe₂ XRD peak corresponding to the (112) plane negatively shifted by only 0.06°. Thus we separated the overlapping peaks to two individual peaks using a triple-axis coupled scan mode, as shown in Fig. 3c. To exclude unexpected variables, which cause analysis error, the 30-CIS sample was slightly etched to remove the secondary phases such as Cu₅Se₆. The glancing angle HR-XRD analysis of the 30-CIS sample prepared without KCN etching revealed that the single peak observed at 26.66° corresponds to Cu₅Se₆ (blue), as shown in Fig. 3c. The colored dotted lines in Fig. 3c indicate the location of the diffraction peaks originating from the corresponding crystal phases. The CuInSe₂ (reference, red) XRD peak is positioned at 26.74°, which is identical to the ICDD data, while the produced 30-CIS (black) shows two distinguishable peaks at 26.74° and 26.80° that are well matched with that of Cu₃InSe₅ and CuInSe₂, respectively. A sample with only one crystal phase can exhibit two peaks owing to unfiltered
We have already demonstrated a uniform atomic concentration from the AES analysis, but the measured atomic ratios were not in agreement with those of typical CIS compounds such as pure CuInSe$_2$ and CuIn$_3$Se$_5$. Moreover, we identified the possibility of the coexistence of two phases in enough volume to be detected in the produced CIS compound by XRD and Raman analyses. Assuming that two phases coexist, the AES results can be anticipated to give a CuInSe$_2$:CuIn$_3$Se$_5$ volume ratio of 1:9. It is also reasonable because the sample exhibited primary photoanodic current and a minor photocathodic current at the same time. To demonstrate the crystal distribution of the two-phase CIS compound, the microstructure of the 30-CIS sample was characterized by high-angle annular dark-field (HAADF) TEM (Fig. 4a and b). Interestingly, a high density of nanoscale crystal nanoparticles uniformly distributed in the CIS matrix was clearly observed. Based on the fundamental property of HAADF image (Fig. 4b), it is expected that the bright contrast nanoparticles consist of heavier elements than does the matrix since the relatively heavy metal scatters more electrons. Therefore, based on the difference between the contrasts of the nanoparticles and matrix and the XRD/AES results, we confirm that the produced CIS compound comprises CuInSe$_2$ nanoparticles in CuIn$_3$Se$_5$ matrix, and not a distribution of tilted CuIn$_3$Se$_5$ grains. The average diameter of these nanoparticles is 66.8 nm and the interval between the nanoparticles is 67.6 nm (Fig. 4b and c). Since the final CIS product has two phases consisting of $p$-type CuInSe$_2$ and $n$-type CuIn$_3$Se$_5$ and shows a remarkably high photoanodic current, we henceforth refer to this structure as a “phase-blended structure”. Additionally, we characterized the relative atomic distribution in the nanoparticles and matrix using an EDS system attached to STEM, as shown in Fig. 4c, where the concentration of three elements is expressed in different colors: Cu (red), In (sky blue), and Se (yellow), and their atomic fractions are summarized in Table 1. The nanoparticles have a higher Cu fraction and a lower In fraction than does the matrix, and the relative Cu/In ratio is approximately 1.08 for the nanoparticles and 0.34 for the matrix. These atomic ratios are in good agreement with the expected atomic ratios of the CuIn$_2$S$_3$ and CuIn$_3$Se$_5$ phases, and thus, our phase identification is verified beyond doubt.

Furthermore, we determined the exact crystal phase from the selective-area diffraction patterns (SADPs) of the phases, as shown in Figs. 4d and 4e, which were obtained from the same zone axis (Z.A. = [100]). The patterns from the matrix revealed diffractions indexed to the (002), (020), (001), and (010) planes (Fig. 4d), while the (001) and (010) planes from the nanoparticles were absent due to the invisible criteria of $h + k + l = 0$ in the body-centered tetragonal structure (Fig. 4e). Consequently, we could distinctly distinguish the phase difference and distribution between CuInSe$_2$ and CuIn$_3$Se$_5$. The dual phase-blended CIS samples (30-CIS and 40-CIS) exhibited remarkably high photocurrents, compared to those of the previous CIS photoabsorbers and pure CuInSe$_2$ and CuIn$_3$Se$_5$ single phases. Thus, we can expect that a correlation between phase distribution and photocurrent enhancement exists, similar to that between an organic photovoltaic cell and a conjugate structure. Typically, high-efficiency photovoltaic cells consist of $p$-$n$ heterojunctions for charge separation through a built-in potential. In particular, our CIS photoabsorber possesses a 3D $p$-$n$ heterophaseic blended heterojunction structure with large grain $n$-type CuIn$_2$S$_3$ matrix and $p$-type CuIn$_3$Se$_5$ nanoparticles. It can efficiently separate the photogenerated electron/hole pairs to the acceptor/donor junction area. Thus, it can be considered that the phase-blended absorber structure is responsible for the remarkably high anodic photocurrent, as compared to that in other photoabsorption layers. It can be also suggested that the small interval between the $p$-type CuIn$_2$S$_3$ nanoparticles and the $n$-type CuIn$_3$Se$_5$ matrix is beneficial for the enhancement in the photocurrent gain owing to the effective built-in potential that efficiently separates the electron/hole pairs.

Thus, we tried to investigate the enhancement in charge transport from the estimation of carrier concentration and depletion width by analyzing the capacitance-voltage (C-V) characteristics of the electrode-electrolyte interface. For the $p$-$n$ phase-blended structure film, the...
entire Mott-Schottky plot shows non-linear characteristic because the overall capacitance in this sample did not consist of a single space-charge region, but was connected with various capacitances such as n-type electrode-electrolyte capacitance ($C_{\text{n}}$), p-type electrode-electrolyte capacitance ($C_{\text{p}}$), and p-n junction capacitance ($C_{\text{pn-p}}$ and $C_{\text{pn-n}}$). In general, the Mott-Schottky plot is a very popular analysis method for the semiconductor/electrolyte interface with a single space-charge capacitance. In some previous works, double-layer structures with p-type and n-type thin films exhibited theoretically and experimentally non-linear C-V profiles with more than two vertexes. Gao et al. demonstrated that p-type and n-type passive double-layer oxide semiconductors, generated on 304-stainless steel due to the corrosion process, formed a p-n junction and exhibited non-linear Mott-Schottky plots [23], which are analogous to the C-V profile of our phase-blended structure, implying that the 30-CIS sample comprises an electrochemically active p-n junction. Even though our phase-blended structure is not a two-dimensional thin film but a 3D nanoparticle embedded junction, the total capacitance can be regarded as a network of a series connection of the semiconductor/electrolyte interface ($C_{\text{n}}$ or $C_{\text{p}}$) and p-n junction ($C_{\text{pn-p}}$ or $C_{\text{pn-n}}$) of the surface conduction type. Until now, there has been no demonstration of a phase-blended structure combining p-type and n-type chalcogenide absorber layers, regardless of the devices, i.e., solar or photo-chemical cells. In the case of n-type semiconductors, the depletion region at the interface is formed at higher applied potentials than at flat band potentials, whereas in p-type semiconductors, the depletion region is produced at low potentials. Thus, in our Mott-Schottky plot, the $C_{\text{n}}$ curve is basically placed in more positive potential than the $C_{\text{p}}$ curve (Fig. 5). In addition, p-n junction capacitance in the phase-blended structure can be effectively produced at the n-type matrix and p-type nanoparticle interfaces, where the assign of capacitance peak was well matched with previous data. Compared to single-phase CIS films, the surface of the n-type CuIn$_3$Se$_5$ matrix in the blended structure is expected to have a relatively lower carrier density due to the compensation from the p-type CuInSe$_2$ nanoparticles, which forms a depletion region. Thus, the flat band potential between the surface and the electrolyte is reduced and shifted close to 1.23 eV, which is the redox potential of the electrolyte, as shown in (Fig. 5 and S3). Using equations S1-4, the depletion region produced within the p-type nanoparticles is much wider than the nanoparticle diameter of ~67.6 nm and thus, the nanoparticles probably become depleted. Similarly, the depletion region formed in the n-type matrix is significantly larger than the interval between the closest nanoparticles, as shown in the TEM images.

Therefore, it can be assumed that the p-n phase-blended structure samples can be sufficiently depleted over the entire area (Figs. 6c and 6d), which can lead to efficient separation of the photo-generated electron-hole pairs and suppression of electron-hole recombination. The synergistic effect of our p-n phase-blended structure in the PEC cells can be clearly elucidated from the charge separation and transport behaviors of the conventional photoelectric devices. A schematic band

![Image of TEM images and Mott-Schottky plot](Figures/figure4.jpg)

**Fig. 4.** (a) and (b) HAADF TEM images of 30-CIS (entire CIS and top region), (c) EDS elemental mapping showing atomic distribution in the nanoparticle and matrix in the 30-CIS sample. SADPs for crystal phase identification in (d) the nanoparticles and (e) the matrix in the 30-CIS sample.

**Table 1** Summary of EDS elemental analysis for Cu (red), In (sky blue), and Se (yellow) in the nanoparticles and matrix.

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![Image of Mott-Schottky plot and fitted curves](Figures/figure5.png)

**Fig. 5.** Mott-Schottky plot (capacitance-voltage) and fitted curves for the phase-blended 30-CIS showing dual photoabsorber characteristics.
diagram of the p-n phase-blended structure for CIS PEC cells is depicted in Fig. 6a. As previously mentioned, since the matrix, which is responsible for primary photocurrent, is an n-type semiconductor, holes will flow from the semiconductor to the electrolyte under light irradiation, while electrons will move to the bottom electrode and circuit, resulting in the generation of anodic photocurrent. In conventional single type PEC cells, a semiconducting material absorbs photons with energies above the band gap, and the electrons are excited from the valence band to the conduction band; however, a lot of electron-hole pairs, which are separated by built-in potential generated at the electrolyte-semiconductor junction, cannot avoid non-radiative recombination (Fig. 6b). Particularly, the unwanted recombination process readily occurs within the absorber because there is no internal driving force to facilitate the transfer of photo-induced holes to the top surface and electrons to the electrode. As a result, the concentration of usable charge carriers is relatively diminished and the photoelectrochemical properties are degraded, despite the high absorption properties of the CIS compounds. On the other hand, in the p-n phase-blended structure, the excited electron-hole pairs can be effectively separated, as the nanoparticles and matrix are partially depleted and a built-in potential is induced in the entire volume, as shown in Figs. 6c and 6d. Furthermore, when the depletion width in the p-type nanoparticles is sufficiently larger than the radius of the nanoparticles, the barrier height at the p-n junction is remarkably suppressed owing to the formation of an incomplete built-in potential, as shown in Fig. 54.

Although electron-hole recombination can occur in the depletion region or at surface defects, the major non-radiative loss mechanism mainly occurs at the bulk region, excluding the minority charge diffusion length and the depletion region. Therefore, our blended structure could suggest a tailored approach to overcome these problems and show high photoelectrochemical properties, as compared to single-phase CIS layers. The valuable photoelectrochemical gain in our phase-blended structure can also be demonstrated by comparing the external quantum efficiency (EQE) of the 30-CIS and 70-CIS samples, as shown in Fig. 7. This result supports the previously suggested theory that effective electron-hole separation occurred due to the formation of a depleted p-n junction and the induced built-in potential that resulted in high photoelectrochemical performances.

Our phase-blended CIS compounds showed a highly enhanced photocurrent; however, the CIS compounds such as CuInSe₂ and CuIn₃Se₅ are severely susceptible to galvanic corrosion by the photoelectrochemical processes in liquid electrolytes. As shown in Fig. S5, under light illumination, the potential-current curve from the cyclic voltammetry sweep in electrolyte showing the magnitude of reduction and oxidation currents clearly reveals the presence of an oxidation potential. On the contrary, the phase-blended CIS was quite stable under the dark condition, which shows its relative stability against electrochemical corrosion. Therefore, the phase-blended CIS is vulnerable to photo-electrochemical corrosion. Some papers have reported that the CIS compounds exhibit weak durability from photo-
electrochemical corrosion. The photoelectrochemical corrosion for the primary CuIn$_2$Se$_3$ phase occurs at around 1.32 V vs RHE by the following chemical reaction:

$$\text{CuIn}_2\text{Se}_3 + b\nu \rightarrow \text{Cu}^{2+} + \frac{2}{3}\text{In}_2\text{O}_3 + \frac{5}{2}\text{Se} \text{surf} (at 1.32 V vs. RHE)$$

The SEM images of the samples before and after the PEC test (Fig. S6) show significant and clearly distinguishable changes due to photoelectrochemical corrosion. The by-product (secondary Se) from the surface of the corroded CIS resulted in highly increased Se ratio from 53.6% to 84.2% (Table S1).

Thus, we additionally coated an Al$_2$O$_3$ passivation layer on the surface. The Al$_2$O$_3$ film suppresses carrier loss by recombination caused by the high density of the surface defect sites and chemical protection, thus enhancing the photocurrent performances and stability as shown in Fig. S7a. This reveals that the carrier transport resistance reduces after surface passivation, as shown in the Nyquist plot result [Fig. S7b]. Consequently, the Al$_2$O$_3$ layer suppressed non-radiative recombination on the surface, and is expected to enhance photoelectrochemical durability. Thus, we carried out chronopotentiometry test with light on/off pulse for 30-CIS with and without Al$_2$O$_3$ passivation (Fig. 8). Although we initially observed almost identical photocurrent values, severe corrosion phenomenon immediately occurred for 30-CIS without the Al$_2$O$_3$ layer. However, the Al$_2$O$_3$ passivated 30-CIS with phase-blended structure maintained 87% of the initial photocurrent even after 1 h, and no significant dark current related to corrosion was observed. Thus, the CIS compounds with phase-blended structure consisting of a p-n junction exhibited remarkably high photocurrents, while their low chemical stability could be partially improved via surface passivation with Al$_2$O$_3$ coatings without significant current drop. In particular, our final CIS photoabsorber ([CuIn$_2$Se$_3$ nanoparticles + CuIn$_2$Se$_3$ matrix] / Al$_2$O$_3$) generated high photocurrents without the aid of metal photocatalysts.

4. Conclusions

The innovative approach for the synthesis of chalcogenide Cu-In-Se compounds presented in this study provides a novel inorganic phase-blended structure consisting of a 3D n-CuIn$_2$Se$_3$ / p-CuInSe$_2$ heterojunction that accords high photoanode performances with dual photoabsorber characteristics. The samples were prepared via a simple one-step annealing process using electrochemically deposited Cu/In bilayer precursors and the supply of plentiful Se vapor with no additional intermediate steps. As a result, the final product is a photoanode with p-CuInSe$_2$ nanoparticles embedded in the n-CuInSe$_3$ matrix. Our phase-blended structure CIS photoanode showed remarkably enhanced photocurrent (12.7 mA/cm$^2$ at 1.23 V vs RHE) and good stability with an ultra-thin Al$_2$O$_3$ protective layer. Based on the TEM and C-V analyses, the enhanced PEC properties were attributed to the depleted nanoparticles and matrix and the induced built-in potential, which effectively separated the photo-generated electron-hole pairs. Contrary to the typical p-type CIGS, CuIn$_5$S$_8$ and Cu$_2$ZnSnS$_4$ compounds, the use of unusual n-type CuIn$_2$Se$_3$ crystals and phase-blended structure afforded unexpected gains for PEC water splitting application.

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Appendix A. Supplementary material

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References

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