

Article

Re-Synthesis of CIGS Nanocrystallites Using Oxidation Roasting Pretreatment from Spent CIGS Targets

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Abstract: The CIGS ($\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$) thin film solar cell sputtering process utilizes only 30% of the original target. The remaining 70% of the target must be recycled to achieve In, Ga, and Se rare metal sustainable use. It is, therefore, very important to establish spent CIGS target recycling technology to reduce environmental damage. CIGS is a tetrahedrally bonded semiconductor with a chalcopyrite crystal structure. Chalcopyrite is resistant to attack by the oxidants used in dissolution due to forming a passivation surface layer. Therefore, increasing the reaction temperature, lixiviating agent, and oxidant concentrations is necessary to enhance CIGS dissolution. The oxidation roasting pretreatment effects on the recovery and leaching of spent CIGS targets are investigated in this study. The results indicated that the proper oxidation roasting pretreatment process could significantly enhance CIGS leaching, reducing costs and increasing the reaction rate. This can be explained by the fact that the chalcopyrite structure was decomposed and transformed into easier dissolvable Cu_2SeO_4 , In_2O_3 , and amorphous Ga_2O_3 after roasting in the air. Cu, In, and Ga recoveries can reach above 99.9% by leaching CIGS roasted at 500 °C in 1 M H_2SO_4 at 60 °C for 1 h. As the roasting temperature was increased to 600 °C, the Ga recovery rate decreased due to the formation of difficult dissolvable $\beta\text{-Ga}_2\text{O}_3$. Mono-dispersed, near-stoichiometric CIGS nanoparticles with a mean crystallite size of 9 nm can be obtained using a direct recycling process combining oxidation, leaching, and re-synthesis processes.



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Keywords: CIGS target; leaching; roasting; nanocrystallites

1. Introduction

Numerous industrial waste materials require conversion into reusable resources or eco-friendly materials to diminish their environmental impact and prevent the exploitation of finite metal resources. One of the most important semiconductor materials used in thin film photovoltaic cells is $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS), which possesses several remarkable advantages, such as high absorption coefficients, good photo-stability, direct band gap semiconductor, and demonstrated high conversion efficiency [1–3]. The sputtering method is frequently used to prepare CIGS absorbers, which offers many benefits, such as easier composition control and suitability for large-scale production. In this popular process, a CuInGa metallic precursor layer is first deposited onto a Mo/glass substrate using CuGa or In metal as the sputtering targets, followed by selenization using Se or H_2Se gases [4–6]. Nevertheless, because of the complexities of employing extremely hazardous H_2Se gas, this procedure incurs costs and causes environmental issues [7–9]. The PV conversion efficiency of CIGS cells can reach 23.35% in laboratory experiments [10]. Sputtering deposition may produce exceptionally dense and well-crystallized CIGS films without extra selenization. Numerous researchers have achieved an efficiency of 7.8% for CIGS thin films made by sputtering from CIGS targets [11,12].

As a result, the availability of a CIGS quaternary sputtering target would simplify the CIGS thin film production process by removing the necessity for selenization [13]. The

initial target usage in the sputtering process for making CIGS thin film solar cells is only approximately 30%. The remaining 70% target must be recycled to achieve sustainable use of rare metals, In, Ga, and Se. Indium and gallium are two essential elements utilized in a variety of industries, including electronics and photovoltaics. Because of their scarcity in nature and the environmental effect of their original manufacturing, indium and gallium recycling is critical. Moreover, recycling indium and gallium can also help reduce the environmental impact of CIGS solar cell manufacturing and disposal, as these elements can be toxic and hazardous when released into the environment. As a result, it is critical to developing wasted CIGS target recycling technology to limit the environmental impact. Currently, wasted CIGS targets are not commonly recycled, resulting in an unsustainable open-loop industrial cycle, necessitating the development of a feasible spent CIGS target recycling process.

Because of its cheap energy costs, minimal air pollution, easy material handling, and low dust and waste disposal, hydrometallurgy has been used to extract important metals for many years. One of the most significant front-end procedures in hydrometallurgy is leaching. The goal of leaching is to dissolve the precious minerals in the concentrate with an aqueous activator solution. CIGS exhibits a chalcopyrite crystal structure that is resistant to attack by the oxidants used in dissolution due to the formation of a passivation surface layer [14]. Therefore, enhancing CIGS dissolution requires increasing the reaction temperature, lixiviating agent, and oxidant concentrations. Oxidation roasting can convert insoluble chalcopyrite (CuFeS_2) into soluble oxides in a dilute sulfuric acid solution [15]. During roasting, chalcopyrite reacts with oxygen to produce copper oxide and sulfur dioxide. The resulting copper oxide can then be leached with sulfuric acid to extract copper from the ore. On the other hand, chalcopyrite remains essentially unreacted under the mild oxidizing conditions of heap leaching due to considerably sluggish leaching kinetics. Dead roasting is an alternative method for converting sulfide concentrates into oxides that can be easily reduced [16]. Alternative chalcopyrite treatment processes have been investigated, including the oxidative roasting of chalcopyrite and its related constituents, such as copper sulfide and iron sulfide [17]. Several technologies have been developed to retrieve valuable constituents from depleted CIGS materials, including pyrometallurgical and hydrometallurgical processes [18,19]. Pyrometallurgical methods are primarily used to remove selenium but do not offer an effective way to separate and recover the remaining valuable metals. Gustafsson et al. [20] studied high-purity selenium recycling from CIGS solar cell waste materials using oxidation roasting at 500–1000 °C. They observed the formation of gaseous selenium dioxide at temperatures above 500 °C, which could be separated from the other elements that remained in the solid state. This study further revealed that almost complete selenium separation was obtained after roasting at 800 °C for 1 h.

However, the effects of oxidation roasting on CIGS leaching and Cu, In, and Ga recoveries have not been reported to the best of our knowledge. On the other hand, hydrometallurgical processes efficiently achieve the high-leaching efficiency of valuable metals. However, the separation of gallium and indium may pose a challenge due to the lack of selectivity in leaching. Amato et al. [21] developed a method for extracting indium and gallium from end-of-life copper indium gallium selenide (CIGS) photovoltaic panels. Various leaching agents (H_2SO_4 , HCl , HNO_3 , citric acid, and NaOH) were employed with an oxidant agent (H_2O_2 and glucose) for efficient metal extraction. It was determined that a combination of citric acid and hydrogen peroxide was the most effective. This study also confirmed the positive effect of hydrogen peroxide on the extraction efficiency of both indium and gallium. The findings indicate that the leaching process typically demands a significant quantity of oxidant, potentially inflating the treatment cost. Hu et al. [22] developed a method for the comprehensive recovery of valuable metals in spent CIGS materials. The method involves three steps: leaching with HNO_3 to separate indium, precipitating to obtain a copper gallium selenite mixture, and calcination to recover selenium. Copper and gallium were almost completely leached in HNO_3 , while indium entered the slag phase as

indium selenite. After leaching, copper, gallium, and selenium can be completely recovered from the leach liquor using magnesium oxide as a precipitant. Subsequently, the separation of Se in the residue and precipitates can be achieved at 800 °C for 30 min. Eventually, the Cu, In, Ga, and Se recovery yields were 99.23%, 96.82%, 98.08%, and 96.38%, respectively. This recovery process, however, is extremely sophisticated, and total separation and recovery of all constituents remain the focus of future studies.

Closed-loop recycling is when a product or material may be consumed and converted back to raw materials endlessly without losing its properties. The advantages of closed-loop recycling include reduced raw material production and usage, reduced environmental impact, and reduced resource depletion. Materials can be recycled forever in ideal conditions with little to no net change in quality or characteristics. Closed-loop recycling is important for conserving precious and scarce metals, such as gallium (Ga), indium (In), and selenium (Se). However, the closed-loop recycling of the CIGS target is rarely reported.

CIGS thin film solar cells are presently mostly manufactured utilizing vacuum methods, which have several drawbacks, including high production costs and difficulties scaling up. As a result, there has been a lot of interest in developing colloidal techniques, such as spin casting or printing, to make CIGS thin film solar cells with well-controlled stoichiometry, high material utilization, and low processing equipment cost [23]. It has been reported that CIGS nanocrystals have been successfully manufactured and employed in the production of CIGS thin film solar cells or targets. The heating-up process has been the most successful and extensively utilized method in nanocrystal production thus far [24,25]. In this study, we investigated the effects of oxidation roasting pretreatment on the recovery and leaching of spent CIGS targets using differential thermal analysis (DTA), thermogravimetry (TG), X-ray diffractometry (XRD), scanning electron microscopy (SEM), and X-ray fluorescence spectrometry (XRF). Additionally, we developed a direct recycling process combining oxidation and leaching processes and the re-synthesis of CIGS nanoparticles to recover CIGS and achieve the closed loop.

2. Materials and Methods

2.1. Materials

Quaternary alloy sputtering targets composed of copper indium gallium selenide (CIGS) were procured for this investigation from Bosin Technology Co., Ltd., Tainan, R.O.C. The constituent of the CIGS target was estimated via an XRF and found to be 17.68% copper, 8.19% indium, 6.71% gallium, and 47.42% selenium by weight. The crystalline phase of the CIGS target is depicted in Figure S1 (Supplementary Material), which illustrates that the sample displays a pure chalcopyrite phase without any secondary phases detected. Subsequently, the sample was ground, smashed, and passed through a 200-mesh sieve. Se powder (99.99%, 200 mesh) and oleylamine (OLA, 80–90%) were acquired from Alfa-Aesar, Ward Hill, MA, USA and Acros Tech., Livonia, MI, USA, respectively.

2.2. Experimental Procedures

The CIGS sieved powders were roasted in the air at 400–600 °C for 30 min. A total of 0.15 g roasted CIGS powder was then added into 30 mL H₂SO₄ aqueous solution (1 M) and heated to 60 °C for 1–4 h. The mixing rate was about 600 rpm.

Following the leaching procedure, the samples were centrifuged and washed with deionized water before being centrifuged again. The washed powders were then dried at 80 °C. Copper (Cu), indium (In), and gallium (Ga) contents in the filtrate were measured using inductively coupled plasma mass spectrometry (ICP-MS) on Hewlett Packard 4500 equipment. The leaching recovery (R_i) of copper, indium, and gallium was estimated using Equation (1)

$$R_i = (C_i \times V_i) / (M_o \times X_o) \times 100\% \quad (1)$$

where M_o (g) and X_o (%) are the mass and element content of wasted CIGS, respectively; C_i (g/L) and V_i (L) are the element concentration and volume of the filtrate, respectively.

The crystalline phase of the roasted and leached specimens was analyzed using an X-ray diffractometer with CuK α radiation from Dandong Fangyuan DX-2700, located in Sandong, China. Furthermore, the chemical compositions of the roasted specimens were identified through the utilization of X-ray fluorescence (XRF) spectroscopy with a ZSX 100e instrument manufactured by Rigaku, Tokyo, Japan.

A filtrate including Cu⁺, In³⁺, and Ga³⁺ ions was produced after leaching 0.9 g of wasted CIGS targets roasted at 500 °C in 1 M H₂SO₄. The metal ions solution was then dried at 100 °C for 12 h before being combined with OLA (20.5 mL) and heated to 100 °C in air. A total of 25 mL of OLA and 8.4 mmol of Se were added to a separate three-neck flask. This combination was then mixed with the metal ions solution. The reaction temperature was raised to 250 °C and maintained for 1 h. After the reaction, the liquid was cooled down to 80 °C, and 30 mL of alcohol was introduced to terminate the reaction. Subsequently, the solution was centrifuged for 5 min at 6000 revolutions per minute. Before being dispersed in toluene, the product underwent an ethanol-washing process. After purification, the CIGS nanoparticles, which were uniformly dispersed, were isolated employing centrifugation at 6000 revolutions per minute for 20 min. An X-ray diffraction (XRD) technique was employed to delineate the nanocrystalline phase of CIGS, utilizing Cu K radiation. Additionally, the morphology, size, and chemical composition of the crystallites were analyzed using transmission electron microscopy (TEM) (Hitachi HF-2000, Chiyoda City, Japan) and energy-dispersive X-ray spectroscopy (EDS) equipment.

3. Results

Table 1 shows the chemical compositions of the roasted CIGS powders determined using XRF. The table indicates that the selenium content decreased with the increasing roasting temperature, and the molar ratio among Cu, In, and Ga remained at 1.00:0.69:0.33. Gustafsson et al. [20] reported that selenium, as selenium dioxide, can be separated from CIGS materials through oxidation at temperatures above 500 °C. These results suggest that selenium was oxidized into volatile SeO₂ gas, and Cu, In, and Ga remained solid during roasting.

Table 1. Chemical compositions of the roasted CIGS powders determined using XRF.

Element	Condition							
	Without Roasting		400 °C		500 °C		600 °C	
	at%	Ratio	at%	Ratio	at%	Ratio	at%	Ratio
Cu	25.59	1.00	29.32	1.00	36.51	1.00	45.79	1.00
In	17.68	0.69	19.74	0.67	25.01	0.68	31.79	0.69
Ga	8.33	0.33	9.80	0.33	12.06	0.33	15.16	0.33
Se	48.40	1.90	41.13	1.40	26.42	0.72	7.25	0.15

The XRD patterns of the samples roasted at different temperatures are shown in Figure 1. For the sample roasted at 400 °C, the chalcopyrite phase was accompanied by a significant In₂O₃ and Cu₉Ga₄ as the main phase. In the case of the sample roasted at 500 °C, the chalcopyrite phase disappeared, and Cu₂SeO₄ and In₂O₃ were predominant with a small amount of Cu_{2-x}Se. As the roasting temperature was increased to 600 °C, all selenides disappeared and transformed into Cu₂SeO₄, In₂O₃, and β -Ga₂O₃.

Figure 2 shows the DTA/TG curves of the sieved CIGS powder. The first exothermic peak, accompanied by the increase in weight loss rate, was observed at about 370 °C. Paszkowicz et al. [26] reported that heating CuInSe₂ in the presence of oxygen produces In₂O₃ and volatile SeO₂ in the 150–300 °C range. Hariskos et al. [27] investigated the CIGS thin film oxidation mechanism. They observed that thermal oxidation in air at 200 °C led to the formation of In₂O₃, Ga₂O₃, and SeO₂ at the surface, and no Cu_xO was detected. Based on the XRD result and previous studies [26,27], the first exothermic peak at 370 °C in the DTA curve can be ascribed to CIGS oxidation at the surface. Note that the Cu₉Ga₄ phase was formed rather than the Cu_xO phase other than In₂O₃ and residual CIGS phase after

roasting at 400 °C for 30 min (Figure 1). This may be due to CIGS oxidation in air at low temperatures (200–400 °C) producing a continuous dense crystalline In_2O_3 and amorphous Ga_2O_3 [28] accumulated layer covering the whole interface. The dense oxide layer inhibits further oxidation, accounting for the residual CIGS in the interior of particles and the simultaneous formation of Cu_9Ga_4 after roasting at 400 °C. This is consistent with the observation of Kazmerski et al. [29], who reported that In_2O_3 with small amounts of SeO_2 were observed on the CuInSe_2 surface after heat treatment over the 100–300 °C temperature range. The DTA curve baseline between 410–455 °C is nearly straight, indicating that an equilibrium in O_2 and SeO_2 gas diffusion through the interfacial layer was reached during that temperature range. A distinct exothermic peak at 510 °C, accompanied by a rapid increase in weight loss, was observed, indicating an intensive oxidation of the inner cores of the CIGS particles and the simultaneous chalcopyrite structure decomposition. A large quantity of mass loss still occurred when the temperature was over 500 °C, which may be attributed to the sublimation of SeO_2 [27].

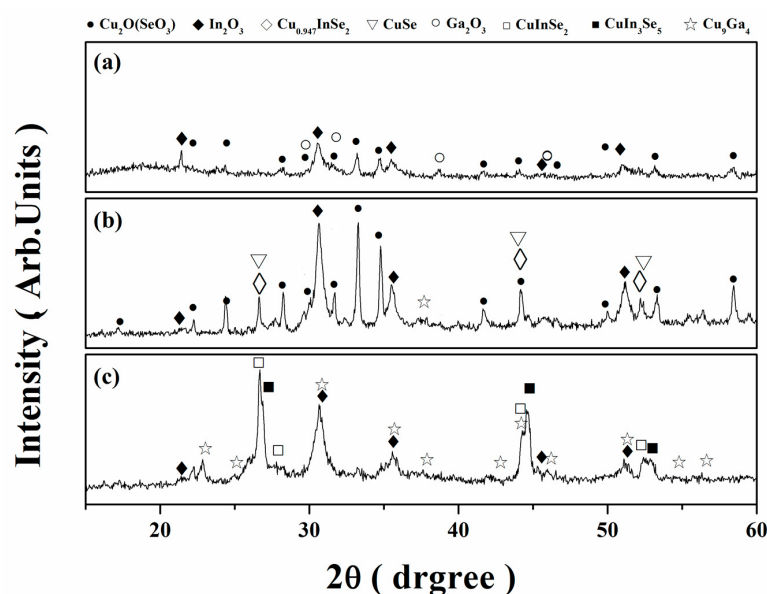


Figure 1. XRD patterns of the samples roasted at different temperatures for 30 min (a) 600 °C, (b) 500 °C, and (c) 400 °C.

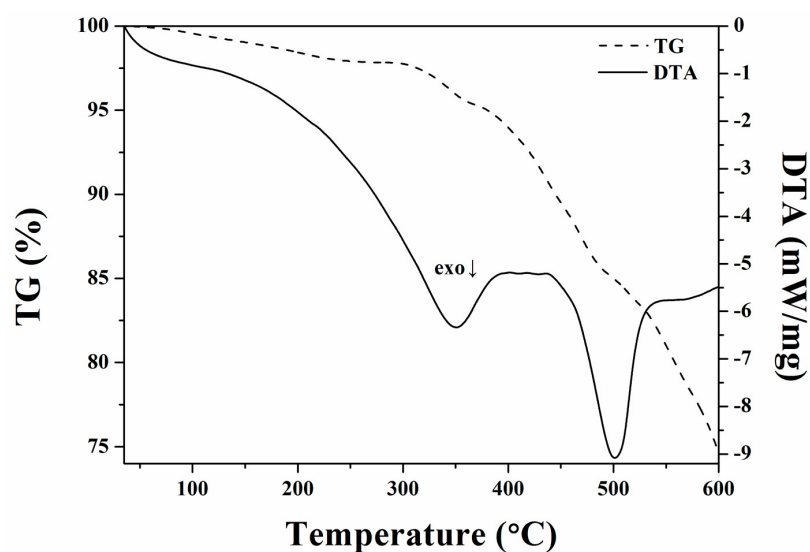


Figure 2. DTA/TG curves of the sieved CIGS powder.

The XRD result of the sample roasted at 500 °C (Figure 1) shows that In_2O_3 and Cu_2SeO_4 were predominant with a small amount of Cu_{2-x}Se . This suggests that the formation of dense In_2O_3 and Cu_{2-x}Se on the CIGS surface increases the SeO_2 partial pressure in the sample interior, promoting Cu_2SeO_4 formation. It is interesting to note that as the roasting temperature was raised to 600 °C, the $\beta\text{-Ga}_2\text{O}_3$ phase was observed in addition to the preformed In_2O_3 and Cu_2SeO_4 at low temperatures, which is consistent with the observations of Wang et al. [30], who reported that after calcination at 630 °C, the $\alpha\text{-Ga}_2\text{O}_3$ phase is converted completely into the $\beta\text{-Ga}_2\text{O}_3$ phase.

Figure 3 shows the leaching time effect in 1M sulfuric acid solution at 60 °C on Cu, In, and Ga recoveries for the samples roasted at different temperatures. The sample without roasting treatment exhibited the lowest Cu, In, and Ga recoveries. For the sample roasted at 400 °C, the Cu and In recoveries were lower than those of other samples roasted at higher temperatures. This occurred due to the presence of the difficult-to-dissolve chalcopyrite phase.

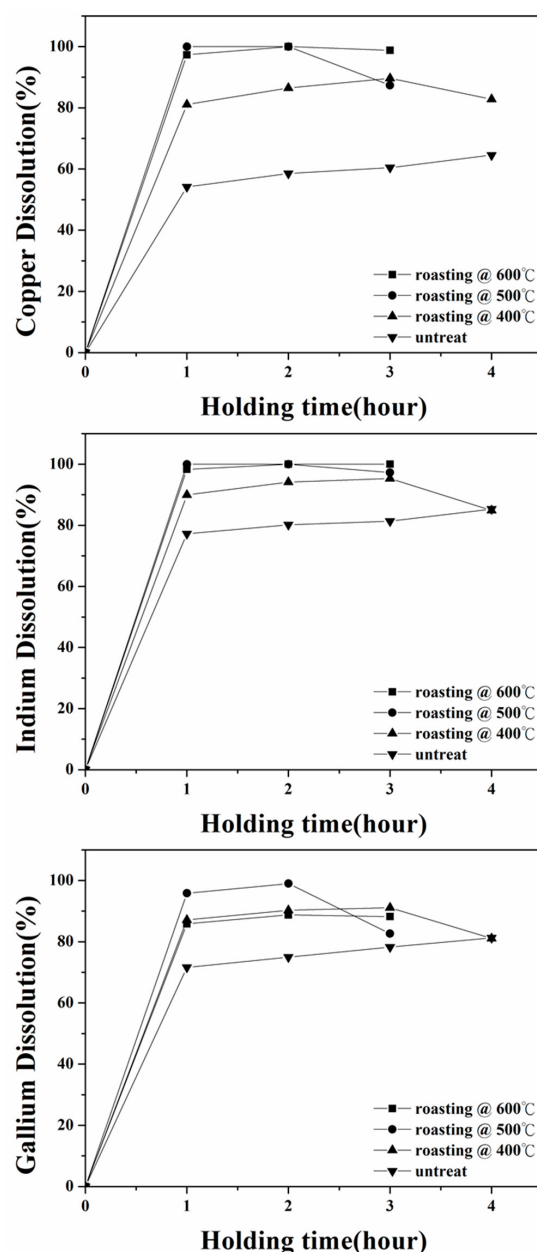


Figure 3. Leaching time effect in 1M sulfuric acid solution at 60 °C on Cu, In, Ga recoveries for the samples roasted at different temperatures.

The XRD pattern for the sample roasted at 400 °C after leaching at 60 °C for 4 h is shown in Figure 4. After the leaching process, the observation of the InSe and elemental selenium phases, along with residual CIGS, confirm that chalcopyrite exhibits a high degree of resistance to the sulfuric acid solution.

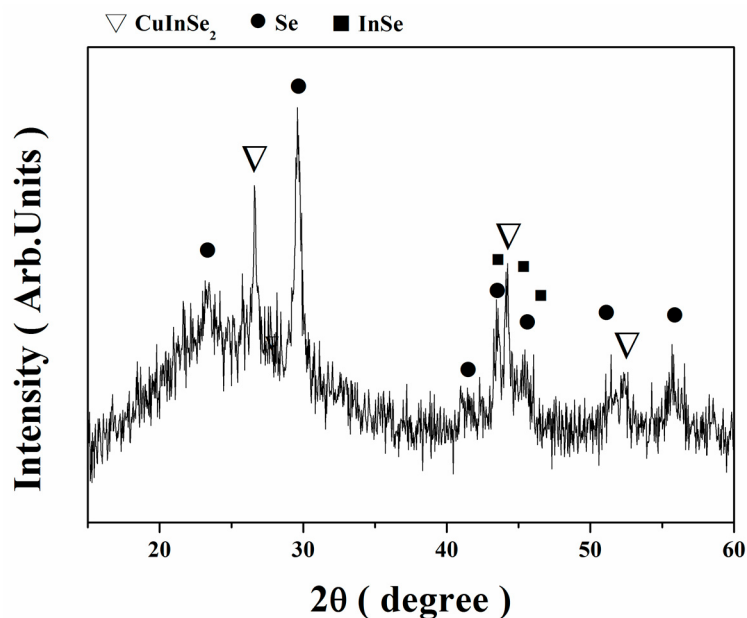


Figure 4. XRD pattern of the residue after 4 h of leaching process at 60 °C, of the CIGS target roasted at 400 °C.

As the roasting temperature was raised to 500 °C, the chalcopyrite structure completely decomposed, leading to Cu, In, and Ga recoveries reaching 99.9% in 1 h. Nevertheless, when the leaching duration was extended to 3 h, the recoveries decreased, and the cause for this reduction remains obscure, requiring additional investigation. In the case of the sample roasted at 600 °C, the Cu and In recoveries reached 99.9% in 1 h. However, Ga recovery declined to about 90%. Ohira et al. [31] investigated the chemical stability of the β -Ga₂O₃ single crystal, explored etchants for wet etching, and observed that β -Ga₂O₃ is chemically stable against attack by acids and alkalis except for aqueous HF and NaOH. As the roasting temperature was increased to 600 °C, β -Ga₂O₃ was formed (Figure 1), accompanied by chalcopyrite phase decomposition, which led to a decline in Ga recovery.

Hu et al. [22] used a hydrometallurgy process to recover valuable metals in spent CIGS materials and reported that under the optimal experimental leaching conditions (temperature: 80 °C, time: 3.5 h, HNO₃ concentration: 3.2 mol/L, Liquid/Solid ratio: 9 mL/g), the leaching yields of Cu, Ga, Se were 98.74%, 95.55%, 60.22%, respectively, while the leaching yield of In was only 3.18%. Amato et al. [21] investigated the recovery of In and Ga metals in spent CIGS using various leaching agents (H₂SO₄, HCl, HNO₃, and citric acid) and found that the leaching efficiency of In was greater than 80%, but the leaching efficiency of Ga was less than 40% for the inorganic acids (H₂SO₄, HCl, and HNO₃). The In and Ga leaching efficiency decreased to 45% and 10%, respectively, for citric acid. Hsiang et al. [19] used the autoclave leaching of CIGS powder in H₂SO₄ solution with H₂O₂ as a strong oxidant. The rate-controlling step in the CIGS leaching process is the decomposition of copper–selenium compounds. Autoclave leaching at 140 °C for 4 h with 3 M H₂SO₄ as the leaching agent and H₂O₂ as the oxidant results in nearly complete CIGS dissolution. The treatment has an immediate effect on the CIGS structure, a tetrahedrally bonded semiconductor with a chalcopyrite crystal structure. Gustafsson et al. [18] on the other hand, investigated the possibility of high-temperature chlorination with NH₄Cl for the separation of Cu, In, Ga, and high-purity Se. The results showed that using temperatures higher than 300 °C resulted in high efficiency. Compared to the literature [18–22], the

complete leaching of Cu, In, and Ga can reach a lower temperature and shorter time using oxidation roasting pretreatment.

Figure 5 presents the X-ray diffraction (XRD) patterns of CIGS that were synthesized at 250 °C for 1 h, using the leachates obtained from leaching waste CIGS targets as the primary raw materials. The figure shows that a pure CIGS phase (JCPDS #35-1102) was obtained.

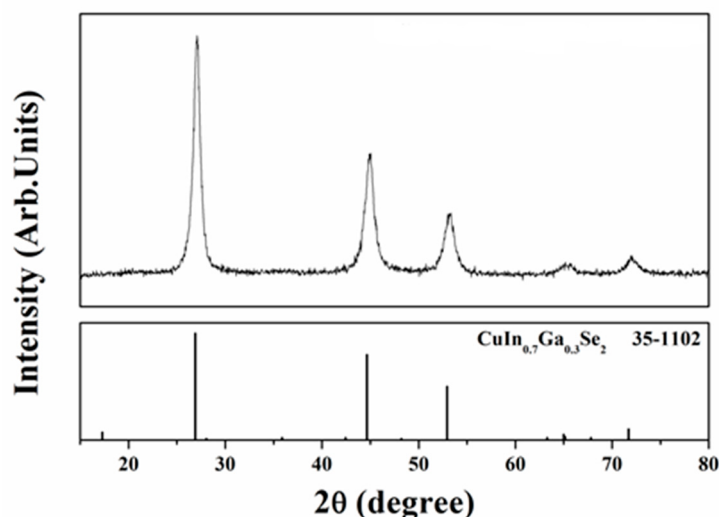


Figure 5. XRD patterns of CIGS powder synthesized at 250 °C for 1 h using the leachates after leaching spent CIGS targets.

Furthermore, the TEM image of the CIGS nanocrystals, synthesized at 250 °C for 1 h, is illustrated in Figure 6. Based on the TEM image, the nanocrystals are essentially monodispersed, and the average size of the crystallites is 9 ± 2 nm. It is worth noting that the average size of the CIGS crystals was estimated using the Scherrer equation, which was based on the X-ray diffraction (XRD) pattern of the (112) peak ($2\theta = 26.897^\circ$). The estimated value was approximately 10.9 nm, which closely agrees with the average size obtained from the TEM results. EDS data (Figure S2 and Table S1, Supplementary Material) confirmed that the chemical composition of the nanocrystallite is similar to Cu:In:Ga:Se = 1:0.66:0.29:2.07. The selected area diffraction pattern matching (112), (220), and (312) lattice planes of the CIGS chalcopyrite phase (JCPDS #35-1102) were detected. Our results suggest that an integrated recycling approach incorporating oxidation and leaching processes and the re-synthesis of CIGS nanoparticles can effectively recover CIGS materials for reintegration into the CIGS supply chain.

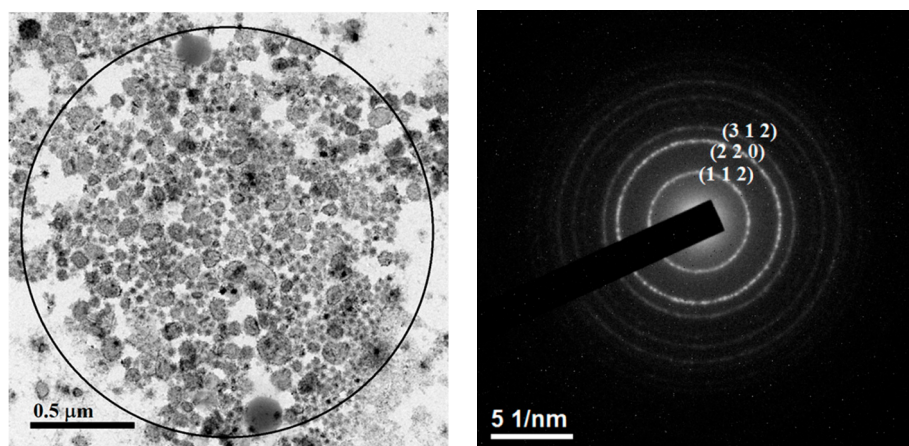


Figure 6. TEM micrograph and selected area diffraction pattern of the CIGS nanocrystals obtained at 250 °C for 1 h.

4. Conclusions

- (1) The proper oxidation roasting pretreatment can significantly enhance CIGS leaching. Compared to the literature, the complete leaching of Cu, In, and Ga can reach a lower temperature and shorter time using oxidation roasting pretreatment;
- (2) After roasting at 400 °C, the chalcopyrite phase was accompanied by significant residual chalcopyrite, In_2O_3 , and Cu_{2-x}Se as the main phase. As the roasting temperature was raised to 500 °C, Cu_2SeO_4 and In_2O_3 were predominant, with a small amount of Cu_{2-x}Se . As the roasting temperature increased to 600 °C, all selenides disappeared and transformed into Cu_2SeO_4 , In_2O_3 , and $\beta\text{-Ga}_2\text{O}_3$;
- (3) For the sample roasted at 400 °C, the Cu and In recoveries were lower than those for other samples roasted at higher temperatures due to the difficult-to-dissolve chalcopyrite phase. The Cu, In, and Ga recoveries reached above 99.9% by leaching CIGS roasted at 500 °C in 1 M H_2SO_4 at 60 °C for 1 h. However, as the roasting temperature was raised to 600 °C, Ga recovery declined to about 90% due to the difficulty of dissolving $\beta\text{-Ga}_2\text{O}_3$;
- (4) A direct recycling process involving oxidation, leaching, and re-synthesis can yield nearly stoichiometric CIGS nanoparticles that are nearly mono-dispersed and have an average crystallite size of 9 nm. This is very helpful in completing the closed-loop recycling of CIGS targets.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met13050893/s1>, Figure S1: XRD pattern of the CIGS target. Figure S2: EDS spectrum of the CIGS nanocrystals, synthesized at 250 °C for 1 h. Table S1: Chemical composition of the CIGS nanocrystals, synthesized at 250 °C for 1 h based on EDS results.

Author Contributions: Conceptualization, H.-I.H. and C.-C.C.; methodology, H.-I.H. and C.-Y.C.; investigation, C.-Y.C.; resources, H.-I.H. and C.-C.C.; data curation, C.-Y.C.; writing—original draft preparation, H.-I.H.; writing—review and editing, C.-C.C.; visualization, C.-Y.C.; supervision, H.-I.H.; project administration, H.-I.H.; funding acquisition, H.-I.H. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available upon request from the authors.

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Conflicts of Interest: The authors declare no conflict of interest.

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