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Research article

A competitive candidate for the Cu_2ZnSnS_4 compound in solar photocatalytic degradation of organic pollutants

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Abstract: This study focused on preparing and analyzing two sulfide compounds: Cu_2ZnSnS_4 and Cu_2BiSnS_4, in order to assess their effectiveness in breaking down pollutants using solar radiation as a photocatalyst method. The results indicated the formation of crystalline phases for both compounds with variations in crystal lattice parameters while closely matching the desired composition ratios. The research also highlighted a nanoparticle morphology with variances in nanoparticle size and distribution observed between the two compounds. The results indicated that both compounds possess an energy gap falling within the visible light spectrum and are thus capable of absorbing radiation effectively. Enough tests under sunlight for photocatalytic purposes demonstrated a superior performance in breaking down organic pollutants with methyl green dye, achieving an 82% degradation efficiency in the Cu_2BiSnS_4 compound compared to the Cu_2ZnSnS_4 compound, which exhibited a photodegradation efficiency of 75%, over a similar exposure duration. The distinct disparity in efficiency between the two compounds is from differences in the size and shape of the nanoparticles as well as their distribution and surface characteristics, influencing the movement of charge carriers and light absorption dynamics. According to the findings, the authors suggest that Cu_2BiSnS_4 shows potential as a catalyst for solar photocatalysis applications due to its unique optical and structural properties, making it an asset in the development of environmentally friendly solutions for water purification and mitigation of environmental pollutants.

Keywords: Cu_2ZnSnS_4 (CZTS); Cu_2BiSnS_4 (CBiTS); sulphide photo catalyst; photo-catalysis; organic pollutant degradation; nanocrystalline materials

1. Introduction

Today, one of the environmental issues that is widely separated around the world is water pollution [1]. These pollutants include dyes that are released from plastics, papers, rubbers, and textile products. Therefore, treating wastewater before releasing it into natural sources is an important matter that should be taken into consideration [2]. To purify the wastewater, catalyst materials are utilized as non-toxic and inorganic materials with the help of sunlight. Various materials have been used as a photocatalyst due to their suitable properties for the purification of wastewater, such as chemical stability, low cost, and low toxicity [3]. The Cu_2ZnSnS_4 (CZTS), TiO_2, Cu_2FeSnS_4, ZnO, ZnS, Cu_2BaSnS_4 CdS, and Cr_2O_3 [4–7] compounds are widely investigated as photocatalyst materials in visible light, in addition to heterojunction $ZnIn_2S_4$–$CdIn_2S_4$ [8] and piezo-photocatalytic oxidation of nitrogen into nitrate $Bi_{24}O_{31}C_{l10}$ [9]. However, these materials have issues limiting their efficiency degradation as photocatalytic compounds in sunlight because of their specific optical properties like a wide band gap and absorption coefficient. Among these materials, the Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ compounds are suitable for the dye gradation and are regarded as an alternative material to other wide band gap compounds [10]. In this regard, authors have focused on the quaternary chalcogenide Cu_2ZnSnS_4 compound. According to the previous reports, the degradation efficiency of different dyes was observed to vary from 5% to 62%, like rhodamine B and methylene blue [11–14]. Meanwhile, in this manuscript, the degradation of methyl green dye with 60 min of light exposure was about 75% by using an aqueous solution of the Cu_2ZnSnS_4 compound mixed with methyl green dye. This indicates the importance of optical property in the synthesized Cu_2ZnSnS_4 nanoparticles by the solvothermal method. In addition, the authors in this manuscript seek to prepare another compound that has optimal optical properties that lead to increasing the efficiency of photocatalytic activity. Therefore, a new durable quaternary chalcogenide Cu_2BiSnS_4 (CBiTS) compound has been synthesized by the solvothermal method as a photocatalyst in the solar radiation of organic pollutants like methyl green dye. This compound has unique properties that make it suitable for use as a photocatalyst. Among these properties is the morphology of nanoparticles, which is enhanced compared with the morphology of nanoparticles in Cu_2ZnSnS_4 as in our previous report [15]. So, it is regarded as a competitor to the Cu_2ZnSnS_4 compound. Specific research on Cu_2BiSnS_4 as a photocatalyst for pollutant removal appears to be limited or not widely available in the scientific literature; however, the authors searched in Science Direct and Web of Science and did not find any articles about this application of the Cu_2BiSnS_4 compound. The Cu_2BiSnS_4 compound has good optical properties such as light absorption and a suitable energy gap, and it has potential for photocatalytic operation in visible light, in addition to other properties that make it a promising candidate in environmental remediation applications, including the destruction of organic pollutants such as dyes. In general, the photocatalytic process is affected by the recombination process generated as a result of light absorption [16]. Therefore, authors believe that the doping process may improve the recombination process, which in turn enhances photocatalysis based on what was proven through our previous study related to the effect of substitution between elements within the compound [17–20]. On this basis, the Cu_2ZnSnS_4 compound was doped by replacing the Zn element with the Bi element to form the Cu_2BiSnS_4 compound. It is a relatively new compound used in photovoltaic and energy applications and is considered environmentally friendly because it consists of non-toxic elements that are abundant in nature. Authors also believe that this compound can be used in photocatalysis to remove pollutants, but there are challenges that need to be addressed, such as improving its synthesis methods, improving the dynamics of charge carriers, and enhancing its stability and operational conditions, among others. Therefore, the importance of the research focuses on studying a new compound that competes with compound CZTS in the photocatalytic process. Therefore, compound CBiTS was chosen because it has physical and chemical properties that make it a good candidate for use in solar photocatalytic degradation of organic pollutants.

2. Materials and methods

2.1. Synthesis of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds

To synthesize by the solvothermal method, we begin with 29.87%, 15.15%, and 21.12% from $CuCl_2$, $ZnCl_2$, and $SnCl_2$, respectively, to prepare the initial solution at 2:1:1 stoichiometry in the 50 mL ethylene glycol (EG) solvent under a magnetic stirrer until a homogenous solution is obtained. Subsequently, we added 33.86% of Ch_4N_2S to the initial solution while stirring continuously. Finally, 0.64 g [21] from polyvinylpyrrolidone (PVP) as a stabilizer was added to the final solution with continuous magnetic stirring for 2 h until a homogenous solution was formed. Meanwhile, the homogeneous solution was transferred into the autoclave at 200 °C for 14 h. After the reaction time ended and the solution had cooled at room temperature, the resulting solution was washed several times using a mixture of ethanol and deionized water (DI water) to remove any impurities or solvent residues. The final stage of the method was to dry the washed solution in a dryer at 80 °C for 3 h. Then a black dried powder was obtained, which returned to the Cu_2ZnSnS_4 compound. The same procedure was repeated to prepare the Cu_2BiSnS_4 compound at the following proportions: 24.94%, 29.24%, 17.58%, and 28.24% of $CuCl_2$, $BiCl_3$, $SnCl_2$, and CH_4N_2S, respectively.

2.2. Characterization

To determine the crystal structure and the crystal phases of the samples, and to ensure the purity of the phases, X-ray diffraction (XRD) was used, and the analysis was performed using an XRD device that operates at a Cu-Ka radiation wavelength of 1.5406 Å. To study the optical properties of the samples and evaluate the optical energy gap, an ultraviolet and visible spectrometer (UV-visible) was used in the wavelength range from 200 to 1100 nm. To view the shape of nanoparticles and investigate their size and distribution in the samples, a field emission scanning electron microscope was used. Finally, to evaluate the photocatalytic activity of the samples and study the photo-degradation rate by stimulating the decomposition of methyl green dye under sunlight, the dye concentration was measured after different periods using a UV-visible spectrometer before and after exposure to sunlight.

3. Results and discussion

3.1. Crystal structure properties

The crystal structure and phase evaluation of Cu_2ZnSnS_4 and Cu_2BiSnS_4 nanocrystals were investigated by an XRD pattern as shown in Figure 1. The dominant diffraction peaks of both samples were obtained at 2θ values of 28.45 and 28.53°, which were indexed to correspond to the (112) plane of the kesterite crystal structure (PDF: 34-1246 ICSD). It is noted from Figure 1 and Table 1 that both compounds have a similarity in the basic crystal structure. However, slight changes in the positions of the peaks or their crystallization may be observed due to the difference in the ionic radius of bismuth compared to zinc, which in turn may lead to a change in the crystal lattice. Different compounds display diffraction peaks at varying angles, signifying crystalline reflections due to the way atoms are arranged in the material. There was a shift in diffraction peak positions toward angles with observations made earlier as in the previous reports [22]. The crystal structure of Cu_2ZnSnS_4 showed crystallinity compared to Cu_2BiSnS_4 due to the difference in ionic radius between the Bi^{3+} and Zn^{2+} ions.

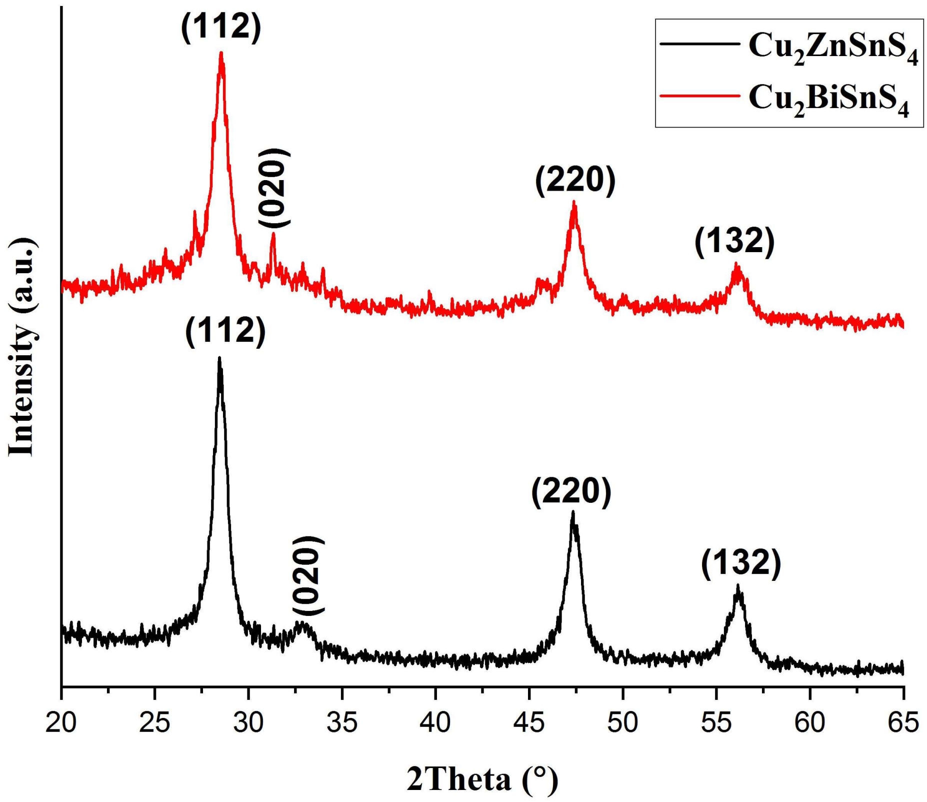

Figure 1. XRD pattern of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds.

It was also noted that replacing zinc with bismuth may result in a small change in the dimensions of the crystal lattice as well as increase in the lattice constants and the unit cell volume. The increase in the unit cell volume is attributed to the expansion of the crystal lattice by bismuth and different interatomic distances between the atomic levels, which lead to an increase in the level of disorder in the crystal lattice, as summarized in Table 1.

Table 1. Crystal structure parameters of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds.

Sample	2θ (°)	Full width at half maximum (FWHM) (°)	Crystal size (Å)	Strain (%)	Lattice constants		Disorder parameter $\eta = c/2a$	Unit cell volume $V = a^2c$
					a (Å)	*c* (Å)		
Cu_2ZnSnS_4	28.45	1.3106	6.26	3.5171	5.653	10.537	0.9319	336.72
Cu_2BiSnS_4	28.53	1.6846	4.57	5.9711	5.661	10.562	0.3929	338.51

When comparing the XRD patterns of both samples side by side, we noticed some peaks in the Cu_2BiSnS_4 compound. These additional peaks could be due to factors like changes in crystal structure parameters and the composition of the Cu_2BiSnS_4 compound altering. The appearance of a phase during the compound's preparation process might be responsible for this change in composition. Also, the larger atomic radius of bismuth contributes to its tendency to form compounds or compounds that contain bismuth. Henceforth, the extra peaks could signify reflections originating from these compounds. Swapping zinc with bismuth generates crystalline levels leading to a potential reorganization of atoms inside the crystal lattice or an augmentation in atomic disorder (distortion) resulting in the emergence of novel peaks. Although there are variations that specifically impact the characteristics of the substance in question, the Cu_2BiSnS_4 compound exhibits absorption capabilities due to bismuth's influence on its electronic structure, resulting in enhanced photocatalytic properties of the compound, a topic that will be explored further in this manuscript.

3.2. Elemental compositions of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds

To investigate the elemental composition of the samples, energy dispersive X-ray spectroscopy (EDS) was used as shown in Figures 2 and 3. The results display the presence of the four primary elements of the compound: copper, zinc or bismuth, tin, and sulfur. The atomic ratios are near the stoichiometric values of 2:1:1:4 for the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds, indicating that the preparation by the solvothermal method became powerful in controlling the ratio of the elements, which is an essential issue in improving the photoelectric properties of the material. It is also stated that there are no enormous impurity elements, which indicates the success of the method, which is exceptionally free of contaminants or secondary phases. The distribution maps for each of the four elements also show a homogeneous spread at the surface of the pattern. This homogeneity contributes to reducing defects within the crystal structure and growing the best of the material from an electronic factor of view. This homogeneity is likewise a crucial indicator of the formation of a homogeneous unmarried segment or an excellent distribution of elements, which helps the formation of the tetragonal shape of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds. We considered that, based on the effects of the EDS examination, the solvothermal approach changed into success in making ready the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds through the matching of the atomic ratios with the stoichiometric values, the homogeneous distribution of elements within the elemental maps, and the absence or negligibility of impurities and secondary levels.

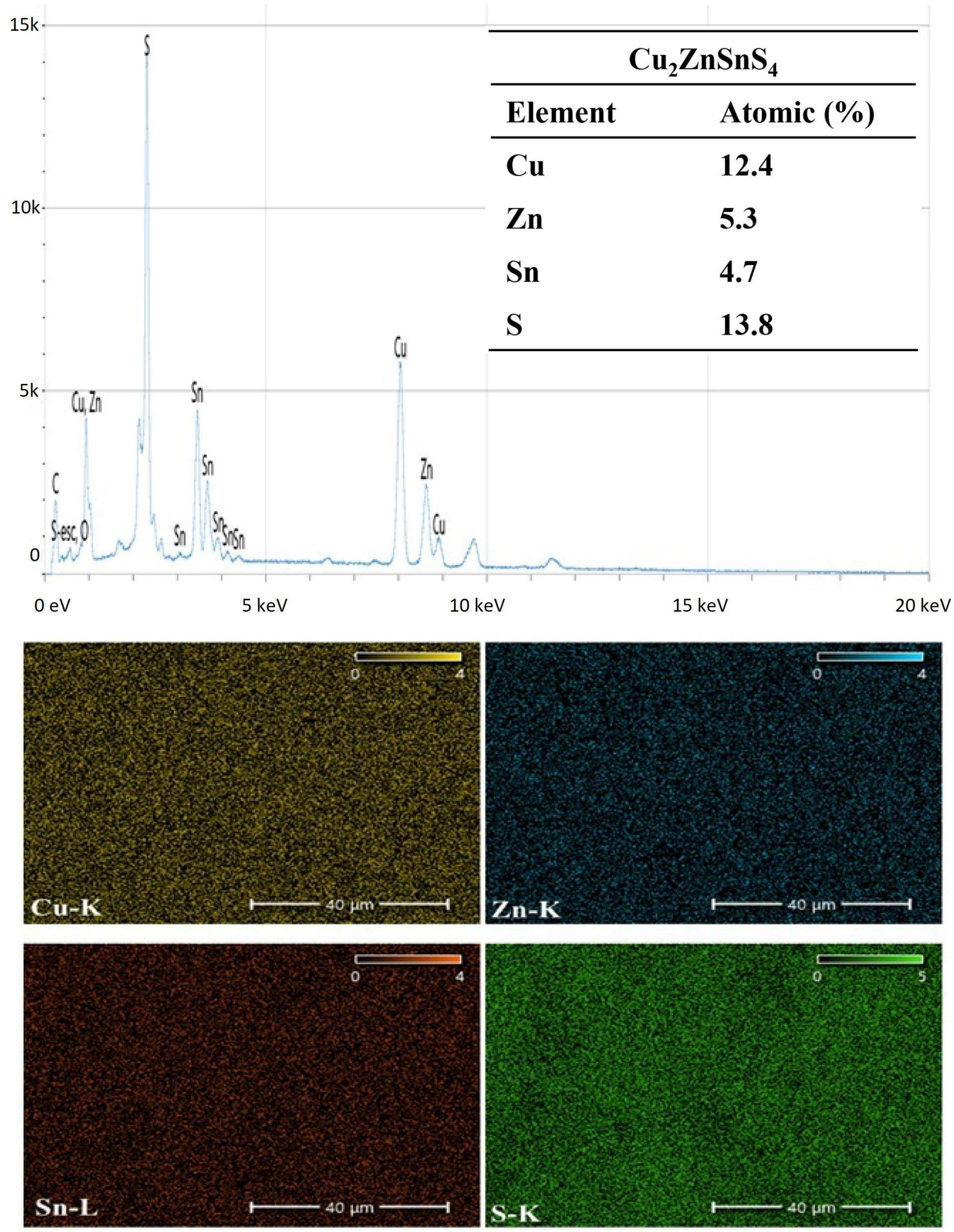

Figure 2. EDS spectrum of the Cu_2ZnSnS_4 compound.

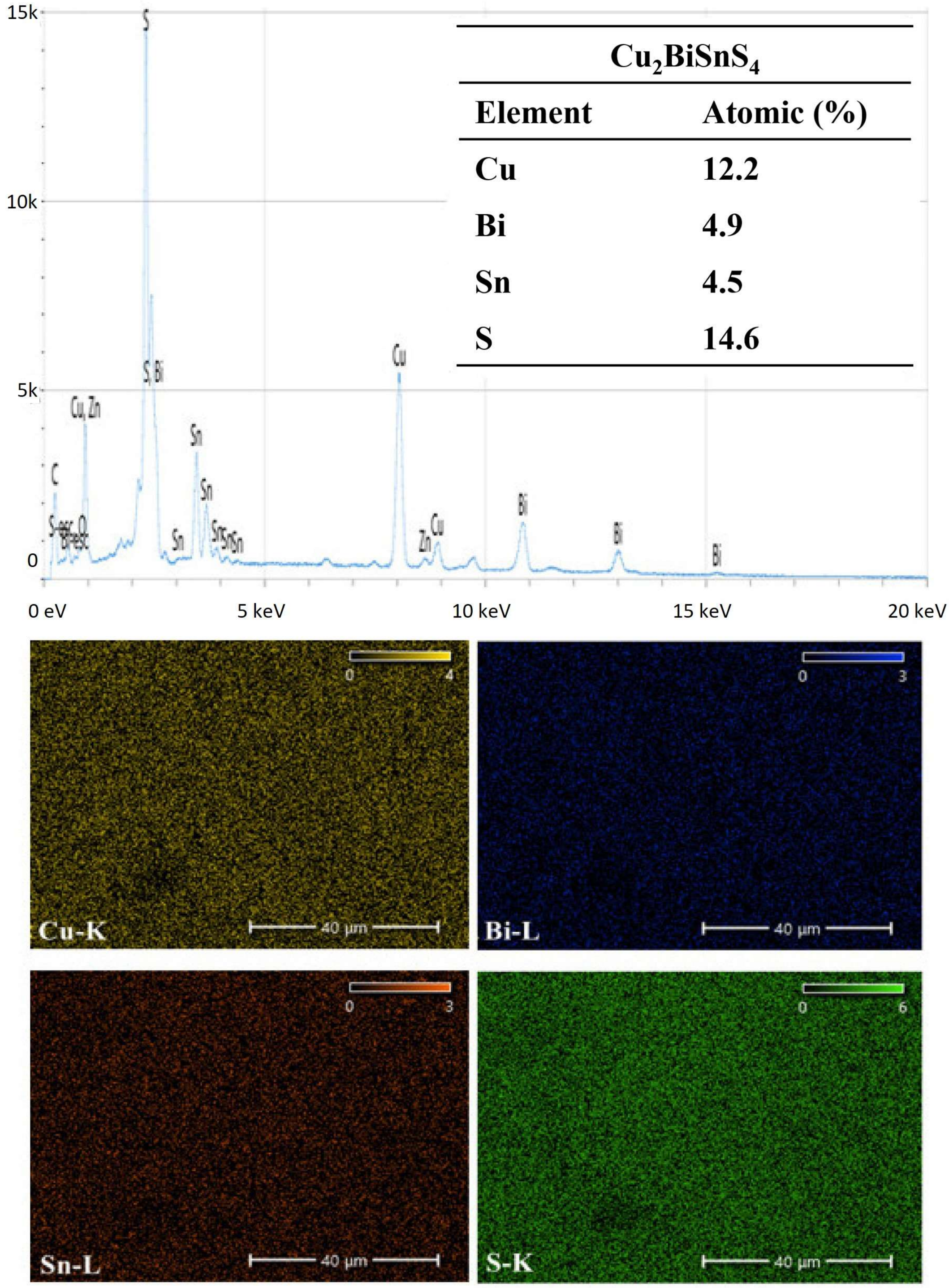

Figure 3. EDS spectrum of the Cu_2BiSnS_4 compound.

3.3. Morphology of Cu_2ZnSnS_4 and Cu_2BiSnS_4 nanoparticles

In general, the high surface area, regular distribution, and crystalline structure are the most important factors in enhancing the photocatalytic efficiency. From Figure 4, field emission scanning electron microscopy (FESEM), it was observed that the nanoparticles of the Cu_2ZnSnS_4 compound are almost spherical and regular shaped, while the nanoparticles of the Cu_2BiSnS_4 compound are in the form of sheets or rough structures. The change in the shape of the particles from spherical to sheets is caused by the replacement of Zn with Bi elements, which vary chemically and physically, affecting the dynamics of the crystalline formation during the preparation process.

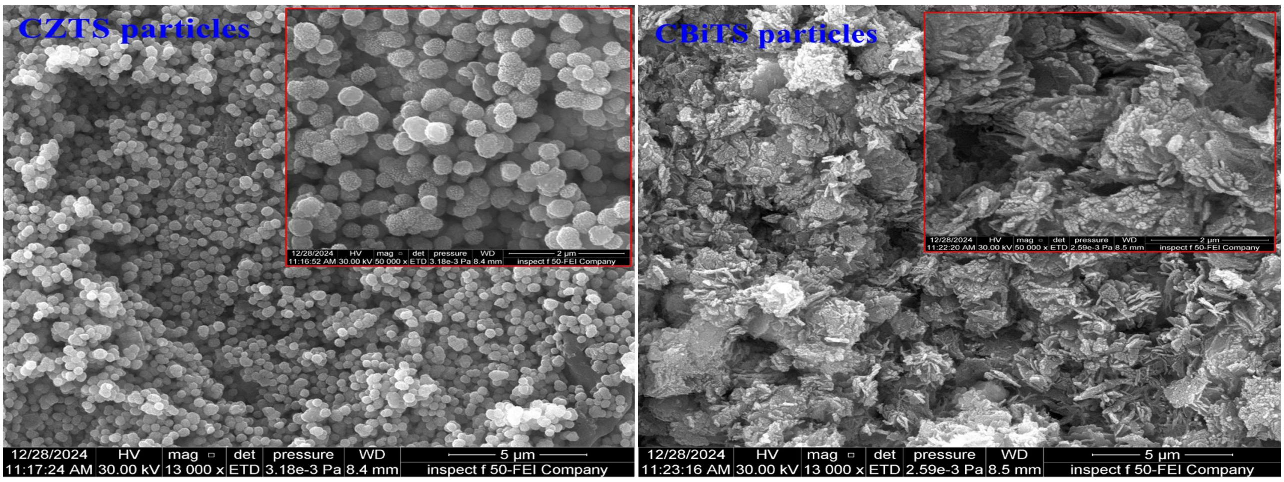

Figure 4. Morphology of the CZTS and CBiTS nanoparticles.

The Cu_2ZnSnS_4 nanoparticles are characterized by a spherical shape due to the small ionic radius of the Zn^{2+} ion, which leads to the formation of a more cohesive and stable structure resulting in spherical particles [23,24]. At the same time, the Bi^{3+} ion has a larger ionic radius, which leads to dynamic changes in the crystallization process, causing the particles to grow in the form of sheets or rough structures. In addition, the oxidation state has an effect on the crystal growth mechanism, as bismuth is in the +3 oxidation state and zinc is +2, which may cause a difference in the electrostatic forces within the crystalline material, which in turn may affect the crystal growth and the final particle shape [25]. The Bi^{3+} ion is characterized by its strong interaction with the sulfur ions during the process of compound formation, which stimulates the formation of structures with low surface energy, as nanoparticles tend to adopt shapes that reduce surface energy [25], such as sheets. The Zn^{2+} ion tends to form more homogeneous and smaller particles due to its tendency to form symmetrical and regular structures, such as the spherical shape. Therefore, we believe that the change in shape from spherical to sheets is not random but rather came from the complex effect of the chemical and physical properties of bismuth compared to zinc on the final crystal structure of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds. By looking at the shape of the Cu_2BiSnS_4 nanoparticles, the sheet or plate shapes of the particles are distributed repeatedly and regularly in all directions. This pattern creates multiple layers, which provide a larger effective surface area that can increase the interaction of light and pollutants. This is very important for improving the efficiency of photocatalytic activity because the sheet shape acts as a multidimensional system for the interaction of light with the catalyst. Therefore, the sheet shape can be considered to increase the regularity of the particle distribution in practice, despite the general appearance that may appear irregular. Therefore, in the Cu_2BiSnS_4 compound, the sheet-shaped nanoparticles are more chemically active, which means they can perform better in photocatalysis because they have a larger surface area to interact with light and pollutants. Conversely, the spherical nanoparticles in the Cu_2ZnSnS_4 compound are thermally stable, but they may not be as effective in photocatalysis because of their limited surface area.

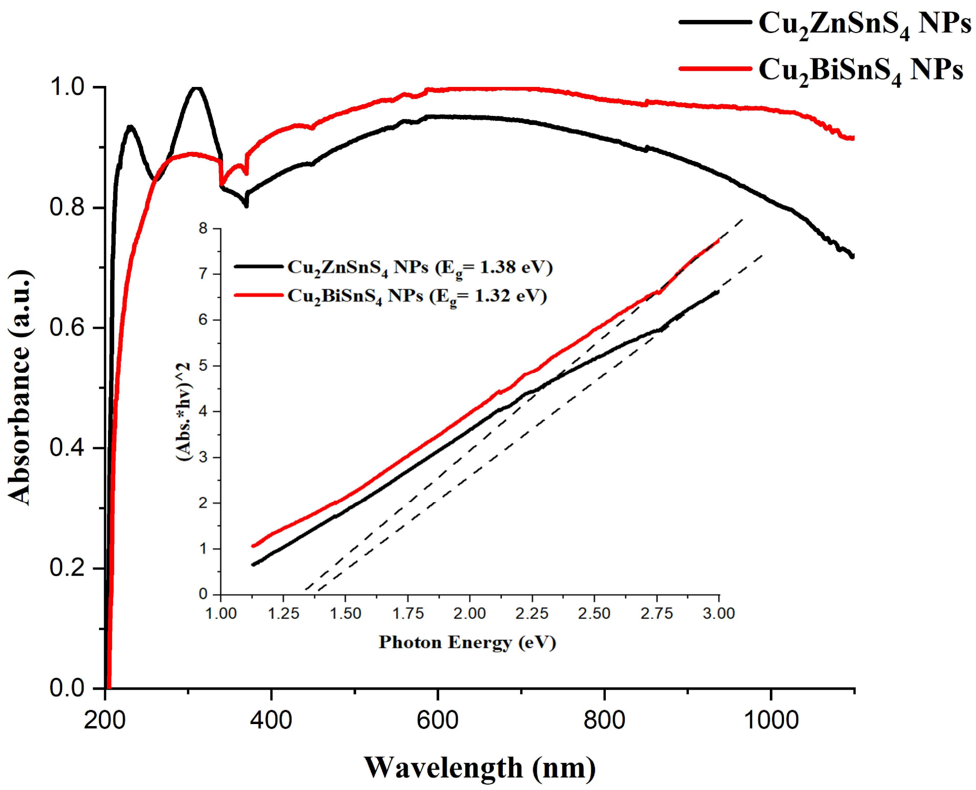

Figure 5. Absorption spectrum and the energy gap (inset) of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds.

3.4. Optical properties

To study and analyze the optical properties of Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds and the effect of Zn replacement with Bi on these properties, the absorption spectrum and energy gap were studied using UV-vis spectroscopy as in Figure 5. The compounds are seen in a wavelength range from 200 to 1100 nm. It is seen from these curves that both compounds have strong absorption in the visible and near-infrared range (NIR) in addition to the UV region, making them a promising candidate for photocatalysis. On the other hand, it was observed that the Cu_2BiSnS_4 compound leads to greater absorption than the Cu_2ZnSnS_4 compound at long wavelengths, indicating a lower energy gap than that of the Cu_2ZnSnS_4. As seen in the inset of Figure 5, which represents Tauc plot analysis to calculate the energy gap, it was observed that the energy gap of the Cu_2ZnSnS_4 compound is equal to about 1.38 eV while it decreased to 1.32 eV after replacing Zn with Bi. This makes the absorption spectrum of the Cu_2BiSnS_4 compound increase as the energy gap of both compounds is ideal for the photocatalytic process in visible light. The factors affecting the effectiveness of the efficiency of photocatalytic activity are the material's ability to absorb light and its energy gap [13]. It is noted that the Cu_2ZnSnS_4 compound absorbs in the visible range with good expansion, which makes it suitable for photocatalysis, while the Cu_2BiSnS_4 compound has a higher absorption at long wavelengths, making its utilization in exploiting near-infrared light more efficient. Since the goal is to take advantage of all visible light, the Cu_2BiSnS_4 compound is considered a better alternative than Cu_2ZnSnS_4 due to high absorption and a small energy gap. According to Figure 5, the absorption edge has shifted from a wavelength of about 950 nm in the Cu_2ZnSnS_4 compound to a wavelength of about 1020 nm in the Cu_2BiSnS_4 compound. This means that the optical energy gap of the Cu_2BiSnS_4 compound is less than that of the Cu_2ZnSnS_4 compound because of the Moss-Burstein effect. The difference in the absorption edge between the two compounds can be influenced by differences in the density of charge carriers resulting from the chemical composition.

3.5. Photocatalytic application

In order to study the efficiency of the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds in photocatalytic removal of organic pollutants, 100 mL of methyl green dye aqueous solution (initial concentration of 10 mg/L) was used with 20 mg of Cu_2ZnSnS_4 and Cu_2BiSnS_4 nanoparticles under sunlight and for different times from 0 to 60 min. Figure 6a,b show that both the Cu_2ZnSnS_4 and Cu_2BiSnS_4 compounds have the ability to act as photocatalysts to degrade organic pollutants in water. A gradual decrease in absorbance at the main wavelength of the dye, 630 nm, is observed with increasing exposure time to sunlight from 0 to 60 min. This decrease indicates the decomposition of the dye [12], which indicates the occurrence of a photocatalytic process by nanomaterials.

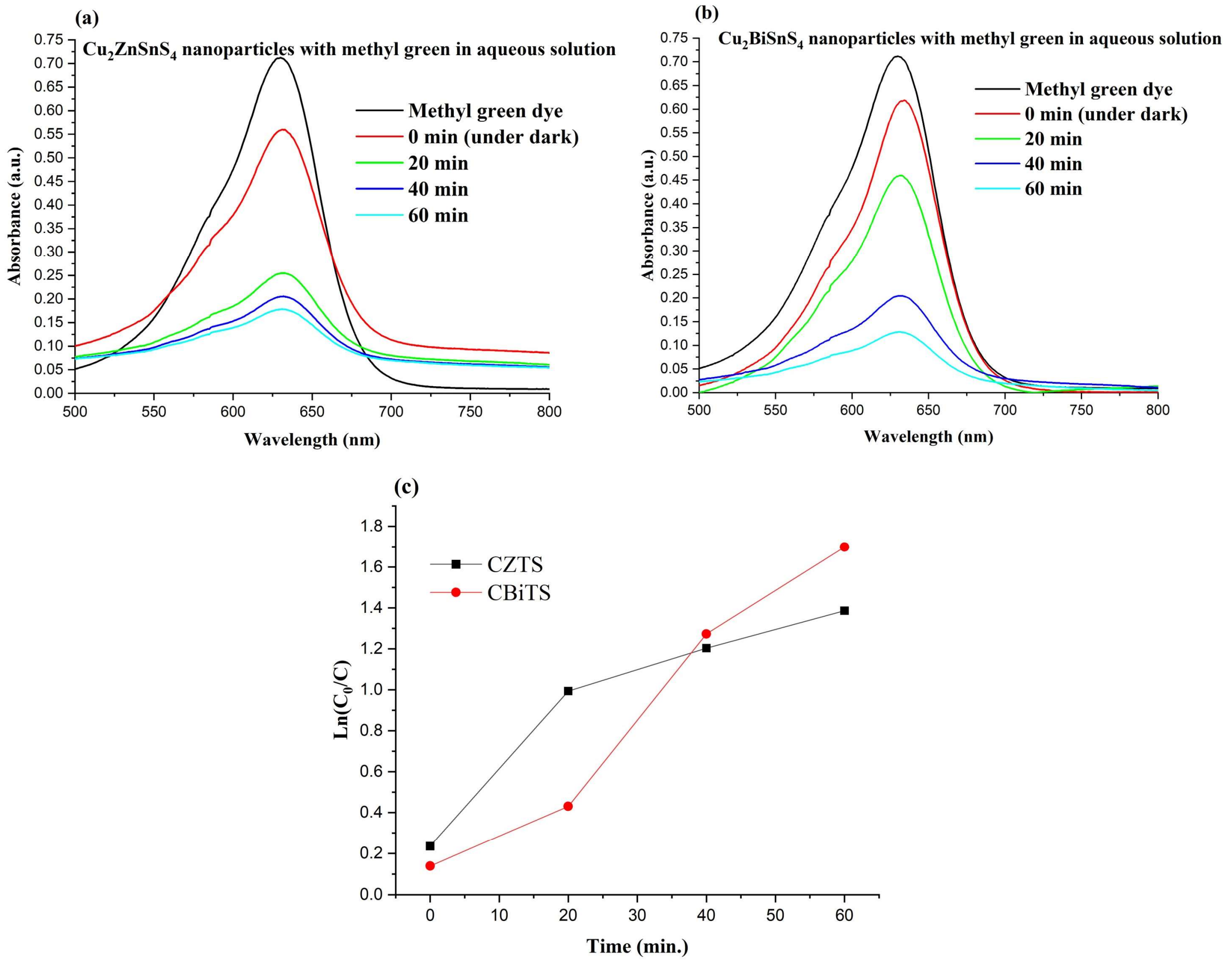

Figure 6. Photocatalysis behaviour of the CZTS and CBiTS compounds.

In general, the photocatalytic process depends on the ability to absorb light and the interaction of electrons and generated holes with the organic pollutant [4], i.e., oxidation-reduction reactions to decompose the molecules of organic pollutants. The holes +h react with water molecules or hydroxide ions −OH to produce hydroxyl radicals OH·, while the electrons −e react with oxygen dissolved in water to produce superoxide radicals. These radicals are strong and superior oxidizing agents that are able to decompose organic compounds (dyes) by breaking the chemical bonds within the dye and decomposing them into simpler compounds or into CO_2 and H_2O [7]. From Figure 6b, it is observed that the Cu_2BiSnS_4 compound has a higher photocatalytic activity and degradation rate. Its absorbance decreases faster over the same time period due to its absorption of a wide spectral range as a result of the favourable energy gap and also the lower recombination rate, which allows more electrons and holes to interact with the medium and thus increases the photo-degradation efficiency. In order to describe the photocatalytic reaction by observing the change in dye concentration with time as in Figure 6c, the Langmuir-Hinshelwood model was used according to the following logarithmic relation: $Ln\ C_0/C_t = kt$ [4], where C_0 is the initial concentration at $t = 0$, C_t is the dye concentration at a time interval t, and k is the photo-degradation rate constant. It is noted that $k = 0.01049$ for the Cu_2ZnSnS_4 compound, while $k = 0.04211$ for the Cu_2BiSnS_4 compound. This means that the compound Cu_2BiSnS_4 has a higher photo-degradation rate compared to Cu_2ZnSnS_4, which indicates its high efficiency in removing the methyl green dye [7]. This is attributed to its high absorption and reduced rate of recombination of electrons and holes. When using methyl green dye as a contaminant in photocatalytic studies, the Cu_2ZnSnS_4 compound works well due to its homogeneous distribution of spherical particles and small size, which improves electron transfer efficiency, but it may face challenges during light absorption. Whereas the Cu_2BiSnS_4 compound has a large surface area that allows for greater absorption of visible light, making it particularly effective with methyl green dye that interacts strongly with light. Authors believe that both compounds act as effective photocatalysts. The degradation efficiency was calculated using the following relation: Efficiency of degradation = $(A_0 - A_t)/A_0$ [4], where A_0 and A_t are absorbance at interval time 0–t min, respectively, and the efficiency of each compound was compared. It was found that the degradation efficiency of the Cu_2ZnSnS_4 compound was about 75%, while it was about 82% for the Cu_2BiSnS_4 compound. These results support the idea that the Cu_2BiSnS_4 compound may be a better choice in the treatment applications of water contaminated with organic dyes.

Table 2 shows that compounds CZTS and CBiTS exhibit high efficiency in degrading methyl green dye compared to other catalysts, without the need for H_2O_2 additions and without the costs or environmental risks. Both compounds are also abundant in the Earth's crust and are non-toxic, enhancing their future applications in sustainable environmental remediation. It is worth noting that due to the presence of bismuth, compound CBiTS exhibited an improved response to visible light, which outperformed CZTS in efficiency.

Table 2. A survey of some photocatalysts.

Photocatalyst	Efficiency (%)	Duration time (min)	Photo-source	Details	Ref.
Mn-ZnO	66.44	60	Sunlight	Bu incorporating Mn into the ZnO	[26]
ZnO	80	-	UV light	By nano rod of ZnO	[27]
TiO_2-P25	50–60	120	Xe lamp	Narrow band absorption depends on UV	[28]
CdS	60–75	90–120	Visible light	Unstable in the light	[29]
$BiVO_4$	68	120	Visible light	Poor solubility	[30]
MoS_2	65–72	120	Visible light	Needs H_2O_2	[31]
ZnO/CuO	75	100	Visible light	Nanocomposite	[32]
CZTS	75	60	Sunlight	Both do not require a cofactor like H_2O_2	Current research
CBiTS	82	60			

4. Conclusions

The results of this article confirm that two sulfide compounds, Cu_2ZnSnS_4 and Cu_2BiSnS_4, have stable crystalline structures and appropriate optical properties that enable them to effectively absorb solar radiation. XRD, EDS, FESEM, UV-visible, and photocatalytic tests demonstrated good crystalline phase formation, regularity in the form of grain, and stability of basic proportions. Therefore, photocatalytic tests show the ability of two compounds to degrade organic pollutants at different rates and at different times, indicating their feasibility in environmental applications, especially in wastewater treatment. The superiority of the Cu_2BiSnS_4 compound over the Cu_2ZnSnS_4 compound is related to the difference in morphological factors and effective surface area. Based on these results, the Cu_2BiSnS_4 compound is a promising alternative for improving the efficiency of photocatalytic treatment under sunlight and can be widely used in the treatment of different pollutants. Therefore, this research helps open new horizons for the development of environmentally friendly and effective technologies to reduce pollution.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Author contributions

The idea of investigation and the manuscript draft were done by corresponding author Hussein M. H. The preparation of samples was done by Nahlah Challob Younus. The interpretation of the results was done by both authors.

Conflict of interest

The authors declare no conflict of interest.

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