Graphene Oxide Boosted: A Multifaceted Examination of CZTS Composite for Enhanced Photocatalysis and Antimicrobial Efficacy

Halit Cavusoglu
hcavusoglu@selcuk.edu.tr

Selcuk University

Marwah Ali Ibrahim
Selcuk University

Hüseyin Sakalak
Selcuk University

Erdogan Günes
Selcuk University

Ahmet Uysal
Selcuk University

Emre Çitak
Konya Technical University

Teoman Öztürk
Selcuk University

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Abstract

Because of their acute toxicity and long-lasting effects on the environment such as chemical accidents, agricultural runoff, and industrial effluents, has raised concerns around the world. Semiconductor-based photocatalysis has gained prominence for its ability to degrade organic contaminants comprehensively, providing a potential solution to the limitations of the conventional methods. This study addresses the environmental repercussions of dye contamination and explores the utilization of active semiconductor photocatalysts for effective wastewater treatment. Our focus lies in synthesizing CZTS through the hydrothermal route, a method gaining traction for its simplicity and environmental viability. To augment the photocatalytic efficiency of semiconductor materials, graphene oxide (GO) has been introduced with varying GO concentrations of 5% and 10%. Additionally, the study explores the performance of CZTS nanoparticles with varying GO concentrations for antibacterial applications against eight Gram-positive/negative bacterial strains and its catalytic prowess in the photodegradation of methylene blue dye under ultraviolet light.

1. Introduction

Water is the source of life on earth and one of the most important natural resources for the survival of life form. According to progress report of World Health Organization (WHO) and United Nations Children's Fund (UNICEF), billions of people across the globe live without safe drinking water services, reliable sanitation facilities and hygiene [1]. Whilst it is known that water is so important for human life, it is still polluted with fertilizers, pesticides, herbicides, insecticides, pharmaceutical, domestic and industrial wastes. Among industrial pollution, the release of textile wastes containing hazardous and carcinogenic dyes poses a threat to aquatic life, including fish, aquatic microorganisms, and mammals [2]. Removing pollutants from water is a major challenge and many techniques are used such as sedimentation, adsorption, filtration, reverse osmosis, coagulation, ozonation and photocatalysis [3–8]. Among these techniques, photocatalysis stands out as a sustainable and potential solution due to its environmental friendliness, efficiency, low-cost and reusability.

Photocatalysis has gained prominence for its efficacy in completely degrading organic contaminants into carbon dioxide, water, and mineral acids [9–13]. Semiconductor-based photocatalysis stands out as a highly promising technology, particularly for its diverse applications, with a primary emphasis on the breakdown of organic contaminants [14, 15]. An important and demanding field of study is the synthesis, characterization, and use of semiconductor photocatalysts in energy and environmental contexts. Although TiO$_2$ is the most widely used photocatalyst since the groundbreaking study of Fujishima and Honda, the search of novel and efficient photocatalyst still continues such as ZnO [16], CuO [17], CdO [18], SnO$_2$ [19], Fe$_2$O$_3$ [20], Ag$_2$CO$_3$ [21], Zn$_2$SnO$_4$ [22], and numerous others.

In recent times, copper-zinc-tin-sulfide (Cu$_2$ZnSnS$_4$ or CZTS) has garnered significant attention as a compelling material, attributed to its notable features. These include excellent photo-stability, reduced toxicity, a direct bandgap spanning from 1.4 to 1.6 eV values roughly corresponding with those of
absorbers in solar cells (1.35 eV), and a significant absorption coefficient throughout the visible range (>104 cm⁻¹) [23–25]. CZTS is employed not only as a photocatalyst but also in various applications such as photodetectors, hydrogen (H₂) production, gas sensors, lithium-ion batteries, and energy storage systems [26, 27]. The discovery of copper-zinc-tin-sulfide (CZTS) was first reported by Katagiri [28], and since then, various synthesis methods have been explored, including sol–gel [29], microwave [30], SILAR [31], solvothermal [32], electrodeposition [33], sputtering [34], and hydrothermal [27]. Among these, hydrothermal synthesis has gained widespread adoption due to its simplicity, environmental friendliness, and cost-effectiveness. Current research is centered on the development of multifunctional materials with applications spanning various domains [35–37]. This emphasis has driven our interest in synthesizing CZTS via the hydrothermal route.

Even though semiconductor materials are widely used, their photocatalytic capabilities are limited by practical issues such as a large band gap energy, rapid recombination rate of electron-hole pairs, and insufficient absorption of visible light. Therefore, it is now more crucial than ever to perform research on the creation and design of semiconductor nanocomposite materials. Notably, to overcome these difficulties and improve the photocatalytic efficiencies of these materials, scientists have resorted to graphene oxide (GO). Graphite represents a three-dimensional form of carbon material characterized by a layered structure. Each individual layer composing graphite consists of a sheet of two-dimensional graphene. Through an oxidation process applied to graphite, graphite oxide is generated, introducing oxygenated functionalities into the graphite structure. This process results in an expansion of layer separation, transforming the material into a hydrophilic substance [38]. This hydrophilicity allows graphite oxide to be exfoliated in water using sonication, eventually yielding single or few-layered graphene, known as graphene oxide (GO). Moreover, the presence of oxygen-containing functional groups in GO creates significant opportunities for accessing heterostructured graphene-based functionalized nanocomposites [39]. The capability to adjust band gaps and promote effective intercalation of diverse compounds positions this innovative material as extremely beneficial in the field of heterogeneous catalysis and support. GO can be utilized to produce composite structures in order to control the size, pore structures, size distributions, and morphologies by incorporating it with semiconductor photocatalysts [40–42]. Since the groundbreaking study by Williams and collaborators [43], there has been a remarkable surge in the volume of publications focusing on the design and advancement of semiconductor photocatalysts based on graphene oxide (GO).

Another use of photocatalysts is as antibacterial, as they can be adsorbed onto the surface of Gram-positive and Gram-negative bacterial strains, thus effectively inhibiting the growth of microorganisms. However, there has been a limited number of antimicrobial studies conducted on CZTS nanoparticles to date. In a study reported by Kumar et al. [24], the antibacterial activity of CZTS nanoparticles were investigated against a range of bacteria using zone of inhibition. According to the results, CZTS particles had as strong antibacterial activity as controls (silver nanoparticles and ampicillin) against the tested bacteria. Chaudhari et al. fabricated CZTS nanoparticles via solvothermal method and carried out the antibacterial activities of the nanoparticles in contrast to a group bacterial strain and obtained significant
antibacterial activity using zone of inhibition [44]. In a study reported by Ceylan et al. [45], hydrothermally prepared CZTS quantum dots were loaded onto PVA/chitosan membranes and the antimicrobial activity of these composite films were examined against *S. aureus* and *E. coli*. According to the results, there is an improvement in antimicrobial properties with the contribution of CZTS. In a remarkable study, Zalneravicius et al. [46] synthesized CZTS particles through molten salts method and performed antimicrobial tests against bacterial (*M. luteus* and *P. aeruginosa*) and yeasts (*C. Krusei* and *C. parapsilosis*). CZTS particles have exhibited 95.9% killing efficiency against *P. aeruginosa* bacteria. In a recent study conducted by Pandey et al. [47], CZTS nanoparticles were produced via a solvothermal route. By investigating the structural, morphological and elemental properties of these nanoparticles, they observed their antimicrobial properties on *B. subtilis* and a *T. indica* strains.

Another critical feature of an antimicrobial agent is its non-toxic impact on human cells within a living organism. Inorganic nanomaterials are recognized for containing essential minerals beneficial to human health. These minerals exhibit lower toxicity, enhanced stability, increased safety, superior heat resistance, and significant activity at low concentrations [48, 49]. In this context, CZTS nanomaterials offer a benefit due to their minimal toxicity and potent antimicrobial activity at low concentrations, rendering them suitable as effective antimicrobial agents across diverse living systems. Prior investigations on different inorganic materials incorporating elements like Cu, Zn, Sn, S, etc., have indicated heightened effectiveness against pathogenic microorganisms while demonstrating minimal influence on human cell lines and tissues. This implies noteworthy antibacterial properties for aforementioned inorganic materials [50–52].

In this study, we present the fabrication of CZTS nanoparticles in pure kesterite phase and CZTS nanoparticles doped with graphene oxide at different concentrations via a hydrothermal route. The obtained composites were characterized by XRD, FTIR, HR-TEM, SEM, EDX and UV-Vis spectrophotometer. Antibacterial activity of these hydrothermally synthesized CZST-GO heterostructures were examined against a group of Gram-positive/negative bacteria (*E. coli, P. aeruginosa, K. pneumoniae, S. aureus, S. enteritidis, S. lutea, B. cereus*) and yeast (*C. albicans*). According to the results, *S. aureus* and *S. lutea*, which are known to be resistant to methicillin, were the most sensitive bacteria against our synthesized heterostructures. Photocatalytic properties of the composite structures were investigated by the photodegradation of methylene blue (MB) dye under ultraviolet (UV) irradiation. As the amount of GO in the composites increased, an enhancement in the photocatalytic activities of the heterostructures was observed.

### 2. Experimental Section

#### 2.1. Materials

Hydrothermal synthesis was used to produce Cu$_2$ZnSnS$_4$ (CZTS) nanoparticles utilizing copper (II) chloride dihydrate (CuCl$_2$•2H$_2$O, 99+%, Thermo Scientific Chemicals), zinc sulfate heptahydrate (ZnSO$_4$•7H$_2$O, 99.5%, Thermo Scientific Chemicals), tin (II) chloride dihydrate (SnCl$_2$•2H$_2$O, 98+%, Thermo
Scientific Chemicals) and sodium sulfide (Na$_2$S, 90+%, Thermo Scientific Chemicals). The chemicals used in the synthesis of graphene oxide comprised graphite powder (Supragraphite C 300, Flake Natural Graphite, Extra Pure), sulfuric acid (H$_2$SO$_4$, 98%, Sigma-Aldrich), phosphoric acid (H$_3$PO$_4$, ≥ 85%, Sigma-Aldrich), potassium permanganate (KMnO$_4$, ≥ 99.0%, Sigma-Aldrich), hydrogen peroxide (H$_2$O$_2$, 30%), hydrochloric acid (HCl, 37%, Sigma-Aldrich), dichloromethane (CH$_2$Cl$_2$, ≥ 99.9%, Sigma-Aldrich), ethanol (CH$_3$CH$_2$OH, 96%, Sigma-Aldrich), diethyl ether ((C$_2$H$_5$)$_2$O, ≥ 98.0%, Sigma-Aldrich) and deionized water. In photocatalytic experiments, methylene blue (MB, C$_{16}$H$_{18}$ClN$_3$S, Merck) was purchased from Merck. All precursors were utilized in their as-received form without any modification or purification.

The purpose of the broth micro dilution experiment was to clarify the possible antibacterial properties of particular substances. For this purpose, seven bacteria and one yeast were used in activity assay. Microorganism strains were from Selçuk University Vocational School of Health Services Microbiology Research Laboratory and these strains were tabulated in Table 1.

### 2.2. Synthesis of CZTS nanoparticles

The synthesis of CZTS nanoparticles was conducted with some modifications to the work in the literature [53]. To obtain CZTS nanoparticles, the molar ratio of 0.24 M CuCl$_2$•2H$_2$O, 0.28 M ZnCl$_2$, 0.16 M SnCl$_2$•2H$_2$O and 0.48 M Na$_2$S•9H$_2$O taken together, were dissolved in 50 mL of DI water. To fully dissolve all the components, the solution was ultrasonically agitated for 60 minutes while being stirred magnetically. The solution was transferred to a 50 mL stainless-steel autoclave and heated to 220°C for a whole day. After the hydrothermal reaction, ambient air was used to cool the autoclave to room temperature. The dark sediment was gathered and centrifuged at 8000 r.p.m. for 15 minutes, after which it was cleaned twice with ethanol and deionized water. After one hour of drying at 90°C, CZTS nanoparticle powder was produced.

### 2.3. Synthesis of graphene oxide (GO)

The graphene oxide synthesis in this study adhered to the methodology outlined in our previous work, utilizing the improved Hummers method [54, 55]. The as-prepared GO flakes were characterized using XRD, SEM, HR-TEM, and FT-IR analysis.

### 2.4. Synthesis of CZTS-GO Heterostructure

The as-synthesized GO flakes and CZTS nanoparticles were disseminated in deionized water simultaneously and independently by using ultrasonication and magnetic stirring. To obtain the CZTS nanoparticle anchored GO composite material, the two stable dispersions were combined, sonicated one more for two hours, centrifuged with an equivalent volume of ethanol, and then dried at 80°C under vacuum. XRD analysis was used to characterize the as-prepared GO, CZTS, and composite in order to determine the phases. Additional characterization uses FT-IR and SEM-EDX. We also confirmed composite formation using SEM-EDX and FT-IR analysis.

### 2.5. Photocatalytic Characterization
We followed a photocatalytic experiment route similar to a previous study performed by Karaduman et al. [56]. In photocatalytic experiments, a 50 ml MB aqueous solution of 8 PPM was prepared with deionized water. 3 ml of the prepared aqueous dye solution was drawn and its absorbance was measured at the 0th minute in the spectrophotometer and the extracted liquid was transferred back to the main solution. Then, 20 mg of CZTS was measured on an electronic analytical balance and placed into the MB solution. The whole solution was transferred to a quartz cell and placed in a photocatalytic reactor and stirred for 30 minutes in the dark for the adsorption-desorption equilibrium. At the end of 30 minutes, some MB solution was taken and placed in 2 ml centrifuge tubes and centrifuged at 7000 rpm for 30 seconds. After this process, the liquid was placed in a quartz cuvette and the absorption spectrum was taken. Afterwards, the centrifuge tubes were shaken with a vortex device, and the photocatalysts and MB liquid in the quartz cuvette were transferred to the main solution in the photoreactor. After that, the solution was exposed to UV light irradiation every 10 minutes and the same procedures were carried out, so that the reduction of MB was investigated by the reduction in the absorption spectrum. The same procedures were repeated for 5% GO: CZTS and 10% GO: CZTS nanoparticles and the absorption spectra were obtained by exposing the MB to UV light at 5-minute intervals.

### 2.6. Investigation of antimicrobial activities

For the determination of antimicrobial potential of the composites, standard microorganisms consisting gram-negative bacteria, gram-positive bacteria and yeast were selected. Then overnight fresh cultures of them were obtained in Brain-Heart Infusion Broth (Merck). The needed microorganism counts (10⁸ CFU/mL) were prepared by adjusting fresh cultures as 0.5 Mc Farland turbidity in sterile physiological water. Finally, the last concentration of the inoculum was 10⁵ CFU/mL by achieving the dilution of main inoculum.

Antimicrobial actions of chemicals were found by broth micro dilution method recommended by Nibras Qader Qader et al. (2022) [57]. At first, the whole wells of the microplate were filled with 100µL Mueller Hinton Broth. Then the chemicals, prepared as 25 mg/mL stock solution, were transferred to the first well of the plate as 100 µL. Two-fold dilutions of the test materials (ranging from 6.25 to 0.0061 mg/mL) were obtained by distributing the mix (chemical and medium) to the remaining wells. After that 100 µL microorganism inoculum transferred to the each well. The Gentamicin was used the killing of microorganisms as positive control. Each plate was incubated in incubator at 37 °C for 18–24 hours. At the end of the incubation period the minimum inhibitory concentration (MIC) values were obtained by dispensing 20µL 2,3,5 TTC (0.5%) to whole wells of the plate and incubated for 30 min again [58]. MIC values were defined as the lowest doses of the chemicals that entirely halted macroscopic growth.

### 2.7. Material Characterization

To examine the morphology of the graphene oxide, high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100F) was employed. For HR-TEM sample preparation, a droplet of colloidal solution was applied to a carbon-covered copper grid. The surface morphologies and elemental compositions of all samples were further analyzed using a Zeiss EVO LS-10 scanning electron microscope (SEM)
equipped with an energy-dispersive X-ray spectroscopy (EDX) system. Using a powder diffractometer Bruker D8-Advance X-ray, measurements of X-ray diffraction (XRD) were made in the 2θ range of 5–60° using Cu Kα radiation (λ = 1.5406 Å). All of the samples' Fourier transform infrared (FT-IR) spectra were captured at a resolution of 4 cm⁻¹ using a Bruker Vertex 70 spectrophotometer (Rheinstetten, Germany). The FTIR spectra were acquired in the 400–4000 cm⁻¹ range. A UV-Vis-NIR spectrophotometer (Jasco Inc., MD, USA) was used to investigate photocatalytic experiments of heterostructures in the 190–1100 nm range.

3. Results and Discussion

3.1. Structural Evaluation

3.1.1. XRD Analysis

X-ray diffraction (XRD) measurements were carried out to examine the structural properties of both GO-doped and undoped CZTS nanoparticles. Figure 1 presents the XRD patterns of graphite and GO were obtained, where GO was obtained with an improved Hummers’ method. The graphite material displayed a distinctive single peak at 2θ ≅ 26°, representing the (002) plane, with an interlayer spacing of 0.335 nm. Conversely, in the case of graphene oxide (GO), this peak vanished entirely, and a new peak corresponding to the (002) crystalline plane emerged at 10.1°, indicating an interlayer spacing of 0.88 nm. Analysis of the XRD data reveals a transformation in the interlayer spacing (d₀₀₂ spacing) from 0.335 to 0.88 nm, providing clear evidence of the transition from graphite to GO. The increased distance between successive carbon layers in GO is ascribed to the incorporation of oxygen-containing functional groups into the carbon basal plane [59, 60].

The determination of phase and crystallinity plays a crucial role in influencing the physical properties of heterostructure nanomaterials. The diffraction patterns of the as-synthesized CZTS nanoparticles exhibit peaks at 2θ = 28.45°, 32.83°, 47.21°, 56.21°, and 58.85°, corresponding to (112), (200), (220), (312), and (224) planes, respectively, characteristic of the single-phase kesterite structure of CZTS (JCPDS 26–0575) as depicted in Fig. 1(a). These XRD peaks align with findings in previously published studies [61, 62]. In the XRD patterns of the composite materials, the diffraction orientations of CZTS and GO affirm the coexistence of both CZTS and GO in the composite (Fig. 2(a) and Fig. 2(b)). The diffraction peak of the CZTS-GO composite indicates an overlap of the CZTS reflection over broad GO peaks, attesting to the presence of both CZTS and GO. In the composite diffraction pattern, the characteristic peaks of GO are distinctly visible, as illustrated in Fig. 2(b).

3.1.2. FTIR Analysis

To verify that the GO can fully conjugate with CZTS nanoparticles, the Fourier transform infrared (FTIR) spectroscopy was used in transmission mode. When examining the pure CZTS peaks in Fig. 3, the bands within the range of 900–1600 cm⁻¹ originate from the stretching and bending frequencies of oxygen. The
faint additional bands at 950 and 884 cm⁻¹ are linked to the resonance interaction between vibration modes of sulfide ions in the crystal. The characteristic absorptions at 2369 cm⁻¹ are ascribed to the S–H thiol functional group. The spectrum of the pure GO shown in Fig. 3 indicates that the peak at 1066 cm⁻¹ is attributed to C–O stretching. The peak at 1288 cm⁻¹ is confirmed to be the C–O–C bending mode, while the C–OH bending is observed at 1587 cm⁻¹. Carbonyl groups are also represented by the C=O stretching peak at 1724 cm⁻¹, and the broad peak at 3448 cm⁻¹ is assigned to the O–H stretching vibrations of C–OH groups and the moisture content in the material. When examining the spectra of CZTS with 5% and 10% GO content, it is observed that as the amount of GO increases, there is an increase in the C–OH group at 3400 cm⁻¹. Additionally, it can be seen that the intensity of the peak at 1587 cm⁻¹, which is attributed to C–OH groups, also increases due to this effect.

3.2. Morphological Analysis

3.2.1. HR-TEM-EDS Analysis

Energy-dispersive X-ray spectroscopy (EDS) with HR-TEM examination of the elemental mapping of prepared the pure GO was performed for analyzing the morphology. The HR-TEM image of the pure GO revealed a structure resembling nanosheets, as illustrated in Fig. 4(a). The image of HR-TEM clearly demonstrated that the margins of the GO sheets were typically partially folded and scrolled. The compositional analysis by EDS-elemental mapping showed that the red and green had constituents of C and O, represented in Fig. 4(b).

3.2.2. SEM-EDX Analysis

SEM-EDX analysis was carried out to obtain insight into how GO doping affected the surface morphology of CZTS nanoparticles. Figure 5 displays the SEM analyses of the pure GO, the pure CZTS, CZTS with 5% GO content, and CZTS with 10% GO content. In the SEM image of the pure GO, the presence of GO layers can be observed in a wrinkled structure. A closer examination at Figs. 5(c) and 5(d) reveals how GO addition affects morphology. It is observed that with the addition of GO, both rod-like and layered structures are present in the morphological structure of CZTS. Furthermore, it is noted that as the amount of GO increases, the layered structure becomes more prominent. In the SEM analysis with 5% GO addition, the rod-like structure is more pronounced, whereas in the sample with 10% GO addition, the layered structure is more prominent. This is attributed to the layered structure of GO. As the amount of GO increases, the layered structure also increases.

Chemical elemental analysis of the undoped CZTS nanoparticles was conducted using EDX analysis. SEM-EDX mapping analysis and the EDX spectrum of the CZTS nanostructures was presented in Fig. S1. Using the relevant SEM–EDX spectra, the contents of the CZTS nanoparticles were determined in relation to the mass fraction composition shown in Table S1. Fig. S1 reveals the presence of Cu (8.16%), Zn (8.34%), Sn (5.68%) and S (28.42%) elements in the undoped CZTS nanoparticles.
3.3. Antimicrobial Analysis

Antimicrobial activity results of the pure CZTS, CZTS with 5% GO content, and CZTS with 10% GO content against pathogen microorganisms were tabulated in Table 1. The activity test findings showed that the pure CZTS nanoparticles were exclusively effective against strains of *S. aureus* and *S. lutea*. The MIC values were recorded as 3.125 and 1.56 mg/mL, respectively. Other strains were resistant to this chemical. After addition of 5% graphene oxide *S. lutea* was affected from the CZTS + 5% graphene oxide at a dose of 0.39 mg/mL. Also, CZTS + 5% graphene oxide was effective against *E. coli*, Gram negative bacterium and methicillin resistant *S. aureus* (MRSA). It revealed antimicrobial activity at concentrations of 6.25 and 1.56 mg/mL for these strains. The CZTS + 10% graphene oxide manifested antimicrobial activity against whole microorganisms at concentrations ranging between 6.25–1.56 mg/mL. The MIC values were determined as 6.25 mg/mL for *P. aeruginosa*, *K. pneumoniae* and *B. cereus*. Antimicrobial action was observed for *E. coli*, *S. aureus* and *S. enteritidis* with a 3.125 mg/mL MIC value. *S. lutea* and *C. albicans* affected from the CZTS + 10% graphene oxide at a dose of 1.56 mg/mL. It was revealed that the CZTS + 10% graphene oxide composite showed antifungal activity against Candida.

**Table 1**

Antimicrobial activity results of chemicals against pathogen microorganisms

<table>
<thead>
<tr>
<th>MIC values of chemicals against pathogen bacteria and fungi (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strains</td>
</tr>
<tr>
<td><em>Escherichia coli</em> ATCC 25922</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em> ATCC 27853</td>
</tr>
<tr>
<td><em>Klebsiella pneumoniae</em> ATCC 700603</td>
</tr>
<tr>
<td><em>Staphylococcus aureus</em> (MRSA) ATCC 43300</td>
</tr>
<tr>
<td><em>Salmonella enteritidis</em> ATCC 13076</td>
</tr>
<tr>
<td><em>Sarcina lutea</em> ATCC 9341</td>
</tr>
<tr>
<td><em>Bacillus cereus</em> ATCC 11778</td>
</tr>
<tr>
<td><em>Candida albicans</em> NRRL Y-417</td>
</tr>
<tr>
<td>1                2         3       Gentamicin (µg/ml)</td>
</tr>
<tr>
<td>2.5             -         -        1.95</td>
</tr>
<tr>
<td>-                     -       6.25                   &lt;0.97</td>
</tr>
<tr>
<td>-                     -       6.25                   7.81</td>
</tr>
<tr>
<td>3.125           1.56      3.125                1.95</td>
</tr>
<tr>
<td>1.56           0.39       1.56                   1.95</td>
</tr>
<tr>
<td>-                     -       6.25                   1.95</td>
</tr>
<tr>
<td>-                     -       1.56                   7.81</td>
</tr>
</tbody>
</table>

1: Pure CZTS  2: CZTS + 5% graphene oxide  3: CZTS + 10% graphene oxide

Methicillin resistant *S. aureus* and *S. lutea* were the most sensitive bacteria against three chemicals. The lowest MIC value observed in the present study was determined for *S. lutea* as 0.39 mg/ml. It was noted that the antimicrobial activities determined in the study ranged from weak to moderate. Nevertheless, the addition of 10% of graphene oxide, made the chemical more effective against other pathogen bacteria and yeast except for *S. aureus* and *S. lutea*.

3.4. Photocatalytic Analysis
The photocatalytic activities of CZTS, 5% GO: CZTS and 10% GO: CZTS nanoparticles which were produced via hydrothermal method were monitored with the help of MB degradation under UV light. In order to obtain maximum degradation of MB using composites, a time period optimization was performed with absorbance measurements. The absorbance spectra of CZTS, 5%GO: CZTS and 10%GO: CZTS nanoparticles were given in Fig. 6, respectively. MB showed a maximum peak around 663 nm, and with the help of this maximum peak, the change in concentration was monitored according to Eq. 1. For CZTS nanoparticles, absorbance measurements were taken per 10 minutes and the intensity of the absorption peak of the MB dye decreased with the exposure time. For 5% GO: CZTS and 10% GO: CZTS composites, absorbance measurements were taken per 5 minutes. As seen in the figures, the absorption peak of the MB aqueous solution decreases with the applied UV light. It is clear from the figures that while CZTS nanoparticles exhibit a remarkable photocatalytic activity, CZTS: GO provides a better reduction than CZTS. The fastest degradation of MB was observed in 10% GO: CZTS composites.

In order to find the degradation in concentration of MB solution, the following equation is used:

\[
\frac{C_0 - C_t}{C_0} = \frac{A_0 - A_t}{A_0}
\]

1

where \(C_0\) is the concentration of MB at launch and \(C_t\) represents the concentration of MB at every given moment. Similarly, \(A_0\) is the initial value of the maximum point in the absorption spectrum and \(A_t\) is the maximum point of the absorption spectrum at any time during the experiment. The change in concentrations obtained by using Eq. 1 is shown in Fig. 7. The decreases in the dark condition can be attributed to the electrostatic interactions of CZTS nanoparticles and GO: CZTS composites with the dye molecules.

The kinetics of the MB solution reduced by UV light is explained by a pseudo first order kinetic model based on the Langmuir-Hinshelwood model. The degradation of the dyes was analyzed by the following equation:

\[-\ln \left( \frac{C_t}{C_0} \right) = k t\]

2

In this model, \(\ln\) gives the natural-based logarithm, \(C_t\) is the solution concentration of the solution at any time, \(C_0\) is the initial concentration, \(t\) is the UV light exposure time, and \(k\) is the pseudo-first-order reaction rate coefficient. The photodegradation kinetics of CZTS nanoparticles versus time \(t\) were depicted in Fig. 8 with scatter plots and linearly fitted. Kinetic coefficients were found from the slopes of these fitted lines.
The kinetic coefficients of CZTS, 5% GO:CZTS and 10% GO:CZTS composites which were found from the slopes of the graphs are $k_{CZTS} = 0.00662$, $k_{5\%GO:CZTS} = 0.01103$ and $k_{10\%GO:CZTS} = 0.01534$, respectively. The column graph of these coefficients was given in Fig. 9. According to these values, the photocatalytic activity of 10% GO: CZTS composites increased approximately 57% and 28% compared to CZTS and 5%GO: CZTS, respectively. The increase in the photocatalytic activity of GO: CZTS composites can be attributed to the reduction of photo-generated electron-hole recombination. In other words, due to its excellent conductivity, GO brings the photo-generated electrons to the surface of photocatalysts very quickly. These electrons form hydroxyl radicals by bonding with H$_2$O molecules. The remaining holes interact with O$_2$ molecules to form superoxide radicals. These radicals cause photocatalytic degradation by breaking down the MB dye.

4. Conclusions

To sum up, elemental Cu, Zn, Sn, and S powders have been effectively converted into CZTS powders via a simple hydrothermal method characterized by X-ray diffraction technique, scanning electron microscope and FTIR spectroscopy. The consistent distribution of the four elements of CZTS (Cu, Zn, Sn, and S) in the nanoparticles is revealed by energy-dispersive X-ray analysis (EDX). Moreover, homogeneous graphene oxide flakes anchored with CZTS nanoparticles which was confirmed using XRD and FTIR. To clarify potential antibacterial activity for the chosen compounds CZTS nanoparticles with different GO concentrations, the broth micro dilution experiment was utilized. In this context, seven bacteria and one yeast were employed in the activity assay. The bacteria that were most sensitive to the three compounds were *S. lutea* and *S. aureus*, which are resistant to methicillin. The chemical was more efficient against various pathogen bacteria and yeast, with the exception of *S. aureus* and *S. lutea*, when 10% GO was inserted. The knowledge gained from this work will undoubtedly be very helpful in understanding cell toxicity and the creation of new drugs based on CZTS nanoparticles. When exposed to visible light, all of the generated compounds showed photocatalytic activity in the MB solution. The 10%GO: CZTS composite sample has the highest photodegradation rate, according to the photodegradation kinetics using the Langmuir-Hinshelwood model, because of its enhanced crystallinity. In conclusion, the outcomes of this study suggest that hydrothermally synthesized CZTS nanoparticles with varying GO concentrations possess a desirable range of antimicrobial and photocatalytic properties, making them suitable for various medical and environmental applications.

Declarations

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CRediT authorship contribution statement

Halit Cavusoglu: Methodology, Project administration, Resources, Supervision, Validation, Visualization, Review & editing. Marwah Ali Ibrahim: Investigation, Methodology, Formal analysis. Hüseyin Sakalak: Conceptualization, Data curation, Investigation. Erdogan Günes: Investigation, Formal analysis. Ahmet Uysal: Conceptualization, Data curation, Investigation, Review & editing, Writing – original draft. Emre Çıtak: Investigation, Formal analysis. Teoman Öztürk: Conceptualization, Data curation, Formal analysis, Writing – original draft.

Declaration of Competing Interests

The authors do not have any personal or financial conflicts of interest that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References


**Figures**
Figure 1

XRD patterns of graphite (a) and graphene oxide (b).

Figure 2

XRD patterns of CZTS nanoparticles, 5% GO: CZTS, 10% GO: CZTS composites (a), and magnified patterns of the materials at $2\theta = 5^\circ$ and $15^\circ$ (b).
Figure 3

FTIR spectra of GO (a), 10% GO: CZTS (b), 5% GO: CZTS (c), and CZTS nanoparticles.
Figure 4

Pure GO HR-TEM pictures (a) and GO HR-TEM-EDS elemental mapping (b).
Figure 5

SEM images of pure GO (a), CZTS (b), 5% GO: CZTS (c) and 10% GO: CZTS (d) nanoparticles.
Figure 6

Time period optimization of the absorption spectra of MB solutions containing (a) CZTS nanoparticles, (b) 5% GO: CZTS and (c) 10% GO: CZTS composites under UV light.
Figure 7

Photodegradation of MB dye aqueous solutions over time.
Figure 8
Photodegradation kinetics of CZTS nanoparticles, 5% GO: CZTS and 10% GO: CZTS composites.
Figure 9

Kinetic values of CZTS nanoparticles, 5% GO: CZTS and 10% GO: CZTS composites.

Supplementary Files

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- SupplementaryMaterial.docx