PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING Cu_2ZnSnS_4 NANOPARTICLES SYNTHESIZED BY SOL-GEL AND HYDROTHERMAL METHODS

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Abstract - Textile wastewater has been recognized as one of the roots that causes environmental problems. Nowadays photocatalysis, in which a photocatalyst absorbs a sunlight and degrades organic molecules, has attracted attention for degradation of organic pollutants in wastewater. Cu2ZnSnS4 (CZTS) is a semiconductor with high absorption coefficient which can be used as an efficient photocatalyst. CZTS nanoparticles can be prepared by several solution-based methods, however, a sol-gel method has never been used to synthesize CZTS photocatalyst for a photocatalysis process. In this study, two different methods of sol-gel and hydrothermal were used to synthesize CZTS nanoparticles and investigated for comparison. CZTS synthesized by hydrothermal method were of high crystallinity with crystallite size of about 23 nm. While CZTS synthesized by sol-gel method had crystallite size of about 5 nm. The photocatalytic activity of CZTS was examined to degrade methylene blue (MB) under visible light irradiation. 91.05% and 51.13% of MB was degraded after 15 h using CZTS nanoparticles synthesized by hydrothermal and sol-gel, respectively. To enhance the photocatalytic activity, hydrogen peroxide (H2O2) was also used with CZTS photocatalyst to generate more hydroxyl radicals for MB degradation.

Keywords - Cu2ZnSnS4, Sol-gel, Hydrothermal, Photocatalysis, Photocatalytic degradation.

I. INTRODUCTION

Textile industries discharge untreated effluent into the environment, causing health and environmental problems due to the toxicity of hazardous organic compounds. Dyes are difficult to decompose in water as they have high thermal and photo stability to resist biodegradation. [1] The traditional wastewater treatment processes such as adsorption on activated carbon process, reverse osmosis process, chemical coagulation flocculation process, ozone oxidation process and electrochemical process cannot treat wastewater contaminated with dye because of its high content of organic compounds and low concentration. Photocatalysis has recently been focused on the removal of dye from wastewater due to its advantages such as being environmentally friendly, cost effective, and capable of destructing various dyes or organic pollutants in waste. Photocatalysis uses light and semiconductor material as a photocatalyst to generate hydroxyl radicals (OH·), which are a strong oxidizing agent to degrade dye from wastewater. [2] TiO2 is a semiconductor that is widely used as a photocatalyst due to its high chemical stability under light irradiation, low cost, and high efficiency. However, due to its wide energy band gap, TiO2 can be activated in the UV range only, which represents a small part of the solar spectrum [3].

Cu2ZnSnS4 (CZTS) is a p-type semiconductor with a high absorption coefficient, nontoxic, low cost and earth-abundant. CZTS research had previously concentrated on its synthesis and photovoltaic performance. CZTS has attracted attention as a photocatalyst in photocatalytic degradation processes because of its narrow energy band gap (1.4-1.6 eV), which allows it to respond to light in the visible range. The CZTS nanoparticles can be prepared by various methods such as sol–gel, sonochemical, solvothermal and hydrothermal.[4] However, different synthesis methods affect the morphology, crystallinity, purity of the resulted nanoparticles and also the photocatalytic activity of the photocatalyst. Among these, sol-gel is considered to be an efficient method to synthesize nanoparticles due to its simplicity and low cost.

So far, there has been no reports on dye solution degradation using CZTS photocatalyst synthesized via sol-gel method. In this study, we used sol-gel (SG) and hydrothermal (HT) method to prepare CZTS nanoparticles for use as photocatalysts, which were then tested to degrade methylene blue under visible light irradiation and in a presence of H2O2. The degradation efficiency of CZTS prepared by different methods was compared and the results were discussed.

II. EXPERIMENTAL

CZTS nanoparticles were synthesized by sol-gel and hydrothermal methods which were improved from Silpcharoen et al. [5] The preparation is as follows.

Sol-gel method

Copper (II) acetate monohydrate (2.395 g, 0.6 m), zinc (II) acetate dihydrate (1.317 g, 0.3 M), tin (II) chloride dihydrate (1.353 g, 0.3 M) and thiourea (1.918 g, 1.2 M) were used to prepare solution containing 20 ml of ethylene glycol as a solvent. After 120 min of stirring at room temperature in the air atmosphere, 0.25 ml monoethanolamide (MEA) was added into the solution and magnetically stirred again for 120 min. The color of the solution was changed from blue green to white and then to brownish colloidal solution during stirring. After 30 min of continuous heating at 250°C the brownish color of the solution turned into the black color of precipitates. The precipitated solution was centrifuged at 6000 rpm by adding additional ethanol and deionized (DI) water to extract the CZTS nanoparticles and impurities. Finally, the particles were dried under air at 80 °C for 240 min.

Hydrothermal method

Copper (II) chloride (0.03 M), zinc chloride (0.015 M), tin chloride (0.015 M) and sodium sulfide (0.06 M) were used as precursors. Dissolved precursors were conducted in 24 ml of DI water and thoroughly mixed using a magnetic stirrer. 6 ml of ethylenediamine was added into the solution and stirred for 20 min. The solution was loaded in Teflon lined stainless steel autoclave and kept in the oven at 220°C for 24 h. After cooling, the black powder was centrifuged at 6000 rpm for 5 min and washed with DI water and ethanol respectively. The final powder was dried at 80°C for 2 h.

Photocatalytic activity

The photocatalytic activity of the CZTS nanoparticles was tested for degradation of methylene blue (MB) dye at room temperature under visible light irradiation. 30 mg of the CZTS nanoparticles was added into a beaker containing 100 ml of MB dye solution (10 mg/L). Then, 0.5 mM of H2O2 was added into the solution to initiate the catalytic process. [6] The solution was sonicated for 5 min in the dark for complete dispersion of CZTS nanoparticles. The mixture was stirred for 30 min in the dark to reach the adsorption-desorption equilibrium. Then, the solution was irradiated with a visible light using a 30 W LED lamp. The lamp was situated 7 cm above the suspension. After a desired irradiation time, a 2 ml sample was taken out, and the catalyst was separated from the solution by centrifugation. The absorption spectrum was recorded by using a UV-Vis spectrophotometer at wavelength of 664 nm to determine the degradation of MB dye in the solution [4]. The degradation efficiency was calculated using the expression in Eq. (1).

$$\eta = \left(\frac{C_0 - C}{C_0}\right) \times 100 \qquad (1)$$

where C_0 is the initial concentration of MB at zero min and C is the concentration after the irradiation time of t min.

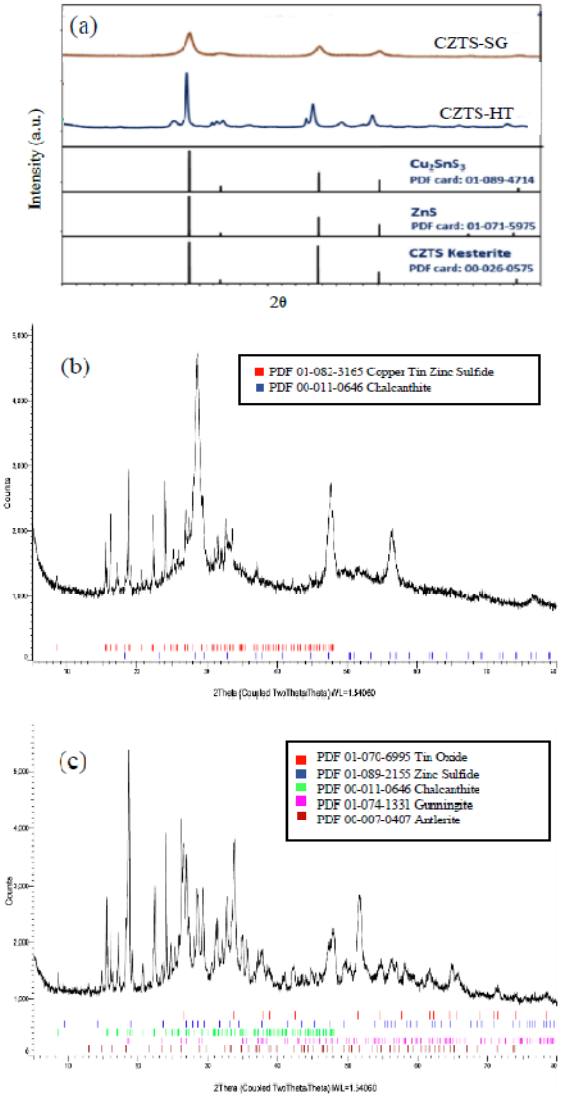


Fig. 1 (a) X-ray diffraction of CZTS synthesized by sol-gel (SG) and hydrothermal (HT) methods, (b and c) X-ray diffraction of CZTS synthesized by sol-gel (SG) and hydrothermal (HT) methods after storage for 2 years.

Characterization

Scanning electron microscope (SEM) was used to determine size and morphology of CZTS nanoparticles. The crystallinity and phase confirmation of CZTS nanoparticles was carried out by X-ray diffraction (XRD). Specific surface area and pore size of CZTS was analyzed by Brunauer, Emmett and Teller (BET). Optical absorption spectra of CZTS and dye solution were carried out by UV-Vis spectrophotometer.

III. RESULT AND DISCUSSION

Fig. 1(a) shows X-ray diffraction (XRD) pattern of as-synthesized CZTS nanoparticles prepared by sol-gel method (CZTS-SG) and hydrothermal method (CZTS-HT). XRD peaks observed at 28.531, 32.990,

47.332, 56.178 and 76.445 correspond to (112), (200), (220), (312) and (332) planes of kesterite phase of CZTS. Intensity and full width at half maximum (FWHM) of peaks indicated that crystallinity of CZTS-SG was less than that of CZTS-HT. The crystallite size for kesterite phase calculated according to Scherrer's equation were 5 and 23 nm for CZTS-SG and CZTS-HT, respectively [5]. The calculated crystallite size corresponds to specific surface area obtained from BET technique. Specific surface area of CZTS-SG and CZTS-HT were 17.582 and 14.197 m2/g, respectively. When the crystallite size of particles increased, the surface area was decreased. It is noted that the CZTS nanoparticles used in this work have been kept for 2 years to investigate their stability.

After 2 years of synthesis, the XRD peaks of CZTS-SG in Fig. 1(b) remain kesterite phase of CZTS, indicating that the material was stable. However, the XRD peaks obtained from CZTS-HT in Fig. 1(c) exhibited a formation of other minerals such as chalcanthite, gunningite and antlerite. The minerals mentioned above were formed by copper being oxidized in the environment condition during storage. Morphology of CZTS synthesized by sol-gel and hydrothermal methods was investigated using SEM. The result demonstrated that different synthesis methods affected the particle morphology. As shown in Fig. 2(a), the flower-like CZTS-SG particles composing of several self-assembled nanosheets were formed [6, 7]. The surface of CZTS-SG shown in Fig. 2(b) represents a uniformly sized spherical particle dispersed on nanosheets. While Fig. 2(c-d) show surface morphology of CZTS-HT, which were spherical in shape with non-uniformity in size. Agglomeration of particles was also observed which could be attributed to 2 year storage, therefore resulting in slightly reduced specific surface area compared to that of CZTS-SG.

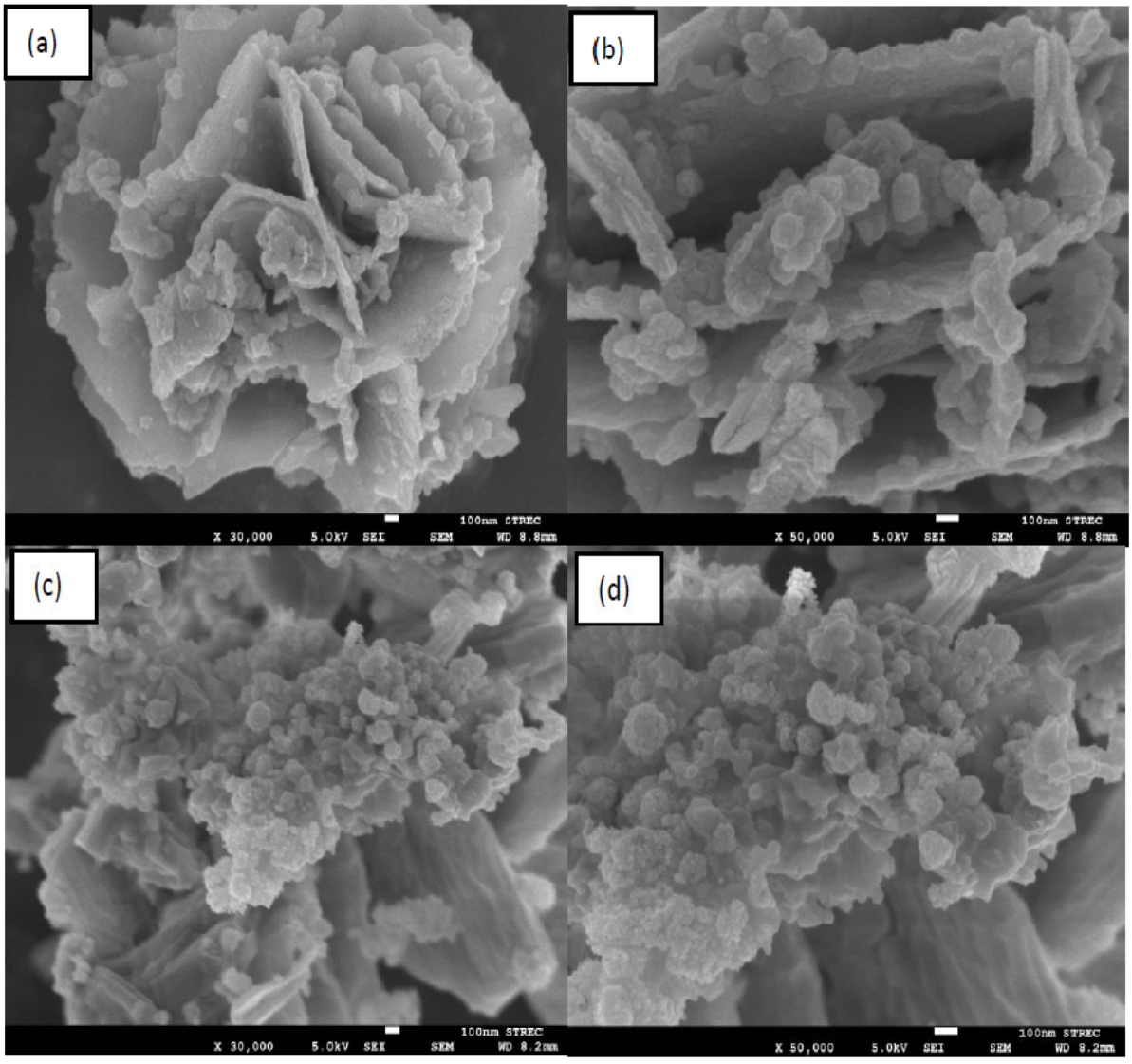


Fig. 2 SEM image of CZTS nanoparticles synthesized by different methods (a, b) CZTS-SG (c, d) CZTS-HT (both are in different angles).

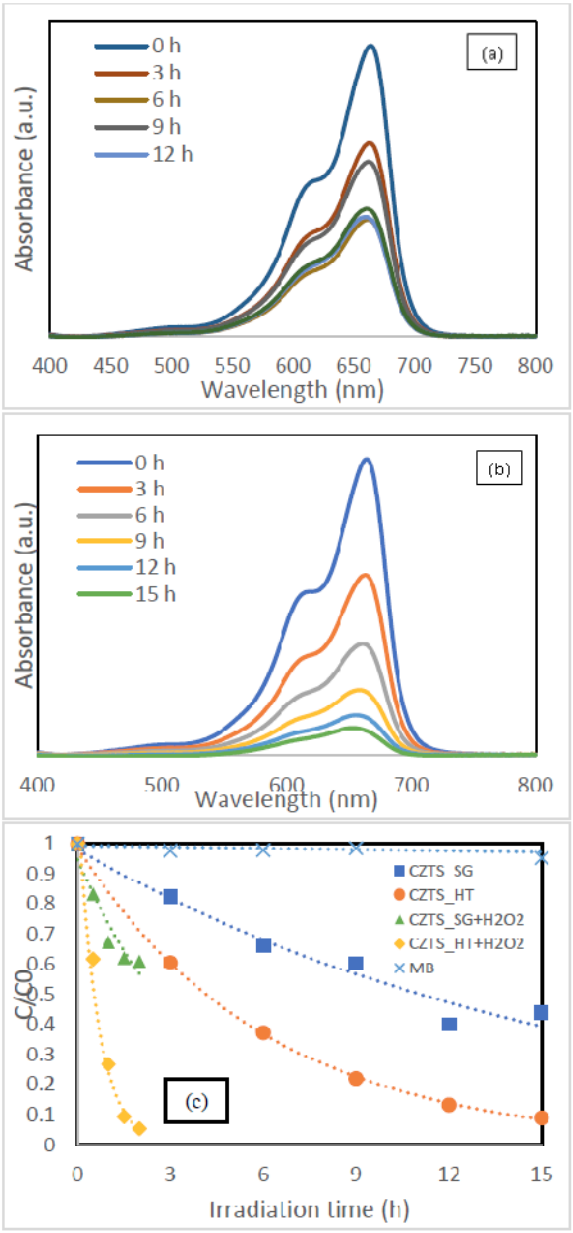


Fig.3 (a) UV-visible absorption spectrum of MB solution with CZYS_SG for different irradiation time, (b) UV-visible absorption spectrum of MB solution with CZYS_HT for different irradiation time, (c) Comparison of photocatalytic degradation of MB using CZTS nanoparticles synthesized by different methods as a function of irradiation time.

To test the photocatalytic degradation using CZTS nanoparticles synthesized from two different methods, methylene blue was used as a model organic pollutant under the visible light irradiation. Fig. 3(a, b) show the absorbance spectra of MB at 664 nm sampling at different time intervals of irradiation. The results show a decrease in the absorbance over time. It is noted that before the photoreaction began, absorption and desorption equilibrium was performed by stirring the solution in the dark for 30 min. As shown in Fig. 3(c), the concentration of MB solution without photocatalyst remained constant after 15 h under visible light irradiation, indicating that the photocatalytic degradation of MB could not proceed without photocatalyst [4, 8]. The photocatalytic process in the absence of H2O2 was successful and led to degradation efficiency of MB to about 51.13% and 91.05% within 15 h upon the addition of CZTS-SG and CZTS-HT, respectively. With a presence of H2O2, the degradation of MB resulted in significantly faster decay within 2 h. Degradation of MB efficiency was 94.62% and 38.88% for CZTS-HT+H2O2 and CZTS-SG+H2O2, respectively.

The difference in efficiency can be explained in terms of the photocatalytic mechanism. The possible mechanism of photocatalytic degradation of MB by using CZTS nanoparticles was proposed and shown in Fig. 4. When CZTS nanoparticles are irradiated by light with energy greater than its energy band gap, electrons and holes were generated as expressed in Eq. (2) [4]

$$Cu_2ZnSnS_4 + h\nu \rightarrow Cu_2ZnSnS_4 + h^+ + e^- \quad (2)$$

Electrons were activated from the valence band (VB) to the conduction band (CB), leaving hole behind in the VB. Electrons reacted with O2 resulting in a formation of superoxide ion ($O2\cdot^-$). While hole on the VB reacted with superoxide ion, which leads to the formation of hydroxyl radicals (OH·) which is a strong oxidizing agent used in the degradation reaction [3]. The reactions for the generation of OH· can be expressed in Eqs. (3-7) as follows [9].

$$H_2O + h^+ \rightarrow OH\cdot + H^+ \quad (3)$$

$$O_2 + e^- \rightarrow O_2^{\cdot -} \quad (4)$$

$$O_2^{\cdot -} + H_2O \rightarrow H_2O_2 \quad (5)$$

$$H_2O_2 \rightarrow 2OH\cdot O_2^{\cdot -} + H_2O \rightarrow H_2O_2 \quad (6)$$

$$OH\cdot + \text{Dye} \rightarrow \text{degrade product} \quad (7)$$

Once OH· radicals are formed, they can degrade MB, which is in contact with the CZTS nanoparticles, to yield carbon dioxide, water, sulfate, nitrate and ammonium ion [10]. To improve the photocatalytic degradation under visible light irradiation, the combination effect of photodissociation of H2O2 was associated with photocatalysis on CZTS surface. This combination process has been previously reported to improve degradation efficiency[11]. Photodissociation of H2O2 can be described by Eq. (8) [12].

$$H_2O_2 + h\nu \rightarrow 2OH\cdot \quad (8)$$

A higher degradation efficiency when H2O2 was added to the process can be explain from the fact that H2O2 acted as a source of OH· radicals. Therefore, it helped generating more OH· radicals for the reaction, resulting in faster degradation rate.

In terms of reaction kinetics, the experimental data was fitted in the following pseudo-first order kinetic equation [13]:

$$-\ln\frac{C}{C_0} = k_{app}t \quad (9)$$

where k_{app} is the pseudo-first order rate constant (min-1). Curve fitted using Eq. (9) was plotted and shown as dotted lines in Fig. 3(c). The rate constants for the reactions using CZTS nanoparticles synthesized from sol-gel and hydrothermal methods and CZTS nanoparticles from 2 methods with a presence of H2O2 are given in Table 1.

Conditions	Rate constants, k_{app} (min^{-1})
CZTS-SG	0.068
CZTS-HT	0.164
CZTS-SG+H_2O_2	0.395
CZTS-HT+H_2O_2	1.321

Table 1. Rate constants of photocatalytic degradation of MB under various conditions.

A significantly higher reaction rate constant of CZTS-HT in the present work compared to the previous work [4, 9] could be due to a high crystallinity of CZTS derived from hydrothermal method. While CZTS nanoparticles synthesized by sol-gel method for photocatalytic degradation has never been researched. Even though the reaction rate constant of CZTS-SG is less than that obtained from CZTS-HT, it is still higher than the previous reported values.

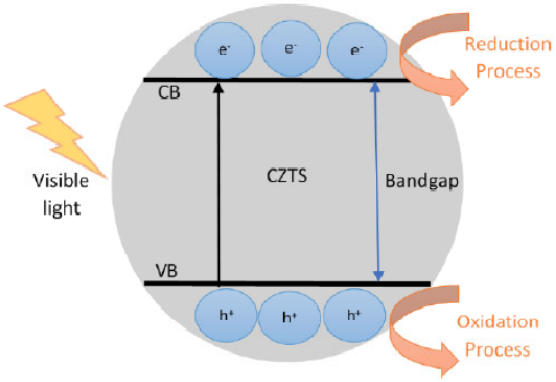


Fig 4 Schematic diagram represents photocatalytic mechanism of CZTS

IV. CONCLUSION

CZTS nanoparticles were successfully synthesized by sol-gel and hydrothermal methods. The result from characterization techniques revealed that the synthesis method affected size and morphology of the particles. CZTS synthesized by hydrothermal method had higher crystallinity in kesterite phase with crystallite size of 23 nm, while CZTS synthesized by sol-gel method had crystallite size of 5 nm. Photocatalytic degradation of methylene blue using CZTS-HT and CZTS-SG under visible light irradiation demonstrated the efficiency of 91.05% and 51.13%, respectively, within 15 h. With a presence of H2O2, photodegradation efficiency were increased to 94.62% and 38.88% for CZTS-HT+H2O2 and CZTS-SG+H2O2, respectively, only within 2 h. Moreover, H2O2 acted as a source of additional hydroxyl radicals, which increased the oxidation of MB.

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