Hydrothermal synthesis of monocopper sulfide for hydrogen peroxide-assisted photodegradation of paraquat

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ABSTRACT
Copper sulfide was prepared by a hydrothermal method at 130°C. The copper to sulfur molar ratio (6-10) and ageing time (24-72 h) were their synthesis parameters. The obtained materials were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), transmission electron microscope (TEM), UV-DR spectroscopy and X-ray photoelectron spectroscopy (XPS). In order to obtain monocopper sulfide, CuS, named as covellite, the molar recipe ratio of sulfur to copper should be less than 8 in any hydrothermal ageing time. The morphology showed spherical-like structure with energy band gap of 1.88-2.04 eV. CuS was tested for its photocatalytic degradation of paraquat under visible light irradiation. It exhibited excellent activities in the presence of H2O2. The kinetic of paraquat degradation was also investigated using Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. The reaction rate constant was three times higher than TiO2 under the same studied conditions.

Keywords: CuS, Solvothermal method, Photocatalytic reaction, Paraquat, Visible light

1. Introduction

Copper sulfide has attracted interest due to the excellence in its optical, electronic, physical and chemical properties [1]. It can be applied in many applications such as p-type semiconductor in solar cell [2, 3], adsorbents and catalysts for sustainable environmental treatment issues. Copper sulfide could be existed in several forms such as covellite (CuS), chalcocite (Cu2S) and villamaninite (CuS2). Copper sulfide can be prepared by many techniques such as hydrothermal or solvothermal methods [4, 5], microwave irradiation [6, 7], sonication [8], sol-gel precipitation [9]. Among those methods, hydrothermal and solvothermal techniques are simple, low cost and friendly to environment.

According to a narrow bandgap ranging of copper sulfide, 1.27 - 1.75 eV [10], copper sulfide could be utilized as a photocatalyst. The photocatalytic degradation by this material was reported over several dye solutions, such as methylene blue (MB), rhodamine B (RhB), malachite green (MG), methyl red (MR), methyl orange (MO) and eosin (E) [11]. Since monocopper sulfide (CuS) is a preference form among those three forms, the study of precursor ratios of Cu and S in the synthesis recipe, therefore, has been interested [12]. Auyoong et al. [13] also mentioned that mole ratio of Cu:S provided an important role in controlling the form of copper sulfide. Adhikari et al. [14] examined the photoreactivity of CuS and Cu2S phases over 4-Chlorophenol. According to the spectra obtained from photoluminescence spectroscopy, it was reported that Cu2S showed less degradation activity than CuS, and high recombination rate of photogenerated charges was concluded as one possible cause. Moreover, dicopper sulfide could be also contaminated in the final product during the synthesis of monocopper sulfide [15, 16]. The recipe range of copper to sulfur ratio in monocopper sulfide synthesis without forming of dicopper sulfide should be interestingly investigated.

Even though organic species in wastewater can be degraded effectively by photodegradation technique, some intermediates found in the effluent have been highly toxic or even higher toxic...
Copper (II) chloride dehydrate (CuCl₂·2H₂O, Carlo Erba Reagents, ≥ 98%), Hexadecyl trimethyl ammonium bromide (CH₃(CH₂)_{15}N(Br)(CH₃)₃, Acros Organics, ≥ 99%) and sodium sulfide nonahydrate (Na₂S·9H₂O, Carlo Erba Reagents, ≥ 99.9%) were used as starting materials for copper sulfide preparation. Methyl viologen hydrate or paraquat (C₂H₂N₂Cl₂·xH₂O, Sigma-Aldrich, ≥ 98%) and hydrogen peroxide solution (H₂O₂, Carlo Erba Reagents, 30 wt% in water) were used as organic probe and electron accepter, respectively, for the photocatalytic activity of the CuS.

2.1. Synthesis of CuS

The preparation of CuS synthesis was adapted from Saranya and Nirmala Grace [22]. A mixture of copper chloride and hexadecyl trimethyl ammonium bromide solution was prepared. A solution of sodium sulfide nonahydrate was added into the prepared copper solution. The ratios of copper to sulfur in the final solution were varied on molar ratio basis of 1:6, 1:8 and 1:10. After the mixing, the solution was stirred for 30 min and transferred into a teflon-lined stainless steel autoclave for further hydrothermal ageing at 130°C in an oven. The autoclave was cured for 24, 48 and 72 h, afterwards, it was cooled down to room temperature before collecting the sample. The as-synthesized material was removed from the teflon-container to centrifugal tubes. The precipitate was isolated by using a centrifuge and washed with deionized water and ethanol for several times until the solution became transparent. Then, the precipitate was dried in a vacuum oven at 60°C for 12 h. Finally, the samples in black powder form were obtained. The as-synthesized samples were assigned as CuS(x-y); where x represents molar ratio of sulfur to copper and y represents ageing period in h. For example: CuS(6-24) means CuS synthesized under copper to sulfur molar ratio basis of 1:6 and hydrothermally aged for 24 h.

2.2. Characterization

The crystalline structure of the synthesized material was identified by an X-ray diffractometer (BrukerAXS Model D8 Discover, Germany) equipped with a Cu Kα monochromatized radiation source in the range of 2θ from 20° to 60°. Scanning electron microscope (SEM, JEOLJSM-6610LV, Japan) and transmission electron microscope (TEM, FEI Tecnai G2 20, Oregon, USA) were used to observe their morphologies of the synthesized materials. The optical property of CuS was studied by UV-diffuse reflectance absorption spectrometer (Hitachi model U-3501, Japan). Surface analysis by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Kratos analytical, UK) was performed with X-ray hybrid mode 700×300 μm spot area and a monochromatic Al Kα radiation at 1.4 keV. The radiation source was operated at 15 kV and 150 W. A base pressure in the XPS chamber was set at 5×10⁻⁹ torr.

2.3. Photocatalytic Activity Tests

The photocatalytic activity of CuS was evaluated over paraquat solution under visible light irradiation. The photocatalytic reaction was performed in a 1.000 mL double-jacket cylindrical vessel. The reactor was fixed 30 cm away from a 6 W light emitting diode lamp (6W-E27, Philips, Germany). The solution was maintained at 25°C. The light intensity was monitored by a solarimeter (SL100, Kimo, France) and a UV meter (UV-meter 5.0, Solartech, USA). It was confirmed that only visible light intensity of 6 W/m² was observed. The initial concentration range of paraquat solution were 0.16-0.38 mM (40-100 mg/L). After adding the studied catalyst into the solution, the mixed solution was magnetically stirred in the dark for 1 h prior to turning the light on. One mL of hydrogen peroxide (30 wt%) was initially added into the solution [19, 23]. For a time interval of 20 min, one mL of sample was drawn out by a syringe and filtered by a PTFE- Millipore disk (0.45 μm) to remove any suspended catalyst particles before the analysis. The remaining paraquat concentration was analyzed by a UV-vis spectrophotometer (JASCO-V630, Japan) under the wavelength of 257 nm. The concentration of paraquat also was double checked with a high performance liquid chromatography (HPLC, Agilent Technologies, USA) equipped with Hypersil C18 ODS (4.0 125 mm, 5 μm) column and diode-array detector (HPLC-DAD 1200 series, Agilent Technologies, USA) with a UV-detector set at λ = 258 nm. The column temperature and injection volume were set at 25°C and 80 μL, respectively.

3. Results and Discussion

3.1. Characterization of CuS

Nine samples of prepared catalysts CuS(x-y) were characterized by XRD, firstly. The XRD patterns of those catalysts are presented in Fig. 1. It was found that all catalysts showed sharp crystalline peaks (2θ) at 27.9°, 32.4°, 46.4° and 55.1°. In regard to JCPDS card no.06-0464, they correspond with the planar of (101), (103),
Fig. 1. XRD patterns of copper sulfide prepared in a variety of sulfite ratios and ageing times. (110) and (108) of CuS or covellite phase [24, 25]. Any formation of Cu2S and CuS2 in this range of synthesis conditions could not be observed. Considering in all samples, the materials synthesized under adding low amount of sulfite for any ageing time [CuS(6-y)] provided stronger sharp peaks, comparative to those under higher amount of sulfite adding for any ageing time [CuS(8-y) and CuS(10-y)]. It was also indicated that ageing period of 24 h would be sufficient to stabilize copper sulfide in covellite phase. According to the XRD patterns, the average crystallite size of catalyst could be approximated by Scherrer’s equation to be 32.52 ± 3.71 nm [26].

Morphologies of copper sulfide in different synthesis conditions were studied by SEM and TEM. The images are shown in Fig. 2. Three structural patterns, including spherical, plate-like and rod-like shape, could be observed. The particles shown in sample CuS(6-y) were formed mostly in spherical type. The distributions of rod-like and plate-like shape for CuS(6-y) were also found, but the distributions were found better when the synthesis were done with higher content of sulfur [CuS(8-y) and CuS(10-y)]. In addition, obtained materials of CuS(6-48) and CuS(10-48) were selected and analyzed by TEM, as shown in Fig. 3. CuS(6-48) provided TEM image in plate-like structure with staggering to each other, while CuS(10-48) possessed more in rod-like structure. The observation of CuO layer was found in the sample with high sulfur ratio in recipe; CuS(10-48). On the other hand, CuO was not detected in CuS with low sulfur content, supported by the EDS results.

Fig. 2. SEM images of CuS(x-y) prepared at 130°C under different sulfur contents and ageing temperatures. (a)-(c) CuS(6-24), (6-48), (6-72); (d)-(f) CuS(8-24), (8-48), (8-72); (g)-(i) CuS(10-24), (10-48), (10-72), respectively.
Fig. 4. UV-DR spectra and Tauc plots of CuS(6-y), CuS(8-y) and CuS(10-y).

To determine whether the material possesses good semiconducting property and be useful for the photocatalytic performance, the diffuse reflectance of UV should be measured. Fig. 4 shows UV-DRs spectra of all CuS samples. The Tauc plots were prepared to estimate the band gap energy of all samples. They were plots of $(\alpha h\nu)^2$, converted from spectra, versus their photon energy $(h\nu)$, where $\alpha$ is absorption coefficient, $h$ is Planck’s constant, and $\nu$ represents light frequency. The tangent lines drawn through the maximum slopes were extrapolated, resulting in intersection values on the X axis [27]. It was found that the average band gap energy of synthesized catalysts was in the range of 1.88-2.04 eV.

As a result, different synthesis conditions on copper to sulfur ratio in the recipe were not significantly affect to the band gap energy. CuS was also analyzed for its chemical states by using X-ray photoelectron spectroscopy (XPS). Fig. 5(a) shows the XPS survey spectra of CuS(6-48) (Top view) and CuS(10-48) (Bottom). The peaks of Cu 2p3/2 and Cu 2p1/2 located at 932.9 eV and 952.7 eV are corresponding to Cu2S. As the ratio of sulfur decreased, the Cu 2p peak shifted negatively to 932.5 eV. This phenomenon described the transformation from Cu2S to CuS [23]. Besides, the peak of S-Cu bond was located at a binding energy 162.2 eV [28] and the peak of S-S dimers was located at 163.6 eV [29] (Fig. 5(b)). It was also found that the position of sulfide peak over CuS(6-y) was shifted negatively to approximately 161.8 eV, demonstrating
the decrease in average Cu-S bond length which is smaller in covellite than in chalcolite [30]. Therefore, it could be concluded that the ratio of copper to sulfur affecting on the formation of CuS. Cu2S and CuS were formed under the conditions of CuS(6-y) and CuS(10-y), respectively.

3.2. Photocatalytic Activity of CuS
The performance of copper sulfide on its photocatalytic activity was tested over paraquat, as a probe chemical. As explained by XPS, mixed recipe ratios of Cu and S could lead to different structures of CuS or Cu2S. All copper sulfide samples were tested for paraquat photodegradation under visible light irradiation. An initial concentration of paraquat was used at 0.16 mM under H2O2 assistance. As shown in Fig. 6, paraquat was completely degraded within 180 min over CuS(6-y) and CuS(8-y). On the other hand, it was taken longer with CuS(10-y), approximately 240 min to complete the degradation. This would confirm that copper sulfide in covellite form (CuS) possessed higher photoactivity than chalcocite form (Cu2S) [16]. This phenomenon is possible due to the effect of Cu2S possesses high recombination rate of photogenerated charges, according to PL spectra explained by Adhikari et al. [14].

It has been proved previously that covellite form (CuS) was preferential to the photocatalytic reaction, therefore, CuS(6-48) was selected as a representative. The comparison of its performance was done against TiO2 powder. Fig. 7 shows the concentration profiles of the studied materials including the blank test. Prior to the photocatalytic test, the solution was kept in the dark environment for 1 h, providing sufficient adsorption on the surface of materials. As observed, paraquat was disappeared onto the surface of TiO2 higher than CuS. It was corresponding to the much higher surface area of TiO2 (50 m²/g) comparing to that of CuS (ca. 4.5 m²/g).

Under visible irradiation, paraquat was barely degraded without photocatalyst, reflecting that paraquat was quite stable. It could be seen that the concentration of paraquat decreased little bit (ca. 2-3 %) in the environment of either CuS or H2O2. The unsatisfactory performance of CuS was probably caused by a rapid recombination of photogenerated charges of CuS [24].
Fig. 7. Photocatalytic degradation profiles of 0.16 mM paraquat solution over a CuS(6-48) with catalyst dosage 1.0 g/L and 1 mL H₂O₂ (30 wt%) under visible light.

Applying a little amount of H₂O₂ into both cases (TiO₂ and CuS), the difference of paraquat degradations could be noticed. Paraquat was degraded significantly higher over CuS assisted with H₂O₂ than over TiO₂ assisted with H₂O₂. A complete degradation of paraquat was found over CuS with H₂O₂ within 2 h irradiation, while only 5% taken place over TiO₂ with H₂O₂. The poor performance of TiO₂ was probably due to low photon energy ($h\nu$) applied from visible light irradiation. The photo energy was not adequate to strike electrons from the valence band to generate any active species [1]. Thus, the declination of paraquat concentration should be based on the adsorption on the surface. Considering CuS assisted with H₂O₂, it seemed that the presence of H₂O₂ played an important role to energize the catalytic degradation activity of CuS. It was expected that two mechanisms would be taken place. One was that H₂O₂ enhanced the reaction through Fenton-like and photo-fenton reactions. Regarding the former reaction, the Cu⁺ in the CuS could react with H₂O₂ to generate hydroxyl radicals, and further improve the photocatalytic property to a Fenton-like reaction [31]. The photo-fenton reaction as the following mechanism, H₂O₂ acted as an efficient electron acceptor reacting with photogenerated electrons to promote the separation of the photogenerated electron and hole and additionally produce hydroxyl radicals [23, 32]. Consequently, paraquat would react with hydroxyl radicals both generated from Fenton-like reactions and photocatalysis. The concentration of remaining paraquat was reconfirmed by HPLC, as shown in Fig. 8. It illustrates paraquat HPLC peaks during photodegradation time; 0-40-80-120 min. The results were corresponded with those shown in Fig. 7. Moreover, the intermediate peak was not observed.

3.3. Kinetic Study

The kinetic study of photocatalytic reaction of CuS was evaluated over CuS(6-48) using an initial rate technique. Various initial concentrations of paraquat solutions of 0.08, 0.16, 0.24, 0.32 and 0.40 mM were performed for the kinetics investigation.

The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model was applied to the photodegradation as shown in Eq (1).
By applying an initial rate technique, all products would be neglected and the rate expression could be written as Eq. (2). To evaluate adsorption equilibrium constant and the surface reaction rate constant, Eq. (2) was rearranged into a linear form, as shown in Eq. (3).

$$-r_{\text{paraq}} = \frac{k_{\text{paraq}}^o - k^i_{\text{prod}}}{1 + K_A t_{\text{paraq}} + K_{\text{prod}} c_{\text{prod}}^o}$$  \hspace{1cm} (1)

$$-r_{\text{paraq}}^0 = \frac{k_{\text{paraq}}^o}{1 + K_A t_{\text{paraq}}}$$  \hspace{1cm} (2)

$$\frac{1}{-r_{\text{paraq}}^o} = \frac{1}{k_{\text{paraq}}^o} + \frac{K_A}{k}$$  \hspace{1cm} (3)

Where a subscription “$o$” represents an initial state.

Fig. S1 shows the plot of $\frac{1}{-r_{\text{paraq}}}$ versus $\frac{1}{k_{\text{paraq}}^0}$. Eventually, adsorption equilibrium constant ($K_A$) and the surface reaction rate constant ($k$) for paraquat degradation were obtained as $10.34 \text{ mM}^{-1}$ and $2.5 \times 10^{-3} \text{ min}^{-1}$, respectively.

4. Conclusions

In the synthesis of copper sulfide by hydrothermal method, the recipe ratio of copper to sulfide was important. It was found that higher portion of sulfide to copper than 8 would generate both forms of CuS and Cu2S. The photocatalytic performance of CuS [from sample CuS(6) and CuS(8)] over paraquat was much better than a combination species of CuS and Cu2S [from CuS(10)]. Aging time was not as a significant factor in the synthesis. The obtained CuS was in nanoparticles and spherical-like structure, provided band gap energy of 2.04 eV. The photodegradation performance of CuS was tested over paraquat solution under the $\text{H}_2\text{O}_2$ assistance. The kinetic of paraquat photocatalytic degradation was revealed by the Langmuir-Hinshelwood-Hougen-Watson kinetic model. The surface reaction rate constant ($k$) was found to be $2.5 \times 10^{-3} \text{ min}^{-1}$, which is higher than that of TiO2.

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Author Contributions

R. K. (Ph.D.) designed and carried out the experiments, contributed to the interpretation of the results, and co-prepared the manuscript. K.W. (Assoc. Prof.) characterized the materials and analyzed the data. N.G. (Assoc. Prof.) supervised the project and co-wrote the manuscript.

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