Enhanced sonocatalytic performance of PEG-modified hierarchical Cu 2 ZnSnS 4 microspheres in Methylene Blue degradation

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Research Article

Keywords: Cu2ZnSnS4, sonocatalysis, hydrothermal, hierarchical microspheres

Posted Date: August 11th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1939443/v1

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Abstract

In this work, hierarchical Cu$_2$ZnSnS$_4$ microspheres were synthesized via a hydrothermal method with the utilization of PEG as surfactant. The as-prepared CZTS samples were systemically characterized by XRD, Raman, TEM, XPS, UV-Vis, PL and BET techniques. The sonocatalytic activity of as-prepared Cu$_2$ZnSnS$_4$ was evaluated by the degradation of methylene blue. The results displayed that the PEG-modified Cu$_2$ZnSnS$_4$ microspheres with smaller optical band gap and lower recombination rate of electrons and holes lead to rapid removal of methylene blue. Over 95.0% methylene blue was sonocatalytically degraded by PEG-modified Cu$_2$ZnSnS$_4$ microspheres after 20 min, while only about 82.1% of methylene blue was degraded over Cu$_2$ZnSnS$_4$ without PEG modification. The effect of radical scavengers on methylene blue degradation process was investigated and clarified that the sonogenerated holes and hydroxyl radicals are the main active oxidative species in sonocatalytic process.

1. Introduction

The increasing water contamination by organic pollutants and dyes has arouse much attention to develop highly efficient and low-cost technology to overcome the water pollution problems. Among various techniques for water treatment, sonocatalytic process has been proved to be a more attractive, simple to operate and clean strategy for wastewater treatment[1]. Notably, the utilization of semiconductors in sonocatalytic process can reduce the activation energy, accelerate the degradation rate and increase the degradation efficiency significantly[2]. Diverse semiconductors including ZnO, TiO$_2$ and ZrO$_2$ have been applied as sonocatalyst and the results showed that the sonocatalytic efficiency highly depends on the type of catalyst[3–5]. Moreover, limited transportation ability of sonocatalyst and high recombination rate of activated electrons and holes in sonocatalyst greatly restrict the sonocatalytic activity through hindered interfacial charge transfer and surface reaction [6, 7]. Therefore, the improvement of sonocatalyst conductivity by surface design or doping become one of promising approaches to improve the catalytic performance.

Quaternary multivalent Cu$_2$ZnSnS$_4$(CZTS) has been considered as one of the most promising materials in solar cells owe to its high absorption coefficient of over 10$^4$ cm$^{-1}$[8], optimum direct band gap (1.4–1.6 eV) [9], natural abundance[10], and favorable electronic band alignment[11]. Impressively, the excellent electrical activity of CZTS can promote the transportation and separation rate of electrons and holes, resulting in the improvement of the photocatalytic activity[12]. It is also reported that the microstructure of CZTS catalyst with additional exposed surface active sites shows visible enhancement in catalytic process[13, 14]. Hydrothermal method has been widely used for the preparation CZTS materials with tunable microstructure and physical properties[15]. PEG has ordered linear molecular structure terminating with multiple coordinating sites which can act as a surfactant and is widely used to control the particle size and morphology of CZTS in hydrothermal process[16].
Herein, we prepared CZTS sonocatalyst through a hydrothermal method by using PEG400 as surfactant to tune its microstructure and conductivity. The composition, microstructure, optical and electrical properties of PEG-modified CZTS microspheres were investigated. The sonocatalytic activity of as-prepared CZTS samples was evaluated by the degradation of Methylene Blue (MB) under ultrasound irradiation.

2. Experiment

2.1. Preparation

Copper(II) chloride dihydrate (CuCl$_2$•2H$_2$O, 99%), zinc chloride (ZnCl$_2$, 95%), Tin(IV) chloride dihydrate (SnCl$_4$•4H$_2$O, 98%), Thiourea (H$_2$NCSNH$_2$, 99.8%), PEG400 and Methylene Blue (MB) were purchased from Aladin China. CuCl$_2$•2H$_2$O (0.467 g, 2.7 mmol), SnCl$_4$•4H$_2$O (0.467 g, 1.3 mmol), ZnCl$_2$ (0.183 g, 1.3 mmol) and Thiourea (0.567 g, 7.4 mmol) were added in distilled water (80 mL) to dissolve under sustained stirring at room temperature for 60 min. PEG400 (1.995 g, 5 mmol) was then added, followed by stirring for an additional 10 minutes. The solution was then transferred to a 100 mL Teflon-lined hydrothermal flask and heated at 483K for 24 hours in a temperature-controlled oven and then allowed to cool down to room temperature. After cooling, the contents of the Teflon-lined hydrothermal flask were transferred to a centrifuge tube and centrifuged at 3000 rpm for 20 minutes. Then discarded supernatant and added distill water, and the precipitate dispersed in water was centrifuged at 3000 rpm for 10 minutes. This centrifugation–redispersion cycle was repeated six times. The obtained product was dried at 378K for 26 hours. The PEG-assisted CZTS sample were denoted as CZTS-P. As a contrast, CZTS sample were prepared as the same procedures without PEG addition and denoted as CZTS.

2.2. Characterization

X-ray diffraction (XRD) measurement was carried out to investigate the phase purity and crystal structure of as-prepared CZTS samples with a Bruker D8 Advance ECO. Raman spectroscopy of the as-prepared CZTS samples was carried out at room temperature using a confocal Raman spectrometer (HORIBA Jobin Yvon). Optical absorption measurement of the synthesized CZTS nanocrystals was carried out using a Perkin-Elmer Lambda 950 UV-Vis spectrophotometer. The surface morphology and compositional analysis of the CZTS samples were characterized by scanning electron microscope (SEM, JEOL, JSM-5600LV). The shape and size of the particles were analyzed using High resolution Transmission Electron Microscopy (HRTEM, JEOL, JEM-1200EX). The photoluminescence (PL) analysis was performed with a spectrometer (MiniPal 4X). The BET surface area was analyzed by nitrogen (N$_2$) adsorption with a MICROMERITICS ASAP 2020M nitrogen adsorption apparatus. The electron transfer resistance of as-prepared CZTS samples was measured by electrochemical impedance spectroscopy (EIS) analysis which was performed in a three-electrode electrochemical cell using a potentiostat/galvanostat (PGSTAT 200, Autolab Eco-Chemie Utrecht).

2.3 Sonocatalytic activity measurement
Sonocatalytic degradation for MB dye was performed by an ultrasonic bath and under the presence of as-prepared CZTS samples. 50 mL of aqueous MB solution was kept in a glass tube and 20mg CZTS catalyst was added. The initial dye concentration was chosen as 5mg/L. Prior to ultrasonic irradiation, the mixed solution was stirred for 1 h in darkness to establish adsorption-desorption equilibrium. Then the mixture was irradiated by an ultrasonic bath (ELMASONIC, P-1004277) with 80 kHz frequency and 300 W output power. At a regular interval of 4 min, 3 mL solution was collected and centrifuged for 10 min and then remnant MB concentration was detected by UV-Vis spectrophotometer at wavelength from 300nm to 800 nm. The degradation efficiency of MB was determined based on Eq. (1)

\[
\text{Degradation Efficiency} = (1 - \frac{C_t}{C_0}) \times 100\%
\]

where \(C_0\) is the initial dye concentration, and \(C_t\) is the dye concentration at time \(t\).

3 Result And Discussion

The crystal structure of CZTS-P and CZTS have been investigated by the XRD and the results are presented in Fig. 1a. The diffraction peaks corresponding to (112), (200), (220), and (312) crystal planes were detected at 2theta value of 28.5, 32.9, 47.3, 56.2 respectively. The observed peaks are in good agreement with the standard XRD data file of kesterite phase Cu$_2$ZnSnS$_4$(JCPDS No. 26–0575)[12, 17]. Moreover, no obvious peaks associated with other crystalline forms were detected, indicating that all of the samples have high purity and crystallinity.

For the XRD peaks of impurity such as Cu$_2$SnS$_4$, Cu$_2$S, SnS, SnS$_2$ and ZnS partially overlapping with CZTS pattern, Raman analysis was carried out to further confirmed the phase purity of as-prepared samples. As shown in Fig. 1b, all the samples demonstrated the most intense peak located at 324cm$^{-1}$, which is consistent with previously reported value of CZTS crystalline form[18]. No more additional Raman peaks related to other crystalline forms such as Cu$_2$SnS$_4$, Cu$_2$S, SnS, SnS$_2$ and ZnS were detected[19], indicating the high purity and crystallinity of as-prepared CZTS samples. This result testified the formation of single phase kesterite Cu$_2$ZnSnS$_4$.

The morphology of as-prepared CZTS samples was investigated by SEM, as illustrated in Fig. 2a and b. Hierarchical flower-like microsphere structure which consists of nanosheets with a diameter of 5–7 um was observed in the CZTS sample. The CZTS-P sample demonstrated a hierarchical mesoporous sphere structure consist of nanosheets connect with each other with 4–5 um in diameter. The crystalline nature of as-prepared CZTS samples was shown in HRTEM images (Fig. 2c and d), which showed continuous lattice fringes throughout a nanoparticle. The d-spacing value of the CZTS nanoparticle calculated from the marked area was found to be 3.1Å, consistent with the theoretical value of 0.31 nm for (112) planes. In contrast, the d-spacing value of CZTS-P nanoparticle corresponding to (112) facets was about 3.1 Å. These results implied that the addition of PEG400 in the hydrothermal process has an effect on microstructure of as-prepared CZTS samples. The mesoporous microstructure of CZTS-P samples might be explained by the kinetically controlled nucleation–dissolution–recrystallization process[20]. The
PEG400 molecules can adsorb on the surface of CZTS nanoparticles, resulted in the steric hindrance effect and confined the growth of CZTS nanoparticles in some orientations, finally inducing the different growth rates in different orientations and determining the final mesoporous microstructure of CZTS-P[21]. The atomic composition of the as-prepared CZTS samples was characterized by energy dispersive X-ray spectroscopy(EDX). The atomic ratio of Cu:Zn:Sn:S was detected to be 2.6:0.6:0.4:4.0 and 1.7:0.6:1.0:4.0 for CZTS and CZTS-P respectively, close to the reported values[22].

N2 physical adsorption–desorption isotherm for as-prepared CZTS samples was performed to investigate the surface area and pore-size distribution and the results were presented in Fig. S1. Two CZTS samples displayed typical type IV isotherms with a H1-type hysteresis hoop, confirming the mesoporous microstructure of the materials. The BET surface areas of CZTS and CZTS-P were calculated to be 29.6 m^2/g and 15.6 m^2/g respectively. The optical property of CZTS samples was investigated by UV-Vis spectroscopy. The optical band gap value was calculated by plotting (αν)^2 versus ν and extrapolating the linear portion of the spectrum in the band edge region, where α and ν represent the absorption coefficient and the photo energy[23]. As displayed in Fig. 3a, the optical bandgaps of CZTS and CZTS-P hierarchical microspheres were estimated about 1.49eV and 1.47eV respectively, which close to the reported values[24]. The obtained band gap of CZTS-P shifted to lower values in contrast with CZTS, and the reason for this shift can be explained by to the particle size and microstructure variation of as-prepared CZTS samples[8].

The electron transfer resistance of hierarchical CZTS microspheres was characterized by EIS measurement and can be determined from the semicircular arc radius of Nyquist impedance plots[25]. In general, a smaller radius of the semicircular arc depicts lower charge transfer resistance which means higher transfer and separation efficiency of electrons and holes. As displayed in Fig.S2, The Nyquist impedance plots of as-prepared CZTS samples showed that the semicircle of CZTS-P is smaller than that of CZTS, suggesting that the PEG modification on CZTS can reduce the charge transfer resistance and promote the electrons and holes transport.

The PL spectra is widely used to study the separation behavior of electron–hole pairs in sonocatalyst for the PL emission arises from the recombination of free electrons and holes[26]. It is well-known that the increased PL intensity implies the higher recombination rate of charge carriers. As presented in Fig. 3b, the PL emission intensity of the CZTS-P microspheres is lower than that of CZTS, which implied a smaller recombination rate of electrons and holes in CZTS-P. Accordingly, PEG modification improves the separation efficiency of charge carriers in hierarchical CZTS microspheres.

The sonocatalytic performance of as-prepared CZTS microspheres was evaluated by the degradation of MB dye, which is a typical organic dye pollutant in textile industry. The sonication effect was also examined by conducting the MB degradation by ultrasound irradiation alone. Fig. S3 exhibited the UV–Vis absorption spectra of MB solution during the sonocatalytic degradation process over the as-prepared CZTS sonocatalyst. It is clearly seen that the characteristic absorption peak of MB dye located at 664 nm reduced with irradiation time increasing and nearly disappeared after 20 min in the presence of CZTS-P,
indicated that the dyes have been completely degraded. While in the UV-Vis spectra variation of MB degradation over CZTS sonocatalyst, the completely degradation of MB take 32 min. The absorption peak intensity of MB at 664nm was reduced with increasing irradiation time without any shift suggested complete cleavage of the MB chromophores[27].

Figure 4a compared the time-dependent degradation efficiency of MB in the presence of different sonocatalyst under ultrasound irradiation. A low degradation efficiency(8.2%) was obtained when MB dye was degrade by ultrasound alone after 20 min in absence of any catalyst, implied sonication effect alone hardly degrade of MB in present experiments. In the presence of CZTS-P as sonocatalyst, 95.1% MB dye was degraded in 20 min under ultrasound irradiation, while 82.6% MB was degraded in the presence of CZTS catalyst at the same time.

Kinetic study of MB sonocatalytic degradation by as-prepared CZTS microspheres was carried out. The MB degradation kinetics by as-prepared CZTS samples both approximately followed a pseudo-first-order model[28, 29], which can be expressed as follows:

$$\ln(C_0/C_t) = kt$$

where $C_0$ and $C_t$ are the dye concentration before and after irradiation respectively, $k$ is pseudo-first order rate constant(min$^{-1}$) and $t$ is the reaction time. The $k$ value can be calculated from the slope of the logarithmic plot of MB degradation linear fitted curve. As seen in Fig. 4b, the $k$ value of MB degradation by the CZTS and CZTS-P sonocatalyst were calculated to be 0.135min$^{-1}$ and 0.089min$^{-1}$, respectively. The rate constant of MB degradation by CZTS-P sonocatalyst is about ~1.52 times higher than that of CZTS, indicating that CZTS-P leads to a rapid sonocatalytic degradation of MB. These results indicated that CZTS is an effective sonocatalyst for the degradation of MB and the PEG-modified CZTS microspheres exhibited enhanced ability for degradation of MB dye under ultrasound irradiation.

It is critical and necessary to investigate the plausible degradation mechanism by identify the main reactive oxygen radicals in sonocatalytic process. It is generally believed that three free radicals including hydroxyl radicals(OH•), superoxide radicals (O$_2$•$^-$) and holes(h$^+$) are main contributed in the sonocatalysis process. Herein, the MB degradation experiments were handled in the addition of 2mM p-benzoquinone (BQ), tert-butanol alcohol(TBA) and Na$_2$EDTA, which acted as scavengers for superoxide radicals, hydroxyl radicals and holes respectively[30, 31]. The effect of different scavengers on the sonocatalytic degradation of MB by the CZTS-P was presented in Fig. 5a. The degradation efficiency of MB decreased from 95.1–89.4%, 36.0% and 70.6% in the addition of BQ, TBA and Na$_2$EDTA respectively. The most obviously decrease of MB degradation efficiency was obtained in the addition of TBA, can be explained by the elimination of hydroxyl radicals by TBA molecules, indicated that the hydroxyl radicals play a major role in sonocatalytic degradation of MB. The reduction of MB degradation efficiency in the addition of Na$_2$EDTA was clearly but smaller than TPA, implied that sonogenerated holes also make a contribution to MB degradation. In contrast, the slightly reduction of degradation efficiency in the addition of BQ suggested that superoxide radicals are involved in sonocatalytic process. These results testified
that the sonocatalytic degradation of MB over CZTS is through the combined action of holes and hydroxyl radicals and the hydroxyl radicals play a major role.

The sonocatalytic dye degradation mechanism is mainly established on the “sonoluminescence” and “hotspot” phenomenon. The ultrasound irradiation in aqueous solution can induce acoustic cavitation effect which consists on the nucleation, growth, and collapse of cavitation bubbles in the liquid medium, leading to the sonoluminescence and hotspot\[32, 33\]. The synergistic effect between hotspot with extremely high temperature and sonoluminescence with a wide wavelength and sonocatalyst can produce electrons and holes in sonocatalyst, which ultimately resulted in the formation of reactive oxygen radicals\[34\]. Finally, a great number of oxygen radicals with high oxidative activity are formed in the reaction media and oxidized the dye molecules to the degradation products. In this mechanism, the superior sonocatalytic activity of the CZTS-P in MB degradation can be ascribed to the synergistic effect of its textual properties. On the one hand, CZTS-P sonocatalyst with a smaller optical bandgap facilitated the generation of electrons and holes under the ultrasound irradiation, which further promoted the formation of oxygen radicals in reaction media\[35\]. On the other hand, as displayed in PL spectrum and EIS Nyquist plots, the PEG-assisted CZTS microspheres exhibited a lower electron transfer resistance and smaller recombination rate of electron-hole pairs, thus boosting the production of more oxygen radicals and finally promoting the sonocatalytic efficiency\[31\].

The stability of sonocatalyst is a key parameter for its practical applications. Therefore, the stability and reusability of as-prepared CZTS sonocatalyst were evaluated by four successive recycling tests. In each recycling test, the sonocatalyst were collected from treated MB solution by centrifugation, rinsed, followed by drying, then reused in sonocatalytic degradation fresh MB process. As shown in Fig. 5b, the reusability results demonstrated that degradation efficiency of MB by the CZTS-P sonocatalyst within three repeated cycles dropped from 95.1–92.3%, 90.2%, and 86.3%. The degradation efficiency of MB by the CZTS sonocatalyst within three repeated cycles dropped from 94.8–92.8%, 91.3%, and 87.6%(Fig.S4). The slight reduction of degradation efficiency can be attributed to either minimal mass loss of catalyst or reduction of the adsorption capacity of catalyst via blocking the pores of the catalyst surface by dyes. This result unveil that the hierarchical CZTS microspheres is stable and durable catalyst for the degradation of MB.

4. Conclusion

Hierarchical CZTS microspheres were synthesized via a hydrothermal method with the utilization of PEG400 as surfactant and used as a highly efficient sonocatalyst. The PEG modified CZTS possess hierarchical mesoporous microstructur with an average particle size of 4–5 um and optical band gap of 1.47 eV. More importantly, the PEG modified hierarchical CZTS microspheres demonstrated enhanced sonocatalytic activity with the pseudo-first-order sonocatalytic reaction constant of 0.135min\(^{-1}\), which is 1.52 times higher than that of CZTS without PEG modification. The superior sonocatalytic performance of PEG modified CZTS can be attributed to the enhanced oxygen radicals production rate and lower recombination rate of sonogenerated electrons and holes.
Declarations

Acknowledgements:

This work was supported by Research Program of Gansu Academy of Science (2014JK-01).

Ethical Approval: Not applicable

Competing interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors’ contributions: Xuemei Hu has been involved in study design, material preparation, data analysis and compiling of the manuscript. Junqiang Qiao has helped in study conception, data analysis and improving the overall quality of the manuscript. Jianping Zhou has been involved in data collection and analysis. Data collection and material preparation were performed by Jianqing Bao and Wei He.

Funding: This work was supported by Research Program of Gansu Academy of Science (2014JK-01).

Availability of data and materials: The data used to support the findings of this study are available from the corresponding author upon request.

References


Figures
Figure 1

The XRD patterns (a) and the Raman spectra (b) of as-prepared CZTS samples
Figure 2

SEM images of as-prepared CZTS samples: (a) CZTS, (b) CZTS-P and HRTEM images of as-prepared CZTS samples: (c) CZTS, (d) CZTS-P
Figure 3

(a) The plot of $(\alpha/hv)^2$ versus $hv$ of hierarchical CZTS microspheres, the inset is the UV-Vis absorption spectra of hierarchical CZTS nanoparticles. (b) PL emission spectra of as-prepared CZTS samples

Figure 4

(a) Degradation efficiency curves of MB dye by CZTS, CZTS-P and ultrasound alone, (b) $\ln(C_0/C_t)$ against reaction time for sonocatalytic degradation of MB in the presence of various sonocatalyst.
Figure 5

(a) Sonocatalytic degradation of MB dye over CZTS-P sonocatalyst in the presence of various radical scavengers; (b) Reusability behavior of hierarchical CZTS-P sonocatalyst in degradation of MB dye

Supplementary Files

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