Preparation and photocatalytic properties of Cu2ZnSnS4 for H₂ production

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Abstract

Cu2ZnSnS4 (CZTS) thin film photocatalytic water splitting for hydrogen production under visible light irradiation has been reported together with CZTS nanoparticles prepared by ultrasonic spray pyrolysis and hydrothermal method, respectively. CZTS thin film provided higher H₂ production rate (68.68 μmol · g⁻¹ · h⁻¹), which was 32 times higher than that of CZTS nanoparticles (2.08 μmol · g⁻¹ · h⁻¹) without loading any noble metals. What’s more, photocatalytic activity of CZTS thin film remained 94% after 48 h which confirmed the good stability and reusability of CZTS thin film. CZTS thin film is a potential and durable candidate for photocatalysis.

1. Introduction

H₂ is an ideal fuel with high combustion caloric value and pollution-free combustion product. Photocatalytic water splitting by solar energy, as an ideal way of hydrogen production, has attracted extensive attention of researchers. How to obtain hydrogen efficiently, cheaply and safely is research hotspot. H₂ production efficiency of most photocatalysts such as TiO₂ [1, 2], ZnO [3, 4], ZnS [5–7] and g-C₃N₄ [8] are limited due to wider band gap which results in larger portion of solar spectrum transmission.

As a kind of narrow band-gap semiconductor, Cu₂ZnSnS₄ (CZTS) owns high light absorption coefficient (∼10⁴ cm⁻¹) and direct band gap (∼1.5 eV). Based on this, Cu₂ZnSnS₄ is considered as candidates for solar cell light absorption materials, and has obtained high photoelectric conversion efficiency (12.6%) [9] at laboratory scale. The high photoelectric conversion efficiency demonstrates that the number of photogenerated-carrier pairs of CZTS based material is considerable in visible light range. Therefore, researchers began to explore the application of CZTS in the photocatalytic hydrogen generation field, since 2010 by Yokoyama [10].

Much work so far has focused on CZTS nanoparticles with various shapes and sizes for photocatalytic water splitting, and improving H₂ evolution activity decorating noble metals nanoparticles on surface [11, 12], composting other semiconductors [13, 14]. There are relatively few studies devoted to application of CSTS thin film for photocatalytic water splitting directly rather than photoelectrochemical water splitting. Herein, in this work, CZTS thin film photocatalytic water splitting for hydrogen production under visible light irradiation was reported together with CZTS nanoparticles prepared by ultrasonic spray pyrolysis and hydrothermal method, respectively. In addition, long-term photostability of Cu₂ZnSnS₄ thin film was also studied in this work.

2. Experimental

2.1. Preparation of Cu₂ZnSnS₄ thin film

Cu₂ZnSnS₄ film was deposited on soda-lime glass substrate by ultrasonic spray pyrolysis. Prior to film deposition, the substrate was washed with acetone, ethanol, and then deionized water in ultrasonic bath. The precursor solution was configured as follows: 0.1705 g CuCl₂·2H₂O (A.R.) was dissolved in 200 ml deionized water and stirred for 5 min to make it dissolved fully, then 0.0682 g ZnCl₂ (A.R.), 0.1128 g SnCl₂·2H₂O (A.R.) and 0.3045 g CH₃N₂S (A.R.) were added under magnetic stirring successively. The precursor solution was pale
2.2. Synthesis of Cu₂ZnSnS₄ nanoparticles

Cu₂ZnSnS₄ photocatalyst was prepared via a hydrothermal process. First, 4 mmol CuCl₂·2H₂O, 2 mmol ZnCl₂, and 2 mmol SnCl₂·2H₂O were added to 70 mL deionized water under magnetic stirring, and ultrasonic treatment 10 min to make it dissolved fully. Next, 8 mmol Na₂S and 4 mmol EDTA-2Na were scattered into the above mentioned mixture successively under magnetic stirring. And then, the blend was transferred to a 100 mL Teflon-lined autoclave and reacted at 180 °C for 8 h. The autoclave cooled to room temperature naturally. After that, the precipitates were centrifuged, washed with deionized water and absolute ethanol until the filtrate was neutral, and dried at 80 °C for 4 h. Finally, Cu₂ZnSnS₄ powders were prepared successfully.

2.3. Characterization

The crystal structure was analyzed by x-ray diffraction (XRD, D/MAX2500PC Rigaku, Cu Kα). The surface morphology was investigated by scanning electron microscopy (SEM, Hitachi S-4800) and high-resolution transmission electron microscope (HRTEM, Joel 2100F). Raman spectrum was detected on a LabRAM Aramis (France) and excited with the wavelength of 552 nm. The atomic valence states were analyzed by x-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 XI).

2.4. Photocatalytic reactions

In photocatalytic H₂ evolution experiment, 50 mg of Cu₂ZnSnS₄ nanoparticles and 10 mg of Cu₂ZnSnS₄ thin film were dispersed and placed on a holder in 100 mL deionized water containing Na₂S (0.1 mol L⁻¹) and Na₂SO₄ (0.1 mol L⁻¹), respectively. The visible light irradiation (λ > 400 nm) was supplied by 100 W xenon lamp (50 mW cm⁻²) with UV-cut filter. The amounts of H₂ production were determined every 2 h by online gas chromatography (GC 2002, Shanghai Kechuang Chromatograph instruments Co., Ltd) equipped with a thermal conductivity detector (TCD), using argon was used as the carrier gas.

3. Results and discussion

The diffraction patterns of nanoparticles and thin film prepared by hydrothermal method and ultrasonic spray pyrolysis have three peaks at 28.5°, 47.3° and 56.2°, corresponding to (112), (220) and (312) of tetragonal Cu₂ZnSnS₄ (ICDD No. 26-575) [15], respectively. The broad peaks especially for Cu₂ZnSnS₄ prepared by hydrothermal method indicate that crystallite size is small. The average crystallite sizes were calculated by Scherrer equation and were found to be about ~3 nm, ~9 nm for nanoparticles and thin film. The intensity of nanoparticles is ostensibly higher inferring that nanoparticles maybe have better crystal quality, but the difference of peaks intensity between nanoparticles and thin film is mainly due to the difference mass during measurement. The thickness of thin film is only 700 nm. Furthermore, no other second phases were detected by XRD as shown in figure 1.

Because the possible existence of ZnS and Cu₂SnS₃ phases with similar XRD peaks to that of the CZTS phase, Raman scattering was performed to confirm the CZTS phase. Raman spectrum for thin film was depicted in figure 2. Characteristic peak at 331 cm⁻¹ belonged to CZTS [16, 17]. Furthermore, no other second phases were detected by Raman spectrum. By combining XRD and Raman analysis, pure CZTS phase was prepared successfully by ultrasonic spray pyrolysis.

Figure 3 shows SEM micrographs of CZTS thin film and nanoparticles, respectively. Both of them were agglomerate to reduce surface energy. CZTS thin film was consist of irregular shape particles roughly in a range of tens to hundreds nanometers. Meanwhile, the thickness of the film is about 700 nm which can be seen from inset of figure 3(a). CZTS nanoparticles consist of spherical roughly 20 nanometers in diameter similar to [13]. This is consistent with the observation from XRD which has broad diffraction peaks. Obviously, the particle sizes of them were larger than the average crystallite size calculated by Scherrer formula. This result suggested that these particles may the aggregations of fine CZTS nanocrystals.

In order to further investigate the morpholgue, high-resolution transmission electron microscopy (HRTEM) was used to characterize CZTS nanoparticles. TEM images in figure 4 show that the subglobular nanoparticles are dense with size about a few nanometers ~20 nm. HRTEM image in figure 4(b) shows the characteristic spacing of 0.31 nm for the (112) [16] lattice plane of tetragonal Cu₂ZnSnS₄. This result is consistent with the observation from XRD (figure 1).
The surface compositions and chemical states of Cu$_2$ZnSnS$_4$ were studied by XPS spectra, and the results are shown in figure 5. Cu, Zn, Sn, S, C and O were clearly displayed in the survey spectra as shown in figure 5(a), and identical result was reported by Ha [11]. Two signals were displayed in figure 5(b) at 951.9 eV and 932.0 eV.

Figure 1. XRD patterns Cu$_2$ZnSnS$_4$ prepared by ultrasonic spray pyrolysis and hydrothermal method.

Figure 2. Raman spectrum of Cu$_2$ZnSnS$_4$ thin film.

Figure 3. Plan view SEM micrographs of CZTS: (a) thin film, inset shows cross-sectional view, (b) nanoparticles.
Figure 4. TEM (a) and HRTEM (b) images of the CZTS nanoparticles.

Figure 5. XPS spectra of Cu$_2$ZnSnS$_4$ thin film (a) survey, (b) Cu 2p, (c) Zn 2p, (d) Sn 3d, (e) S 2p.
which corresponded with the binding energies of Cu 2p3/2 and Cu 2p1/2 with a binding energy splitting of 19.9 eV, confirming the states of Cu+ in Cu2ZnSnS4. Two characteristic Zn 2p peaks located at 1045.3 and 1022.1 eV with a binding energy splitting of 23.2 eV indicated the presence of Zn2+. Sn4+ state was identified from the peaks at 495.2 and 486.8 eV with a peak splitting of 8.4 eV. S 2p peaks appeared at 162.8 eV and 161.8 eV with its characteristic peak separation of 1.0 eV which confirmed S2− state. These results above confirmed formation of CZTS [11, 17, 18].

Combined with XRD and SEM results, it can be concluded that the CZTS nanoparticles prepared by hydrothermal method have smaller size. So when Cu2ZnSnS4 nanoparticles dispersed to form aqueous suspension, the contact area with water was larger than that of the film. Usually, smaller size could be beneficial to light absorption and reaction sites number. Nevertheless, contrary to expectation, CZTS thin film produced higher H2 production rate (68.68 μmol g−1 h−1), which was 32 times higher than that of CZTS nanoparticles (2.08 μmol g−1 h−1). H2 production rate of CZTS nanoparticles was lower because it had larger grain boundary ratio as a result of smaller crystallite size. Recombination is particularly problem for polycrystalline materials with small grain sizes, owing to the exceptionally large density of dangling bonds at the grain boundaries [19] which act as carrier recombination centers according to literature [20]. Therefore, crystallite size is not as small as possible; especially considering carrier diffusion length was 350 nm of CZTS [21]. It should not increase specific surface area unilaterally, but balance between it and carrier recombination probability [22]. The research of Chang [22] indicated H2 evolution rate increased with the increase of crystalline size in a certain range. H2 production rate of CZTS nanoparticles is significantly different by different researcher. Jiang [13] considered CZTS without activity for photocatalytic H2 evolution, because in his work no H2 was measured when CZTS irradiation for 6 h. Ha [11] reported H2 evolution rate of CZTS nanoplate and nanorods were about 16 μmol g−1 h−1 and 43 μmol g−1 h−1, respectively. Yu [12] reported H2 evolution rate of CZTS nanocrystals was 0.13 mmol g−1 h−1. For comparison purpose, photocatalytic water splitting for hydrogen production rates of different CZTS form. Irradiation system Amount of catalyst References

| CZTS form  | H2 production rate | Irradiation system | Amount of catalyst | References |
|------------|--------------------|--------------------|--------------------|------------|
| nanoplate  | 16 μmol g−1 h−1    | Xe lamp (100 mW cm−2) | 10 mg              | [11]       |
| nanorods   | 43 μmol g−1 h−1    | Xe lamp (100 mW cm−2) | 10 mg              | [12]       |
| nanoparticles | 0                   | Xe lamp (300 W)    | 50 mg/100 ml       | [13]       |
| nanocrystals | 0.13 mmol g−1 h−1 | Xe lamp (300 W)    | 10 mg/50 ml        | [12]       |
| Nanoparticles-Pt | 82 μmol g−1 h−1 | Xe lamp (300 W)    | 40 mg/50 ml        | [22, 23]  |
| nanoparticles | 2.08 μmol g−1 h−1 | Xe lamp (50 mW cm−2) | 50 mg/100 ml       | Our case   |
| film       | 68.68 μmol g−1 h−1 | Xe lamp (50 mW cm−2) | 10 mg/100 ml       | Our case   |

To examine the photostability of Cu2ZnSnS4 thin film, three cycles of the photocatalytic experiment of hydrogen production had been conducted, and one cycle lasted 16 h. After each cycle, Cu2ZnSnS4 thin film was
washed and re-placed in a new deionized water solution containing fresh scavengers. The photocatalyst remained with 94% activity after 48 h of reaction as shown in figure 6, which signified efficient reusability. CZTS nanoparticles also exhibited analogous long term activity for photocatalytic H2 evolution, when loaded with expensive Pt or MoS2 as a co-catalyst [12, 14]. Undoubtedly, photocatalyst in the form of thin film is very easy to recycle.

4. Conclusions

In summary, CZTS thin film has been studied photocatalytic water splitting for hydrogen production under visible light irradiation for the first time together with CZTS nanoparticles prepared by ultrasonic spray pyrolysis and hydrothermal method. H2 production rate is higher for CZTS film (68.68 µmol·g⁻¹·h⁻¹) than for CZTS nanoparticles (2.08 µmol·g⁻¹·h⁻¹) without loading any noble metals. More importantly, photocatalytic activity of CZTS thin film remains 94% after 48 h. CZTS thin film shows good candidate for further applications in photocatalytic fields.

Acknowledgments

This work was financially supported by Youth fund of Hebei Province Education Department (No. QN2017117), Hebei Natural Science Funds for the Joint Research of Iron and Steel (No. E2019209374).

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References

[1] Gao M, Zhu L, Ong W L, Wang J and Ho G 2015 Structural design of TiO2-based photocatalyst for H2 production and degradation applications Catal. Sci. Technol. 5 4703–26
[2] Dholam R, Patel N, Adami M and Miottello A 2009 Hydrogen production by photocatalytic water-splitting using Cr- or Fe-doped TiO2 composite thin films photocatalyst Int. J. Hydrogen Energy 34 5337–46
[3] Zhang Q S, Xiao Y, Li Y M, Zhao K Y, Deng H F, Lou Y B, Chen J X, Yu H and Cheng L 2020 Efficient photocatalytic overall water splitting by synergistically enhancing bulk charge separation and surface reaction kinetics in Cu2O-x decorated ZnO@ZnS core–shell structures Chem. Eng. J. 393 124681
[4] Sharma M D, Mahal a C and Basu M 2020 Sensitization of vertically grown ZnO 2D thin sheets by MoSx for efficient charge separation process towards photoelectrochemical water splitting reaction Int. J. Hydrogen Energy 45 12277–82
[5] Tie L N, Liu Y M, Shen S J, Yu C F, Mao C J, Sun J Y and Sun J H 2020 In-situ construction of graphene oxide in microsphere ZnS photocatalyst for high-performance photochemical hydrogen generation Int. J. Hydrogen Energy 45 16606–13
[6] Puentes-Prado E, García C R, Oliva J, Galindo R, Bernal-Alvarado J J, Díaz-Torres L A and Gomez-Solis C 2020 Enhancing the solar photocatalytic hydrogen generation of ZnS films by UV radiation treatment Int. J. Hydrogen Energy 45 12308–17
[7] Poornaprakash B, Chalapathi U, Kumar M, Ramu S, Vattikuti S V P and Park S H 2020 Enhanced photocatalytic degradation and hydrogen evolution of ZnS nanoparticles by (Co, Er) co-doping Mater. Lett. 273 127887
[8] Si H Y, Deng Q X, Yin C, Zhou J X, Zhang S Q, Zhang Y X, Liu Z C, Zhang J B, Zhang J and Kong J 2020 Gas exfoliation of graphitic carbon nitride to improve the photocatalytic hydrogen evolution of metal-free 2D/2D g-C3N4/graphdiyne heterojunction J. Alloys Compd. 833 155054
[9] Wang W, Winkler M T, Gunawan O, Gokmen T, Todorov T K, Zhu Y and Mitzi D B 2014 Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency Adv. Energy Mater. 4 1301465
[10] Yokoyama D, Minegishi T, Jimbo K, Hisatomi T, Ma G, Katayama M, Kubota J, Katagiri H and Domen K 2010 H2 evolution from water on modified Cu2ZnSnS4 photoelectrode under solar light Appl. Phys. Express 3 101202
[11] Ha E, Lee I Y S, Wang J C, Li H, Wong K Y and Tsang S C E 2014 Significant enhancement in photocatalytic reduction of water to hydrogen by Cu2O/Cu2ZnSnS4 nanostructure Adv. Mater. 26 4946–500
[12] Yu X, Shavel A, An X, Luo Z, Ibáñez M and Cabot A 2014 Cu2ZnSnS4–Pt and Cu2ZnSnS4–Au heterostructured nanoparticles for photocatalytic water splitting and pollutant degradation JACS 136 9236–9
[13] Jiang F, Pan B, You D, Zhou Y, Wang X and Su W 2016 Visible light photocatalytic H2 production activity of epitaxial Cu2ZnSnS4/ZnS heterojunction Catal. Commun. 85 39–43
[14] Gogoi G, Arora S, Vinothkumar N, De M and Quekeshi M 2015 Quaternary semiconductor Cu2ZnSnS4 loaded with MoS2 as a co-catalyst for enhanced photo-catalytic activity RSC Adv. 5 40475–83
[15] Wang J, Li S, Cai J, Shen B, Ren Y and Qin G 2013 Cu2ZnSnS4 thin films: facile and cost-effective preparation by RF-magnetron sputtering and texture control J. Alloys Compd. 552 418–22
[16] Kush P, Deori K, Kumar A and Deka S 2015 Efficient hydrogen/oxygen evolution and photocatalytic dye degradation and reduction of aqueous Cr (vi) by surfactant free hydrophilic Cu2ZnSnS4 nanoparticles, J. Mater. Chem. A 3 8098–106
[17] Burhanuzz Zaman M, Mir K A and Poolla R 2019 Growth and properties of solvothermally derived highly crystalline Cu2ZnSnS4 nanoparticles for photocatalytic and electrocatalytic applications Int. J. Hydrogen Energy 44 23023–33
[18] Singh A, Geaney H, Laffir F and Ryan K M 2012 Colloidal synthesis of Wurtzite Cu2ZnSnS4 nanorods and their perpendicular assembly JACS 134 2910–3
[19] Moniruddin M, Ilyassov R, Zhao X, Smith E, Serikov T, Ibrayev N, Asmatulu R and Nuraje N 2018 Recent progress on perovskite materials in photovoltaic and water splitting applications Materials Today Energy 7 246–59

[20] Matthews T S 2013 Growth and Characterization of Transition Metal Oxide Semiconductors for the Photoelectrochemical Oxidation of Water Using Visible Light University of California, Berkeley (https://escholarship.org/uc/item/51k0p1tc#main)

[21] Dhakal T P, Peng C Y, Reid Tobias R, Dasharathy R and Westgate C R 2014 Characterization of a CZTS thin film solar cell grown by sputtering method Sol. Energy 100 23–30

[22] Chang Z-X, Chong R-F, Meng Y-N, Zhou W-H, Kou D-X, Zhou Z-J and Wu S-X 2015 High temperature recrystallization of kersterite Cu2ZnSnS4 towards enhanced photocatalytic H2-evolution Int. J. Hydrogen Energy 40 13456–62

[23] Wang J, Yu N, Zhang Y, Zhu Y, Fu L, Zhang P, Gao L and Wu Y 2016 Synthesis and performance of Cu2ZnSnS4 semiconductor as photocathode for solar water splitting J. Alloys Compd. 688 923–32