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Electrophoretic behavior of solvothermal synthesized anion replaced $Cu_2ZnSn(S_xSe_{1-x})_4$ films for photoelectrochemical water splitting

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ABSTRACT

Quaternary $Cu_2ZnSn(S_xSe_{1-x})_4$ ($CZT(S_xSe_{1-x})_4$) compounds have drawn a great deal of attention for being used in the fabrication of optoelectronic devices such as solar cells, photocatalysts, and photoelectrochemical water splitting. However, one major challenge facing the utilization of this material is to reduce the production cost of synthesis and fabrication of high quality $CZT(S_xSe_{1-x})_4$ films. In the present study, a facile and beneficial solvothermal route has been reported for synthesis of $CZT(S_xSe_{1-x})_4$ compounds. The process of electrophoretic deposition (EPD) of synthesized $CZT(S_xSe_{1-x})_4$ nanoparticles, is systematically compared with each other in order to obtain high quality films with appropriate porosity. The XRD patterns, EDS and Raman spectra confirm the formation of $CZT(S_xSe_{1-x})_4$ phases with no trace of impurities and appreciable crystallinity and also with near stoichiometry composition in all the samples. The obtained particle size for CZTS, CZTSSe and CZTSe samples was in the range of 50–100 nm and also for some agglomerate particles was in the range of 500 nm to 2 μm. Based on the obtained results for thin films prepared using EPD in the present study, the best EPD parameters for each CZTS, CZTSe and CZTSSe samples with 120 V and 5 min as applied voltage and deposition time were reported as the best samples. The obtained photocurrent-potential and current-time curves of $CZT(S_xSe_{1-x})_4$ thin film samples demonstrate that the photocurrents of each CZTS, CZTSe, CZTSSe thin films, are different in the range of −2.1 to −6 mA/cm^2 and also the CZTS and CZTSe samples show a detectable current under the exposure of sunlight that can have an appropriate stability for 3000 s but the CZTSSe sample showed a stable photocurrent just for 2000 s. According to the mentioned results in this study, the CZTS and CZTSe samples can potentially be suitable candidates for further applications.

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Introduction

Climate change and the need to diminish fossil fuel consumption are, today, two of the biggest challenges facing the planet [1]. It is beyond dispute that among the energy resources, renewable energies are the most reliable and plentiful and will potentially be very cheap once technology and infrastructure improve. Among the economically sustainable clean energy technologies, direct conversion of sunlight into electricity or storage of its energy in chemical bonds for generation of renewable fuels may be the most powerful and potential alternative to fossil fuels [2,3]. Today, there exists a remarkable effort aiming at making the process cheaper and more beneficial to achieve photovoltaic and photoelectrochemical (PEC) cells with high efficiency and low cost [4,5]. Although many reports on PEC water splitting have been published each year by using oxide semiconductors such as $BiVO_4$, carbon-doped TiO_2 nanotube, $SrTiO_3$, WO_3, ZnO, Fe_2O_3, the efficiency of those systems still need further improvements [6–10]. It seems that the efficiency of this system can be increased by tuning the band gap, morphology, and porosity of the thin films.

The thin film chalcopyrite semiconductors such as $Cu_2ZnSn(S_xSe_{1-x})_4$ have drawn world-wide attention due to their earth abundant and non-toxicity of their constituents compared to $CuInGa(S,Se)_2$ [11,12]. These quaternary p-type compounds are known for their exceptionally high optical absorption coefficient ($>10^5$ cm^{-1}), tunable direct band gap energy ($1.05 < E_g < 1.63$ eV) [13–17], which is well matched with the solar spectrum, and long-term stability [18], which makes them a promising absorber for photocatalytic solar water splitting [19,20]. Thus, CZTSSe is an environmentally friendly and low-cost material, which has been demonstrated to be an excellent light absorber in photocatalytic generation of hydrogen and other value-added chemicals. However, some improvements in the synthesis of these materials are still necessary to achieve an efficient versatile environmentally friendly semiconductor, which can overcome the obstacles hindering their wide spread applications [21,22].

One major challenge which has not been totally addressed yet is reducing the production cost of high quality CZTSSe compounds and their thin films compared with current gas phase deposition methods such as pulsed laser deposition [23,24], sputtering [25,26], and evaporation of precursor sources [27], which require high vacuum chamber, controlled atmosphere, or post selenization annealing step. Recently, a diverse range of synthesis methods with different synthesis parameters have been developed and reported to overcome this challenge, such as doctor-blade coating [28], paste coating [29,30], dip coating [31], spin coating [32,33], hydrazine solution processing [34], and in-situ method [35]. Although, some of the mentioned methods such as hydrazine base method show promising efficiencies, they still suffer from utilization of toxic solvents or complex apparatus [36]. However, electrophoretic deposition (EPD) requires a simple apparatus, and includes some noticeable economic benefits including versatility, suitability for deposition of various materials, short deposition time, low material losses, improved adherence, proper control on thickness, ability to deposit large area coatings, and ability to fabricate complex shapes with high density on the surface, which makes it an attractive method for different applications [37,38]. The EPD process is based on the movement of charged particles in a suspension of nanoparticles in a liquid media under the influence of static-electrical field and then the subsequent deposition of nanoparticles on the substrate [39]. There exists a wide effort for fabricating chalcopyrite semiconductors with EPD method due to its benefits. For instance, EPD has been used for deposition of quantum dots and utilizing them in solar cells [33]. Also, EPD has been widely used for fabricating $CuGaS_2$ films for electro-optical devices or infrared radiation and detection applications [40]. Recently, this method has attracted tremendous attentions to fabricate CZTS compounds [41]. However, systematic investigation of EPD process for fabricating $CZT(S_xSe_{1-x})_4$ films has never been reported.

These compounds have the potential of being used in water splitting due to their suitable band gap, absorption coefficient, and consisting of non-toxic elements. In the present article, we utilize a facile EPD method to fabricate $CZT(S_xSe_{1-x})_4$ thin films, investigate the EPD parameters for $CZT(S_xSe_{1-x})_4$, and compare the optimum deposition parameter of different samples. CTZS films have been used for PEC water splitting. For instance, Yang et al. dissolved the precursors in 2-methoxyethanol, prepared the ink of CZTS, and deposited films of 1 μm thick with doctor blade. A photocurrent of 166 $\mu A/cm^2$ for bare CZTS and improved photocurrent of 21.5 mA/cm^2 for $Pt/TiO_2/CdS/CZTS$ configuration was achieved [42]. In another work performed by Chong et al. CZTS nanoparticles were synthesized by hot injection method and combined with SiO_2 nanoparticles. The H_2 evolution rate was greatly enhanced in the composite sample [43]. Suryawanshi et al. also synthesized the CZTS nanoparticles through green synthesis method using vegetable oil and achieved the photocurrent density of 16 mA/cm^2 [44]. The films prepared by spin coating [45] or electroplate technique [46] show lower values of photocurrent densities. In this paper, $CZT(S_xSe_{1-x})_4$ nanoparticles are synthesized by modified solvothermal method with mix solvents of ethylene glycol (EG) and triethylentetramine (TETA). As it is explicit, solvothermal synthesis allows the precise control over the size, shape, morphology, and crystallinity of the nanostructures [47,48]. Next, the obtained nanoparticles are deposited by EPD method and the EPD behavior of $CZT(S_xSe_{1-x})_4$ for different x values are systematically compared. The thus obtained films with precisely tuned band gap, porosity, and morphology are utilized for solar water splitting system. These semiconductors can potentially pave the way for solar energy storage in hydrogen bonds for infinite humankind energy demands.

Material and methods

Materials

Anhydrous copper (II) chloride ($CuCl_2$, >98%), zinc acetate dehydrate (ZAD, $Zn(CH_3COO)_2\cdot 2H_2O$, >99.5%), tin (II) chloride dehydrate ($SnCl_2\cdot 2H_2O$, >99%), sulfur powder, sodium sulfate anhydrous (Na_2SO_4, >99.5%), selenium (IV) chloride (>99.5%, Alfa Aesar), triethylenetetramine (TETA, >99%), ethylene