

Doping effect of copper zinc tin sulphide counter electrode for dye-sensitized solar cells



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ABSTRACT

The exploration of more efficient counter electrode (CE) is of great significance for the development of dye-sensitized solar cells (DSSCs). Here, the catalysis of I_3^-/I^- by $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and its derivatives have been investigated using density functional theory (DFT). By studying the geometrical and electronic properties of iodine atom adsorbed on CZTS, $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ (CZTSSe), and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe), it was found that the charge transport performance of CZTS can be significantly enhanced when the S in CZTS was replaced by Se. Further investigation on the different cation sites of CZTS doped with K, V, Ir, or Pt reveals that the formation of V-substituted CZTS is energetically favorable. Adsorption energies of iodine atom and desorption energies of iodine anion on various surfaces were further calculated. The results indicated that the designed material shows a high catalytic activity for the reaction of I_3^-/I^- when the Cu2 atom in CZTS is replaced by V ($\text{V}_{\text{Cu}2}$). Thus, the findings could help to promote novel, high-efficiency CZTS-based CE in DSSCs.

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1. Introduction

To satisfy increasing global energy demands, scholars mainly focused on the development of renewable energy sources [1]. Solar energy has been a popular renewable energy source for applications in the field of energetic. Dye-sensitized solar cells (DSSCs) are an important device to harness solar energy [2–4]. DSSCs feature lower cost, easy fabrication, and environment friendliness compared with conventional silicon-based solar cells [5–7]. Numerous studies increased the conversion efficiency of DSSCs by improving the properties of sensitizers [2,8,9], photoanode materials [10–12], and counter electrode (CE) materials [13–16]. It is well known that in order to achieve a high-efficiency DSSCs, platinum (Pt) is coated on a fluorine-dope tin oxide glass due to its excellent catalytic activity, good electrical conductivity, and high stability [17–19]. However, Pt is relatively expensive, which limits the potential large-scale application of DSSCs. In this regard, researchers developed numerous low-cost CE materials with high catalytic activity and ready availability over the past 20 years [4,20,21]. Among these materials, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has been suggested to be a promising alternative because it is earth-abundant, low-cost and environment-friendly [13,22–26]. Recently, a DSSC cell with CZTS as CE fabricated by Fan et al. achieved a power con-

version efficiency (PCE) of 7.94%, which is comparable to those with a Pt CE (8.55%) [25].

The quaternary semiconductor CZTS is an ideal candidate as the superior photovoltaic (PV) p-type absorber materials with a direct band gap ($E_g = 1.4\text{--}1.5$ eV) and a large absorption coefficient of over 10^4 cm^{-1} [27–29]. Sn and Zn are naturally abundant in the earth's crust and have very low toxicity. CZTS has widely used in thin film solar cells [30–32]. Wang et al. reported that CZTS is a promising new candidate for photovoltaic applications [33]. Solar cells based on thin films of CZTS have achieved efficiencies of 9.6% [34], 10.1% [35], and 11.1% [36]. Xin et al. [22] first introduced CZTS film as a catalyst for the tri-iodide reduction, however, the DSSC PCE was very low (3.62%). It is noteworthy that the DSSC showed a remarkably higher PCE of 7.37% after the selenization of the CZTS CE, which was superior to a PCE of 7.04% using the Pt CE under the same conditions [22]. These findings imply that the replacement of S by Se leads to a significant improvement of the DSSC PCE. Recently, Chen et al. [13] reported a high-efficiency DSSC with a large-grain $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ (CZTSSe) CE, which had a 13% increased PCE (7.43%) than that of Pt-coated DSSC (6.58%). The optimization of the thickness of the $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanocrystal film exhibited a higher efficiency of 7.82% [24]. However, so far there is no theoretical study on the differences of the I_3^-/I^- reduction on the CZTS, CZTSSe, and CZTSe surfaces.

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It was indicated by a combined experimental and theoretical study that the substitution of cation by other metal (K, Na, V, Cr, Ir, etc.) is able to improve the efficiency of the CZTS thin film solar cells [37–40]. Tong et al. [38] showed that the K doping can enhance the (1 1 2) preferred orientation and reduce the second phase of ZnS in the CZTS thin film. Tablero [39] reported that the substitution of cations by V and Ir create a partially-full intermediate band. This opens a new avenue to design advanced catalysts based on CZTS. Moreover, even though the CZTS have been successfully prepared the controlling of composition and phase in experiments remains challenging. The systematic studies by Chen et al. [41,42] suggested that the chemical potential region where CZTS could form stoichiometrically is very small and that it is very important to control the growth conditions for obtaining high-quality CZTS samples. With this situation, theoretical investigations can help us to further understand the catalytic performance of the doped CZTS systems.

There have been some reports on charge injection process of interface [43–45]. In the present work, we calculated the charge transfer amount based on the Bader charge analysis [46] to elucidate the charge transport performance. We have investigated the I_3^-/I^- reduction on the CZTS (1 1 2), CZTSSe (1 1 2), and CZTSe (1 1 2) surfaces, respectively. The calculations reveal that the charge transport performance of CE material is very important for the reaction. Subsequently, various metal-substituted CZTS (1 1 2) (M-CZTS (1 1 2)) surfaces (metal = K, V, Ir, and Pt) were made in order to design potential high-efficiency CE materials. By comparing adsorption energies of iodine atom and desorption energies of iodine anion on various surfaces, it has been demonstrated that, when the Cu₂ atom in Cu₂ZnSnS₄ is replaced by V (V_{Cu2}), the designed material shows a high catalytic activity for the reaction of I_3^-/I^- . The results here provide helpful information for improving the photoelectric conversion efficiency of DSSCs by the doping of CE materials.

2. Computational details

2.1. Computational methods and models

All DFT calculations were performed using projector-augmented wave (PAW) [47,48] pseudopotentials as implemented in the Vienna ab initio simulation package (VASP) [49,50]. The electron wave function was expanded in plane waves up to a cutoff energy of 380 eV and a Monkhorst-Pack k-point mesh [51] of $4 \times 2 \times 1$ was used for geometry optimization. The exchange-correlation

functions were computed within a uniform generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [52].

For CZTS, kesterite phase (space group $\bar{1}4$) has been reported to be more thermodynamically stable than stannite phase (space group $\bar{1}42m$) [53,54]. Using the computational method described earlier, the lattice constants of pure kesterite CZTS (Fig. S1, Supporting Information) are calculated to be $a = b = 5.43 \text{ \AA}$ and $c = 10.95 \text{ \AA}$, which are very close to the experimental values [55,56] of $a = b = 5.43 \text{ \AA}$ and $c = 10.89 \text{ \AA}$. This implies that the computational methods employed in the present work are reasonable. The four occasionally exposed facets in natural kesterite structure CZTS are (1 1 2), (2 0 0), (2 2 0) and (3 1 2) (Fig. S1, Supporting Information) [57]. The peak intensity of (1 1 2) is stronger than others, and a preferential (1 1 2) orientation is observed [57]. In CZTS system with a kesterite structure, the thermodynamically preferred growth direction will be along (1 1 2) orientation, which is the close-packed plane in CZTS system [58]. In fact, several groups have reported the preferential crystallization effect along (1 1 2) plane in CZTS films [59,60]. Recently, Yu and Carter [61] had reported that the cleavage energies of (1 1 0), (1 1 2), and (1 0 2) surfaces are significantly lower than those of the (1 0 0) and (0 0 1) surfaces. The cleavage energy can be considered as a reference for the stability of the surfaces created, and it was confirmed that the (1 1 2) surface is the most preferable growth direction for CZTS films on either Mo or glass substrates [62–70]. The CZTS (1 1 2) surface was modeled with a 1×2 48-atom supercell. The CZTS (1 1 2) surface was simulated using a slab of three layers by fixing the bottom layer, and a vacuum region of 30 Å thickness was used.

2.2. Adsorption energy and desorption energy

The I_3^- reduction reaction could be written as:



where I^* means the iodine atom adsorbed on the electrode surface. The process (1) is fast [71], so the whole reaction is rate-determined by the steps of (2) and (3). It has been reported that the barriers for I_2 dissociation and I^* desorption are related to the adsorption energy of iodine atom on the electrode surface [72], that is, the binding strength of iodine atom on the counter electrode plays a key role in determining the catalytic activity. Therefore, the adsorp-

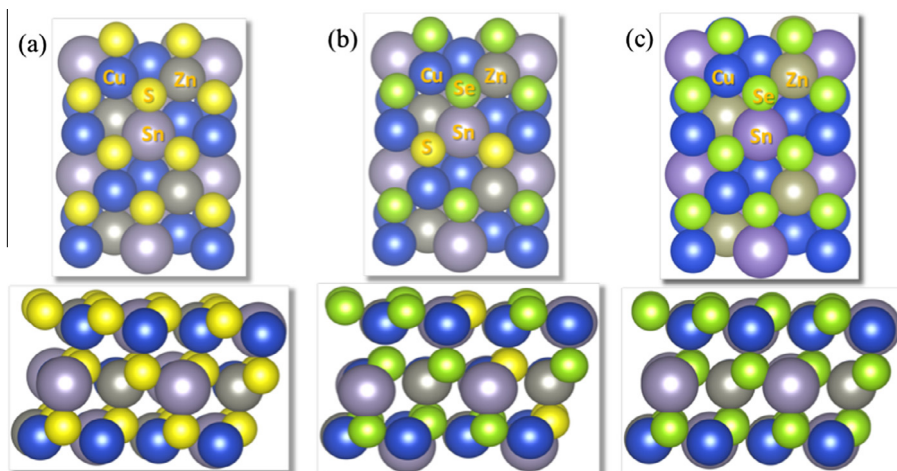


Fig. 1. Top view and side view of CZTS (1 1 2) surface (a), CZTSSe₃ (1 1 2) surface (b), and CZTSe (1 1 2) surface (c).

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