UDK 620.3:549.641:621.383.51
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 52(4)483(2018)

# HIGH-EFFICIENCY PEROVSKITE SOLAR CELLS IMPROVED WITH LOW-COST ORTHORHOMBIC $Cu_2ZnSnS_4$ AS THE HOLE-TRANSPORTING LAYER

## VISOKO UČINKOVITE PEROVSKITNE SONČNE CELICE, IZBOLJŠANE Z NIZKOCENOVNIM ORTOROMBSKIM $Cu_2ZnSnS_4$, DELUJOČIM KOT TRANSPORTNA PLAST ZA PRAZNINE

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*Prejem rokopisa – received: 2017-10-17; sprejem za objavo – accepted for publication: 2018-02-15*

doi:10.17222/mit.2017.178

Quaternary copper chalcogenide $Cu_2ZnSnS_4$ (CZTS) nanoparticles (NPs) were synthesized with the sol-gel technique and used as the hole-transporting layer (HTL), achieving a power-conversion efficiency (PCE) of 13.41 %, which is the highest PCE for Cu-based inorganic HTLs. The effects of the CZTS HTL on the optical absorption, crystallinity, crystal plane orientation and hysteresis of the J-V curve for the devices with a perovskite film were investigated and compared with spiro-OMeTAD, revealing the role of CZTS in efficient hole transporting in perovskite solar cells. In addition to the traditional use of the light absorber, this study reveals a new role of CZTS in photovoltaics, acting as an HTL, providing a completely different insight into the CZTS development.

Keywords: $Cu_2ZnSnS_4$, perovskite, solar cells, hole-transporting layer

Avtorji prispevka so sintetizirali nanodelce (NPs; angl.: Nano-Particles) kvaternarnega bakrovega halkogenida $Cu_2ZnSnS_4$ (CZTS) s sol–gel tehniko in jih uporabili kot transportno plast za praznine (HTL; angl.: hole transporting layer). S tem so dosegli 13,41 % učinkovitost pretvorbe moči (PCE; angl.: Power Conversion Efficiency), kar je do sedaj najvišja dosežena PCE z anorganskimi HTL-ji na osnovi Cu. Avtorji so raziskali vpliv CZTS HTL na optično absorpcijo, kristaliničnost, orientacijo kristalne ravnine in histerezo J-V krivulje za naprave s perovskitnim filmom in ga primerjali s spiro-OMeTAD ter odkrili vlogo CZTS pri učinkovitosti transporta praznin v perovskitnih sončnih celicah. Ta študija, dodatno k tradicionalni uporabi svetlobnih absorberjev, odkriva nov pomen CZTS v fotovoltaiki kot HTL, kar omogoča popolnoma nov pogled v razvoju CZTS.

Ključne besede: $Cu_2ZnSnS_4$, perovskit, sončne celice, transportna plast praznin

## 1 INTRODUCTION

In recent years, new energy materials have attracted more and more attention of the researchers.[1–4] Solar energy is seen as one of the most promising renewable energy forms in the 21st century. The trend towards a widespread affordable use of solar energy has aroused the researchers' attention to thin-film-based solar cells.[5] Especially metal halide perovskites (CH3NH3PbX3, X=Cl-,Br-,I-) perovskite-based hybrid solar cells are currently one of the most competitive candidates for the fabrication of solar cells as they were reported to achieve a remarkably high PCE of 26 %.[6]

Different types of hole-transport materials (HTMs) such as poly(triarylamine)(PTAA), poly (3-hexylthiophee-2,5-diyl(P3HT), poly[2,6-(4,4-bis(2-ethylhexyl)-4Hcyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)(PCPDTBT), spiro-OMeTAD, poly (3-hexylthiophene-2,5-diyl) (P3HT), 4-(diethylamino)-benzaldehyde diphenylhydrazone (DEH), $MoO_3$ and CuSCN were developed to fabricate perovskite-solar-cell devices.[7–10] Organic HTMs called spiro-OMeTAD and PTAA have been widely used and achieved a PCE reaching 20.54 %. However, these materials are easy to degrade and expensive for fabricating solar cells because of their complicated synthetic procedures and high-purity requirement.[11,12] Inorganic materials are advantageous in terms of a facile synthesis, high stability and low cost. Up to now, a few inorganic HTMs were incorporated into PSCs, including $MoO_3$, CuI and CuSCN. For instance, Seigo Ito et al. used CuSCN as the HTM for solar cells and achieved a PCE of 4.86 %, which was lower than that obtained for the spiro-OMeTAD HTM-based device.[10] After that, the CuI HTM was also applied by Qin et al. to fabricate high-efficiency and stable perovskite solar cells using a low-temperature solution-process deposition method, leading to a high PCE of 6.6 %.[11] These limited reports demonstrate the great potential of Cu-based inorganic HTMs for fabricating perovskite solar cells. But, the PCE of the devices using inorganic HTMs are lower than in the case of organic HTMs. Therefore, large-scale applications of perovskite solar cells are impractical, and it is preferable to develop other HTMs with lower costs.

The CZTS belonging to the colloidal semiconductor, which is similar to CuSCN and CuI, exhibits a combination of attractive electronic and optical properties, such as low toxicities, the band gaps (~1.5 eV) suitable for the solar-energy conversion, earth-abundant elemental constituents and low costs. Now, the best PCE of thin-film solar-cell devices using CZTS as the light absorber was over 9 %.[13] Few papers reported on perovskite solar cells based on CZTS HTL. In this work, we synthesized smooth CZTS NPs with different phase structures and employed them on a perovskite layer as an HTL in a perovskite solar cell. The results of X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis spectroscopy and PCE experiments suggest that CZTS could be a good choice for the HTL to replace expensive spiro-OMeTAD in large-scale applications of perovskite solar cells.

## 2 EXPERIMENTAL PART

The $TiO_2$ compact-film precursor solution in ethanol consists of 0.3 M titanium isopropoxide (Sigma–Aldrich, 99.999 %) and 0.01 M HCl. A dense $TiO_2$ film was applied onto an F-doped $SnO_2$ (FTO) substrate by spinning titanium precursor at 5000 $min^{-1}$, followed by annealing at 500 °C for 1 h. The precursor solution was deposited onto the $TiO_2$/FTO substrate by spin-coating at 3000 $min^{-1}$ for 18 s. During this period, 40 µL chlorobenzene was dropped on the perovskite film to recrystallize it in 13 s. After annealing the film on a hotplate at 100 °C for 0.5 h, the color of the film turned from yellow to black, indicating the formation of perovskite. Subsequently, CZTS was deposited on the perovskite film to function as the HTL. For comparison, a reference PSC device based on a spiro-OMeTAD HTL was also fabricated following the procedure reported in the literature.[10] Finally, an Ag electrode was thermally evaporated as an electrode. All of the layers were fabricated inside an $N_2$-filled glove box. A schematic diagram of the fabricated FTO/ $TiO_2$/perovskite/HTL/Au cell is presented in **Figure 1**.

## 3 RESULTS AND DISCUSSION

The structure and optical properties were first studied to probe the effect of the CZTS NP film as a HTL. **Figure 2** shows the XRD pattern and EDS image of CZTS NP thin films. The positions of diffraction peaks

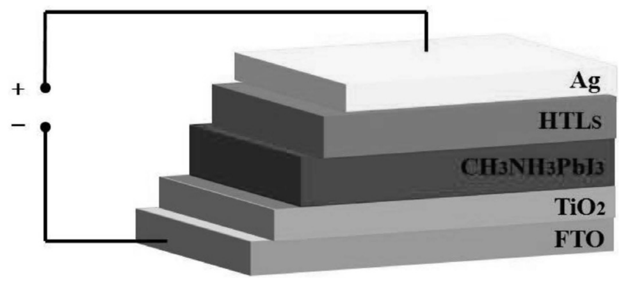


**Figure 1:** Schematic representation of a perovskite solar cell

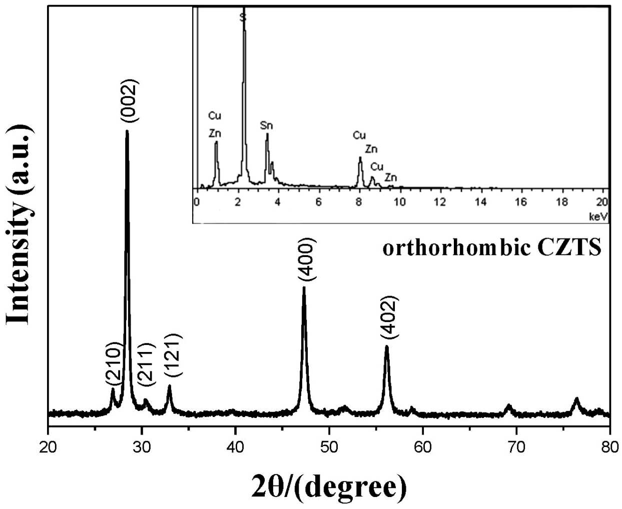


**Figure 2**: XRD pattern and EDS image of CTTS NPs

indicate that CZTS NPs are polycrystalline with the preferred in-plane orientations of the (210), (002), (121), (400) and (402) planes, with an orthorhombic structure matching the JCPDS file (#26-0575). The EDS image shows a ratio of different atoms in the CZTS to be 2.05:1:1:4.05, which reveals that the CZTS is synthesized successfully.

Ultraviolent-visible (UV-vis) spectroscopy results for the $TiO_2/CH_3NH_3PbI_3$ films before and after the CZTS HTL incorporation are compared in **Figure 3**, which also includes the $TiO_2$/CZTS and $TiO_2/CH_3NH_3PbI_3$/spiro-OMeTAD films for comparison. A huge improvement in the light absorption of $TiO_2/CH_3NH_3PbI_3$/CZTS can be seen in the visible spectrum after the incorporation of the CZTS HTL. This can be partly attributed to the absorption of the CZTS, having a relatively small bandgap of 1.49 eV as seen from its absorption spectrum. In addition, after the incorporation of spiro-OMeTAD HTL,

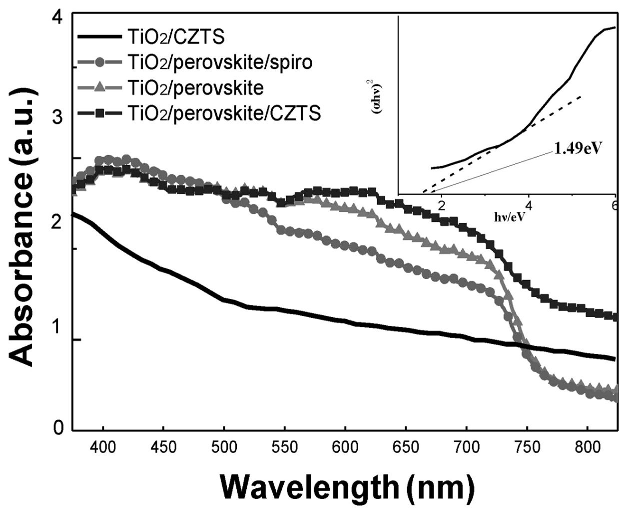


**Figure 3:** UV-vis absorption spectra for: a) TiO2/perovskite/CZTS, b) TiO2/perovskite, c) TiO2/perovskite/spiro-OMeTAD, d) TiO2/CZTS films and band gap of CZTS

the $TiO_2/CH_3NH_3PbI_3$/spiro-OMeTAD film exhibits an absorption decrease, indicating a negative effect on the light absorption of the solar cell. Therefore, the dramatic absorption increase upon the CZTS incorporation shows a path for solving the high cost of the HTL used in perovskite solar cells.

Recently, it was found that the crystallization and crystal-plane orientation, especially a more preferential in-plane orientation of the (110) plane, of a perovskite film could improve the corresponding device performance.[14] GIXRD (grazing incidence X-ray diffraction) experiments were carried out to study the HTM effect on the perovskite crystallization and crystal-plane orientation. Snapshots of the in-situ GIXRD experiments on the perovskite film on spiro-OMeTAD and CZTS are shown in **Figures 4a** and **4b**. All the GIXRD patterns are at the same incidence angle and exhibit a relatively strong scattering background on the amorphous glass substrate in a range of $q$ = 10–25 $nm^{-1}$, where $q$ is the scattering vector ($q = 4\pi\sin(\theta)/\lambda$, $\theta$ is half of the diffraction angle, and $\lambda$ is the X-ray wavelength. After the calibration, the key features of the perovskite diffraction pattern could be observed at $q \approx 10.04\ nm^{-1}$, $19.74\ nm^{-1}$ and $22.21\ nm^{-1}$. These are consistent with the reflections from the (110), (220) and (310) lattice planes, respectively,[15] demonstrating that the textured perovskite crystals with a well orthorhombic crystal structure[16] were found in the perovskite film on both spiro-OMeTAD and CZTS.

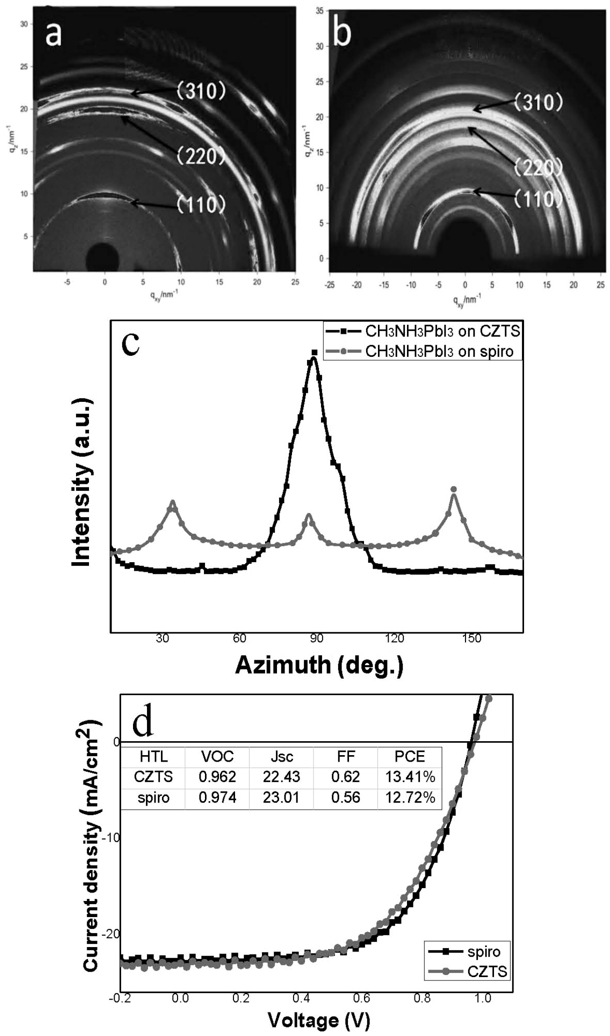


**Figure 4:** GIXRD pattern of $CH_3NH_3PbI_3$ deposited on: a) CZTS, b) spiro-OMeTAD, c) the corresponding radially integrated intensity plots along the ring at $q \approx 10\ nm^{-1}$ for the two films derived from a) and b), respectively, d) *J-V* characteristics of the champion perovskite solar cells using spiro-OMeTAD and CZTS as HTLs

**Figure 4c** reports on the azimuthally integrated intensity profiles for the two films derived from **Figures 4a** and **4b**, respectively. The strong and sharp (110) peaks in **Figure 4c** imply that the films exhibit good crystallization and a large crystal size. Compared with the perovskite film on spiro-OMeTAD, the perovskite film on CZTS has a higher and sharper perovskite (110) diffraction peak, indicating its higher quality crystallization. Thus, the improved crystallization of the present film obviously contributes to the performances of the present champion perovskite solar cells.[14,16] The current density-voltage (J-V) curves of CZTS and spiro-OMeTADHTL-based device are shown in **Figure 4d**. The device based on spiro-OMeTAD HTL shows a *Voc* of 0.974 V, a *Jsc* of 23.01 mA $cm^{-2}$, an *FF* of 0.56, and a PCE of 12.72 %. On the basis of the CZTS HTL, the PCE of the device reaches 13.41 %, calculated from the *Voc* of 0.962 V, *Jsc* of 22.43 mA $cm^{-2}$, and *FF* of 0.62, representing the highest PCE of Cu-based inorganic HTLs reported up to now. These results indicate that CZTS acts as a low-cost and efficient HTL, being an appropriate candidate to be used as a photoelectric material for future perovskite solar-cell applications.

**Table 1** summarizes the photovoltaic parameters of the devices with different HTLs in different scan directions measured under AM 1.5G solar illumination at 100 mW $cm^{-2}$. Regarding the device employing spiro-OMeTAD as the HTL, the hysteresis of the PCE of 29.0 % was obtained. When the CZTS NP layer was introduced into the solar cell, the hysteresis of the PCE of 16.3 % was obtained, indicating a better effect on the hole transporting, a dramatic improvement in the charge extraction and reduced recombination.[13,17] Therefore, the CZTS NP layer is proved to be a suitable HTM for the use in perovskite solar cells.

**Table 1:** Photovoltaic parameters of FTO/TiO2/$CH_3NH_3PbI_3$ perovskite/HTM/Ag devices with different HTLs in different scan directions

| HTL | Scan direction | $J_{SC}$/ ($mA/cm^2$) | Voc/V | FF | $\eta$(%) |
|---|---|---|---|---|---|
| Spiro | Reverse | 23.01 | 0.974 | 0.56 | 12.72 |
| | Forward | 13.47 | 0.921 | 0.72 | 9.08 |
| CZTS | Reverse | 22.43 | 0.962 | 0.62 | 13.41 |
| | Forward | 21.02 | 0.925 | 0.57 | 11.22 |

## 4 CONCLUSIONS

In summary, in order to tackle the problem of high-cost organic HTMs in perovskite solar cells, we successfully demonstrated an orthorhombic structure of CZTS NPs, using the XRD and EDS results, and employed it as the HTL in the perovskite solar cells. Its champion efficiency of up to 13.41 % was demonstrated. The CZTS NP layer can efficiently extract holes out of perovskite and help improve the perovskite crystal structure in the preferred in-plane orientation of the (110) plane, as indicated by the GIXRD measurement. The low-cost CZTS NPs with good opto-electrical properties have a promising future in large-scale industrial applications.

### Acknowledgement

We gratefully acknowledge the financial support from the Natural Science Foundation of the Jiangsu Province (BK20160566), China Postdoctoral Science Foundation (2016M601754), Jiangsu Planned Projects for Postdoctoral Research Funds (1421601085B), and Jiangsu Provincial Department of Education Fund (15KJB430009).

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