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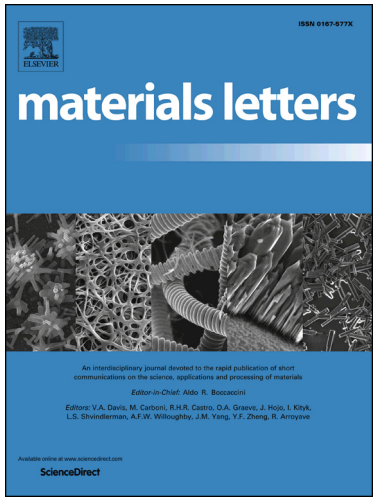

Jet-nebulizer-spray coated copper zinc tin sulphide film for low cost platinum-free electrocatalyst in solar cells

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Jet-nebulizer-spray coated copper zinc tin sulphide film for low cost platinum-free electrocatalyst in solar cells

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Abstract:

The copper zinc tin sulphide (CZTS) alloy is a promising p-type earth abundant alloy that received profound attention as an electron driven dark catalyst in electrocatalytic reduction reaction. We report about fabrication of p-type CZTS film with the jet nebulizer assisted spray (*JNS)* coating technique. The electrocatalytic activity of the as-synthesized CZTS electrode is studied at tri-iodide reduction reactions and is tested as Pt-free electrocatalyst in proof-of-concept type device. Under identical experimental conditions the CZTS counter electrode- and platinum electrode-based dye-sensitised solar cells result similar photocurrent density of ~ 10 $mAcm^{-2}$. These results encourage applications of the aero-sol controlled spray coated CZTS films as the Pt-free electrocatalyst, where reduction reaction takes a key role in energy conversion and biosensing.

Keywords: Jet-nebulizer spray; CZTS; dye-sensitized solar cells; tri-iodide reduction; Pt-free electrocatalyst.

Introduction:

Dye-sensitized solar cells (DSSCs) is a promising device to transform the solar energy into electricity using the semiconductor materials and organic dye molecules [1]. The photoelectrons or oxidative electron carriers collected from the photoanode will be transported to the cathode, which initiates catalytic reduction reactions with target electrolyte and thus sustain the electricity or fuel generation in the cell. This clearly implies that the electron driven catalyst platinum (Pt) is an indispensable component to demonstrate electrochemical process in dye-sensitized solar cells (DSSCs). However, availability and materials cost limits industrial deployment of Pt catalyst at large scale.

The less expensive semiconductor materials are proposed as the Pt-free catalyst in DSSCs [2, 3]. Compared to Pt, the cathode electrodes of transition metal oxides, sulphides, nitrides and carbides exhibited promising electrocatalytic performance in DSSCs. In particular, sulphide based electrocatalysts have the merits in easy synthesis, chemical stability, and excellent electrocatalytic property [4-6]. Recently, the quaternary semiconductor CZTS perceived profound attention as the Pt-free electrocatalyst in DSSCs owing to its abundance, low toxicity [7-10], and high hole concentration[11] of ~1.2×10^{15} to 3.1×10^{20} cm^{-3} providing high p-type electrical conductivity. This may anticipate high appealing class of electron-driven catalyst materials in electrochemical reduction reaction at DSSCs.

The CZTS films can be either synthesized directly on substrates or deposited from the already available nanocrystals. Among the available coating techniques, spray coating attracted much interest in catalyst and photoabsorber industry owing to its technical merits of low cost, the fabrication on large area, precise controllability of the electrode thickness, and possibility of doping and of hetero/multilayer formation. Compare to conventional pneumatic spray coater, our recent efforts on *JNS* coating showed more technical advantages on precise controllability in aerosol distribution, which results in smooth film surface and well-defined crystallite edges [12]. This may anticipate to produce homogenous and highly reactive CZTS catalyst film. In the present work, we demonstrate CZTS films directly grown using the *JNS* spray coating. We examine the structural and optical properties of the as-synthesised CZTS films, demonstrate their catalytic activity in DSSCs.

Experimental:

*JNS spray coated CZTS film***:** All the chemicals were received from Alfa Aesar India, and utilized without further purification. The typical precursor solutions are copper

chloride, zinc chloride, tin (II) chloride, thiourea taken in the ratio of 2:1:1:8 and dissolved in 35 mL of distilled water and stirred constantly under room temperature for 30 min. The filtered precursor solution was taken in the pocket size nebulizer as demonstrated in our previous work [13] and spraying was carried out on the FTO substrate for 5 minutes.

The crystalline structure of CZTS thin film was examined by x-ray diffractometer (XRD) (Rigaku Denki, Japan) using CuKα radiation. The surface morphology of CZTS was characterized using a field emission scanning electron microscope (FE-SEM, JSM 7600F, JEOL, Tokyo, Japan. The composition of the resultant CZTS film is examined using energy dispersion spectra and found to be 25:9:18:48.

Results and discussion

Structural and morphology analysis: The XRD spectra (**Figure 1a**), shows a predominant peak at 28.5˚ corresponding to (112) crystallite plane. Relatively smaller crystallite peaks were observed at 47.3˚ and 56.2˚ are corresponding to (220), and (312) crystallite planes. These (112), (220), (312) crystallite peaks implies the kesterite structure of CZTS (JCPDS–26-0575). Further, this film was examined by Raman spectra (**Figure 1b**). The observed broad Raman peak at 322 cm^{-1} indicates the kesterite CZTS structure. A small shift in Raman peak position is often observed at 337 cm^{-1} due to difference in preparation technique and composition.[14] **Figure 1c** shows the surface morphology of the CZTS film at 1 μm scale. In close proximity, the CZTS surface seems to be compact packing of nanoscale crystallites. The rugosity of the film surface might be related to the spray coating at low substrate temperature [15].

Dye-sensitized solar cells: The schematic device structure of DSSC is depicted in **Figure 2a**. Under solar light irradiation, the photoelectrons and holes will be generated

in photoanode. Further, the photoelectrons will be transported into the counter electrode and will reduce the redox carriers at the counter electrode. In order to examine catalytic activity of the as-synthesised CZTS electrode in tri-iodide reduction, CV of CZTS coated FTO electrode (CZTS/FTO) was tested with iodide containing electrolyte. The resultant CV plot is compared with conventional Pt electrode (Pt/FTO) in **Figure 2b**. The distinguished peak observed at negative potential region -0.34 V vs Ag/AgCl of CZTS electrode demonstrates the catalytic activity in the trioxide reduction ($I_3^- + 2e^- \leftrightarrow 3I^-$) [16]. Further, the catalytic performance of CZTS film is tested in DSSC device. For further details about DSSC device please refer supporting information. The *J-V* measurements have been performed and results presented in **Figure 3a**. The CZTS counter electrode based DSSC results in the photocurrent density of J_{sc}=10.5 mAcm^{-2}, open circuit voltage V_{oc} =0.65 V, fill factor F.F=39 and efficiency η=2.7 %. The DSSC with the Pt counter electrode results in the photocurrent density of J_{sc}=10.6 mAcm^{-2}, open circuit voltage V_{oc} =0.78 V, fill factor F.F=56 and overall efficiency η=4.5 %. The photocurrent generated by the CZTS based device is almost the same as that based on Pt. The effective electronic conductivity (N_b= 3.76 x 10^{17} cm^{-3}) and high electrocatalytic activity is responsible for the photocurrent generation by the CZTS based device as it is discussed in **Fig. 2b**. However, the smaller fill factor of this device as compared to the Pt-based cell might originate from larger electrical resistivity at the counter electrode/electrolyte interface.

This argument can be further examined through electrochemical impedance spectra. The resultant Nyquist plot is further simulated with the equivalent circuit as presented in the inset of **Figure 3b**. The simulated charge transfer resistance value (Rct_1) of CZTS electrode is 48.7 Ω.cm^{-2}, this is four times larger than that of Pt electrode (11.7 Ω.cm^{-2}). The high charge transfer resistance at CZTS electrode might

be responsible for the small fill factor of this device. The charge transfer resistance of CZTS film can be further reduced by varying the composition, substrate temperature, or probing thickness of the electrode.

Conclusions

In conclusion, aero-sol controlled CZTS film has been fabricated through low cost, JNS coating technique. The as-deposited CZTS film prepared at 250 °C substrate temperature exhibits kesterite crystallite structure. Under identical experimental conditions, the CZTS films showed reasonable electrocatalytic performance in tri-iodide reduction reactions, which encourages its implementation as Pt-free electrocatalyst in solar cells as well other catalysis applications.

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References:

[1] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films, Nature 353 (1991) 737.

[2] M. Wu, X. Lin, Y. Wang, L. Wang, W. Guo, D. Qi, X. Peng, A. Hagfeldt, M. Grätzel, T. Ma, Economical Pt-Free Catalysts for Counter Electrodes of Dye-Sensitized Solar Cells, Journal of the American Chemical Society 134(7) (2012) 3419-3428.

[3] J. Briscoe, S. Dunn, The Future of Using Earth-Abundant Elements in Counter Electrodes for Dye-Sensitized Solar Cells, Advanced Materials 28(20) (2016) 3802-3813.

[4] J. Xu, H. Xue, X. Yang, H. Wei, W. Li, Z. Li, W. Zhang, C.-S. Lee, Synthesis of Honeycomb-like Mesoporous Pyrite FeS2 Microspheres as Efficient Counter Electrode in Quantum Dots Sensitized Solar Cells, Small 10(22) (2014) 4754-4759.

[5] Z. Yang, C.-Y. Chen, C.-W. Liu, C.-L. Li, H.-T. Chang, Quantum Dot–Sensitized Solar Cells Featuring CuS/CoS Electrodes Provide 4.1% Efficiency, Advanced Energy Materials 1(2) (2011) 259-264.

[6] Z. Shi, K. Deng, L. Li, Pt-free and efficient counter electrode with nanostructured CoNi2S4 for dye-sensitized solar cells, Scientific Reports 5 (2015) 9317.

[7] S. Chen, J. Tao, H. Tao, Y. Shen, L. Zhu, J. Jiang, X. Zeng, T. Wang, Fabrication of low cost kesterite Cu2ZnSnS4 (CZTS) thin films as counter-electrode for dye sensitised solar cells (DSSCs), Materials Technology 30(5) (2015) 306-312.

[8] X. Xin, M. He, W. Han, J. Jung, Z. Lin, Low-Cost Copper Zinc Tin Sulfide Counter Electrodes for High-Efficiency Dye-Sensitized Solar Cells, Angewandte Chemie International Edition 50(49) (2011) 11739-11742.

[9] X. Zhang, X. Wu, A. Centeno, M.P. Ryan, N.M. Alford, D.J. Riley, F. Xie, Significant Broadband Photocurrent Enhancement by Au-CZTS Core-Shell Nanostructured Photocathodes, Scientific Reports 6 (2016) 23364.

[10] S. Chen, A. Xu, J. Tao, H. Tao, Y. Shen, L. Zhu, J. Jiang, T. Wang, L. Pan, In-Situ and Green Method To Prepare Pt-Free Cu2ZnSnS4 (CZTS) Counter Electrodes for Efficient and Low Cost Dye-Sensitized Solar Cells, ACS Sustainable Chemistry & Engineering 3(11) (2015) 2652-2659.

[11] S. Chen, A. Walsh, X.-G. Gong, S.-H. Wei, Classification of Lattice Defects in the Kesterite Cu2ZnSnS4 and Cu2ZnSnSe4 Earth-Abundant Solar Cell Absorbers, Advanced Materials 25(11) (2013) 1522-1539.

[12] S.S. Latthe, P. Sudhagar, C. Ravidhas, A. Jennifer Christy, D. David Kirubakaran, R. Venkatesh, A. Devadoss, C. Terashima, K. Nakata, A. Fujishima, Self-cleaning and superhydrophobic CuO coating by jet-nebulizer spray pyrolysis technique, CrystEngComm 17(13) (2015) 2624-2628.

[13] C. Ravidhas, B. Anitha, A. Moses Ezhil Raj, K. Ravichandran, T.C. Sabari Girisun, K. Mahalakshmi, K. Saravanakumar, C. Sanjeeviraja, Effect of nitrogen doped titanium dioxide (N-TiO2) thin films by jet nebulizer spray technique suitable for photoconductive study, Journal of Materials Science: Materials in Electronics 26(6) (2015) 3573-3582.

[14] Z. Li, A.L.K. Lui, K.H. Lam, L. Xi, Y.M. Lam, Phase-Selective Synthesis of Cu2ZnSnS4 Nanocrystals using Different Sulfur Precursors, Inorganic Chemistry 53(20) (2014) 10874-10880.

[15] M. Valdés, G. Santoro, M. Vázquez, Spray deposition of Cu2ZnSnS4 thin films, Journal of Alloys and Compounds 585 (2014) 776-782.

[16] P. Sudhagar, S. Nagarajan, Y.-G. Lee, D. Song, T. Son, W. Cho, M. Heo, K. Lee, J. Won, Y.S. Kang, Synergistic Catalytic Effect of a Composite (CoS/PEDOT:PSS) Counter Electrode on Triiodide Reduction in Dye-Sensitized Solar Cells, ACS Applied Materials & Interfaces 3(6) (2011) 1838-1843.

Figure Captions

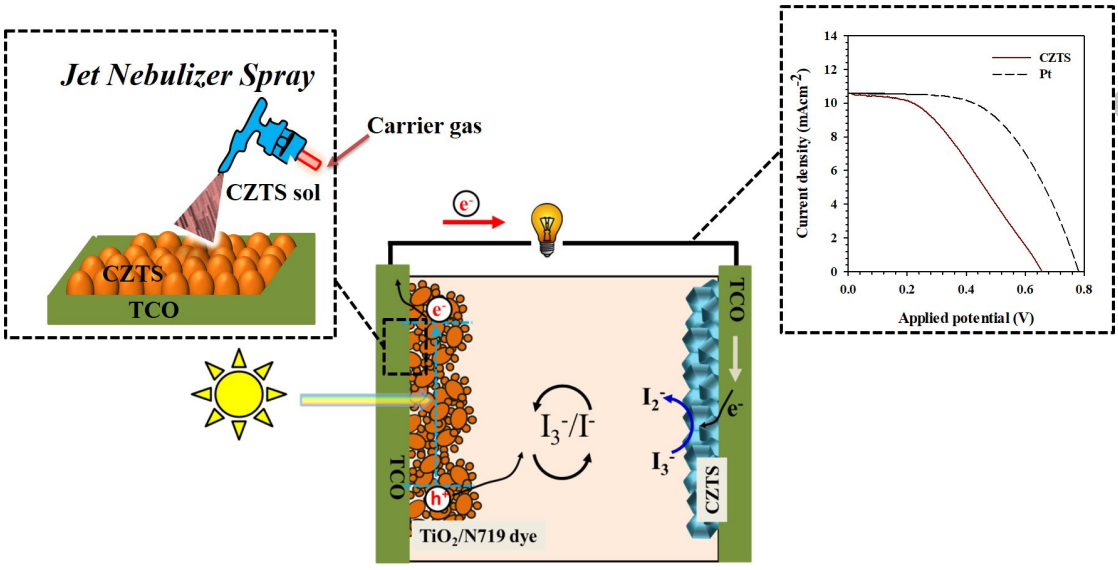
Figure 1. (a) X-ray diffraction pattern; (b) Raman spectra and (c) SEM image of JNS spray coated CZTS film (inset photography of the sample).

Figure 2. (a) Schematic illustration of dye-sensitized solar cells associate with CZTS counter electrode; (b) cyclic voltammogram of CZTS and Pt counter electrodes measured using a three electrode configuration (Note that the electrolyte containing methoxypropionitrile solvent with 10 mM LiI, 1 mM I_2 and 0.1 M $LiClO_4$ measured at a fixed scan rate of 100 $mV.s^{-1}$).

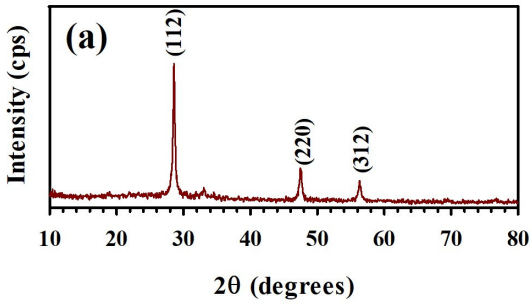
Figure 3. (a) J-V plot of dye-sensitized solar cells fabricated with different counter electrodes (CZTS and Pt); (b) Nyquist plots of dye-sensitized solar cells with different counter electrodes (CZTS and Pt) [the measurements were carried out under 1 sun AM1.5 illumination; inset shows the equivalent circuit for simulation].

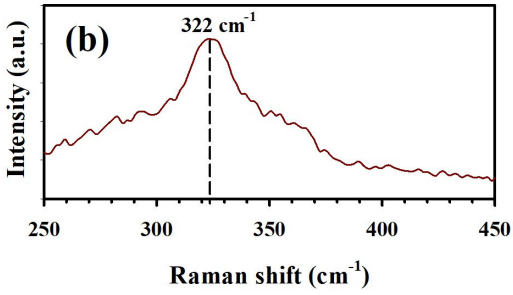
Highlights

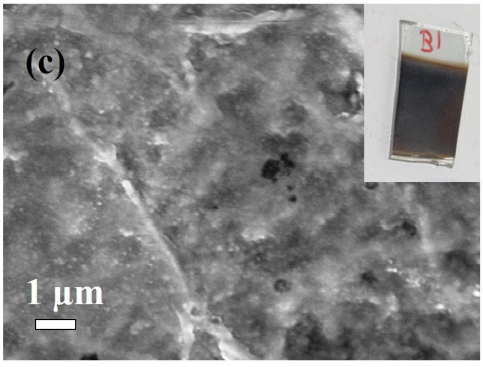
- Less expensive CZTS film coating is demonstrated through jet-nebulizer spray technique.
- Highly oriented (112) CZTS phase is achieved at low processing temperature.
- Electrocatalytic activity of triiodide/iodide reduction is demonstrated.
- CZTS based DSSC exhibits feasible photocurrent generation compared to Pt.

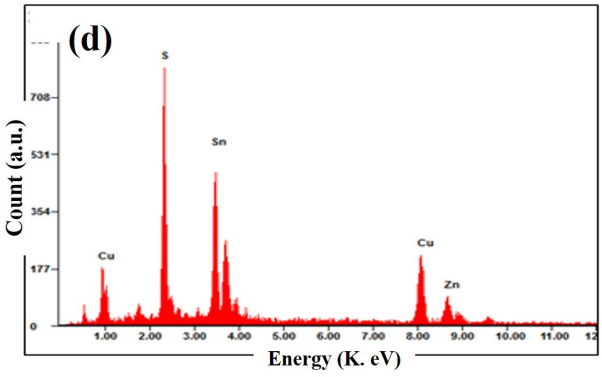


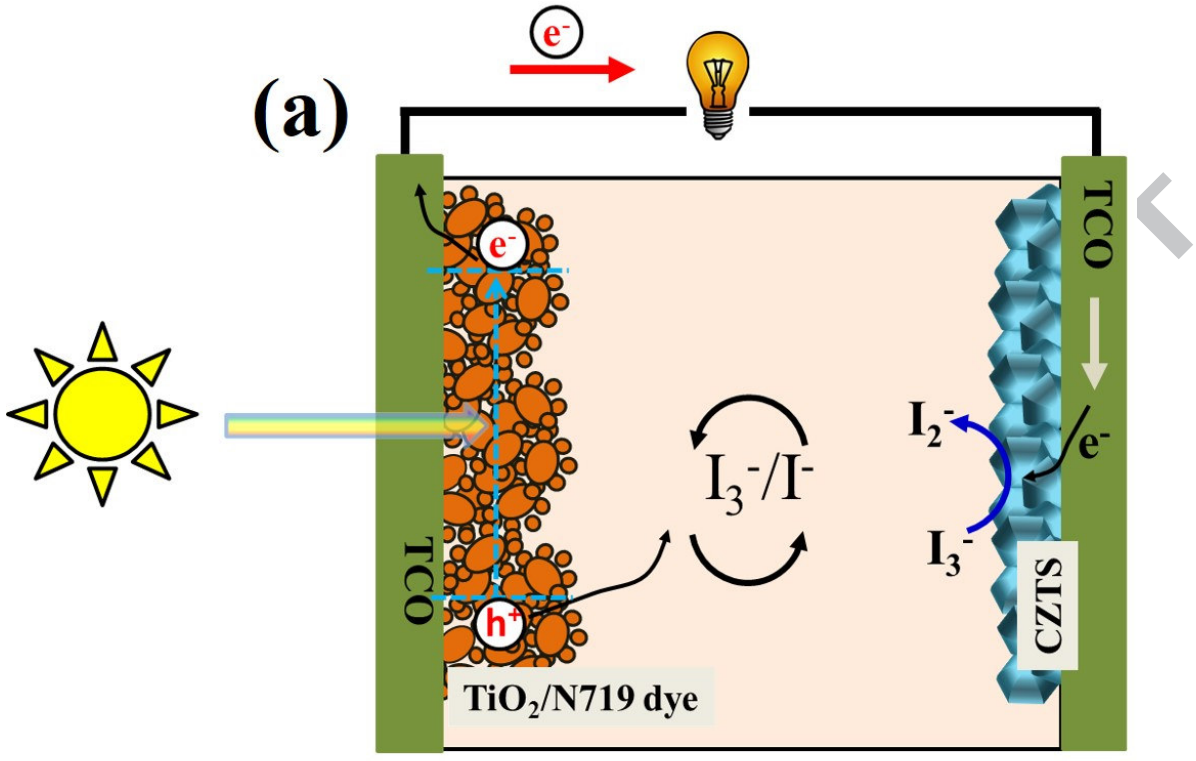
CZTS Counter Electrode based Dye-sensitized Solar Cells

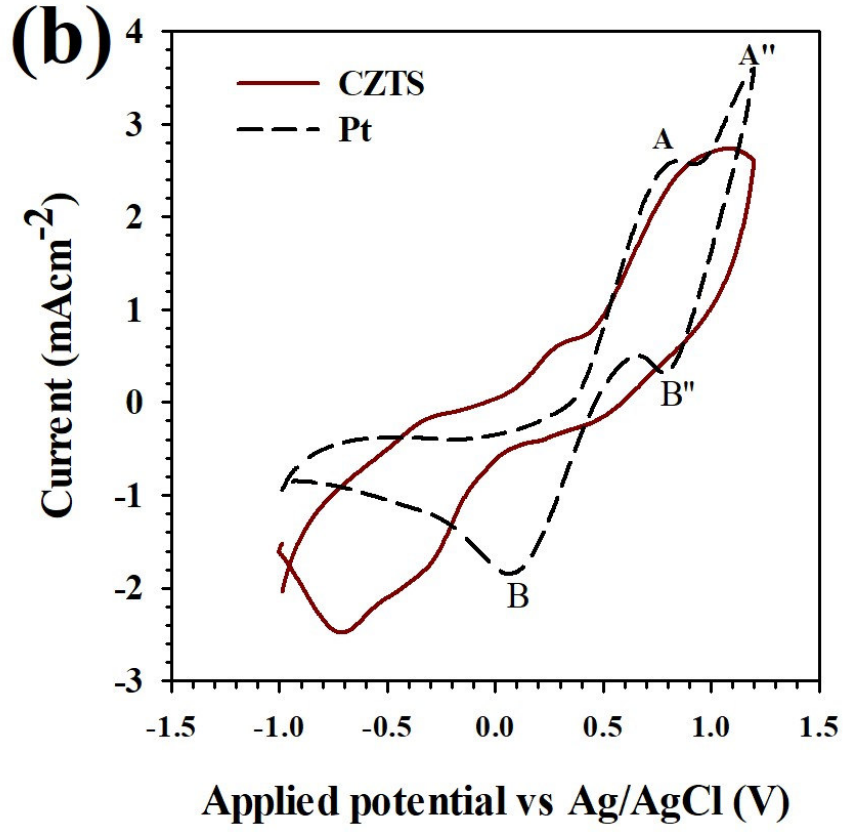


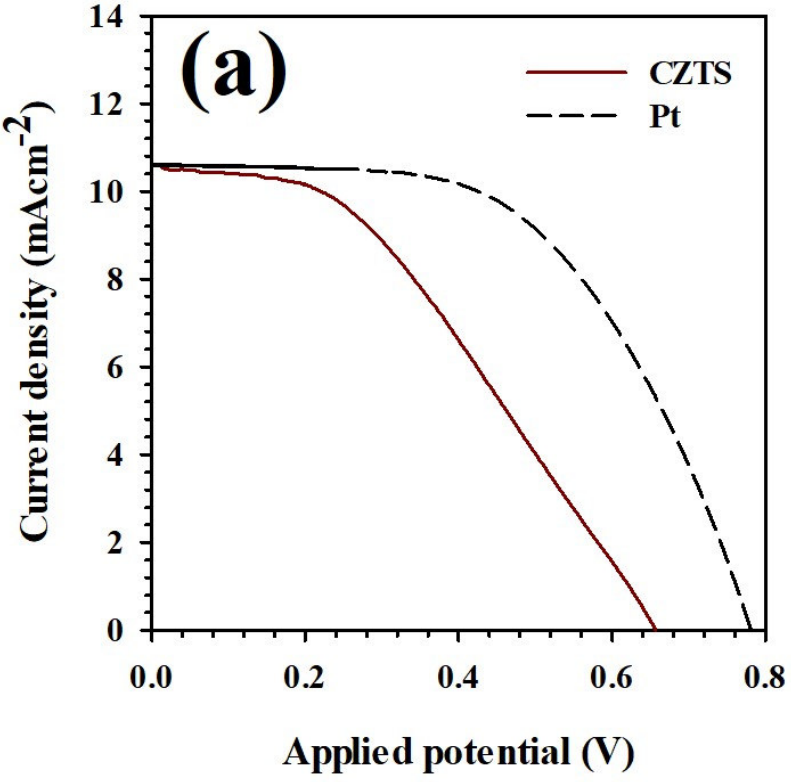


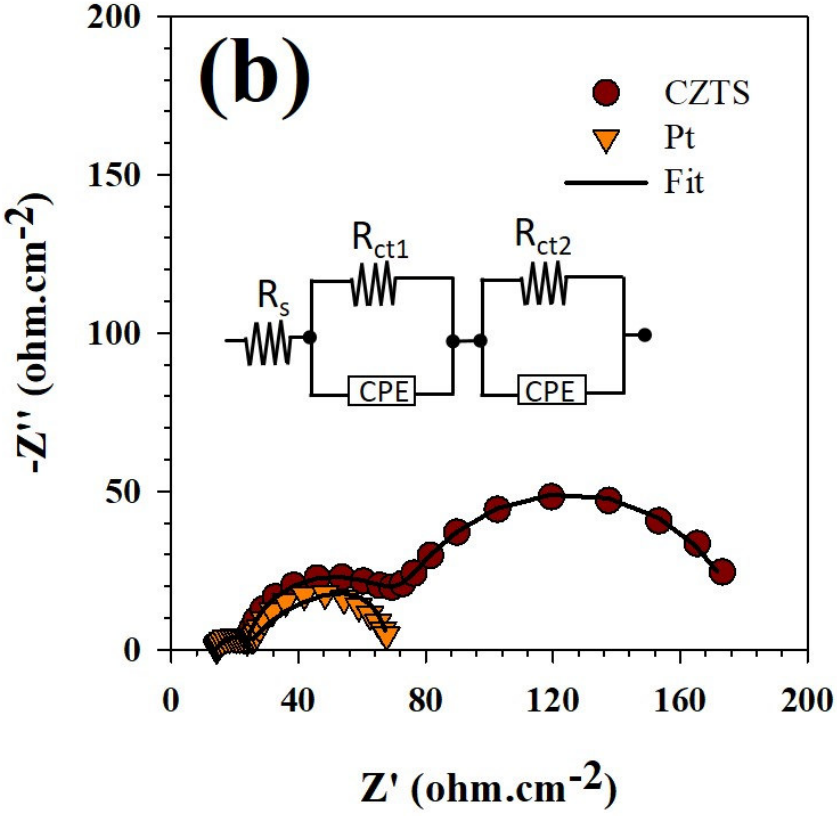





(a)
e⁻
TCO
e⁻
I₃⁻/I⁻
I₂⁻
e⁻
I₃⁻
CZTS
h⁺
TCO
TiO₂/N719 dye


(b)
CZTS
Pt
A
A"
B
B"
Current (mAcm⁻²)
Applied potential vs Ag/AgCl (V)
4
3
2
1
0
-1
-2
-3
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5


(a)
CZTS
Pt
Current density (mAcm-2)
Applied potential (V)
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8


(b)
CZTS
Pt
Fit
Rct1
Rct2
Rs
CPE
CPE
-Z'' (ohm.cm-2)
Z' (ohm.cm-2)
0
50
100
150
200
0
40
80
120
160
200