

Improving photocurrent of continual mesoporous dye-sensitized solar cells using tin ions

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Continual mesoporous TiO₂ films doped with various tin contents were prepared by simple and cost effective spray pyrolysis method for application in photoanodes of dye-sensitized solar cells. The results indicated that the presence of tin ions in TiO₂ lattice led to deterioration of anatase crystalline structure, increased light absorption in ultraviolet and visible regions and films' enhanced specific surface area. Thus with doping 1.5 mol% tin, cell overall conversion efficiency increased 36% and reached to 5.65% which was due to electron production increment as a result of improved dye adsorption on film surface and enhanced electron injection to TiO₂ conduction band as a result of reduction in its Fermi level.

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1. Introduction

One of the strategies that can help commercializing dye-sensitized solar cells (DSSCs) through decreasing manufacturing costs and simplifying production process is applying continual mesoporous TiO₂ films (CMTFs) prepared by spray pyrolysis method in fabricating photoanodes. In addition to simple coating process and low production cost, these films have advantages such as high specific surface area for dye adsorption, fine and uniform pores for electrolyte carries' diffusion, and continuous pathways for electron movements; however their light harvest efficiency is low [1-3].

The most effective method which has been employed in recent decades to improve photoanode function of DSSCs is doping TiO₂ films with different elements. It has been reported that doping tantalum and niobium in anatase phase enhances photovoltaic conversion efficiency 17.6% and 10.5%, respectively [4, 5]. Adding zinc to anatase phase improves light conversion efficiency 23% in low intensity [6]. Doping magnesium in anatase phase with crystallinity improvement and reducing band gap leads to improved cell efficiency, while adding cobalt and copper decrease photovoltaic performance [7]. The presence of metal ions in lattice of non-porous TiO₂ films along with a change in defects content, traps density, inducing oxygen vacancy, and reducing Ti⁴⁺ to Ti³⁺ lead to alteration in structural and optical properties. Nevertheless, in CMTFs surface properties like specific surface area and pore size considerably change which can have a dominant effect on other properties. These variations in solar cell and gas sensor applications whose function is dependent on surface properties are truly important [8-11].

There is not sufficient information yet made available on the effect of tin ions on CMTFs properties for application in DSSCs, therefore in this study the effect of tin content on CMTFs properties prepared by spray

pyrolysis method, and their performance as DSSC photoanode have been investigated. Regarding to the ionic radius differences imposed on the TiO₂ lattice, it is expected that tin doping causes remarkable change on characteristics of the CMTFs.

2. Experimental

2.1. Preparation of films and DSSCs

CMTFs were deposited onto transparent conductive substrate (FTO, 10 Ω/cm², Solaronix) using spray pyrolysis technique. The precursor solution was obtained by dissolving 5 g titanium tetraisopropoxide (Merck) with 3.2 g hydrochloric acid (Merck) in 21 g ethanol (Merck) which contained 1 g Pluronic P123 (Aldrich) under stirring for 12 h. Tin chloride (SnCl₄.5H₂O, Merck) was added to the solution with varying molar ratios of Sn/Ti (0%, 0.5%, 1% and 1.5%). Samples were denoted as Sn0, Sn0.5, Sn1 and Sn_{1.5}, respectively. During deposition, nitrogen was used as carrier gas (P_{N₂} = 3 bar) and the substrate temperature was maintained at 450 °C. The films were thickened about 7 μm after deposition for 15 min. The DSSCs were fabricated using, N719 (cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) –bis-(tetrabutylammonium, solaronix) dye-sensitized CMTF as the photoanode, platinum catalyst (solaronix) as the counter electrode and AN50 (solaronix) as the electrolyte.

2.2. Characterization

Structural properties and morphology of the films were examined using grazing incidence X-ray diffractometer (GIXRD, MPD, PANalytical) and transmission electron microscope (TEM, CM200 FEG, Philips), respectively. Quantitative analysis of the

compounds was performed by atomic absorption spectroscopy (AAS, AAnalyst 400, Perkin Elmer). Absorption spectra were recorded by UV-Vis spectrophotometer (Lambda 25, Perkin Elmer). Surface area analysis was evaluated through nitrogen adsorption/desorption isotherms (Belsorp II). Photovoltaic measurements were performed under 1 sun AM 1.5G simulated sun light using a solar simulator (luzchem) and a potentiostat/galvanostate (PGSTAT 302N, Autolab, Eco-Chemie).

3. Results and discussion

3.1. Microstructure analysis

Fig. 1 shows the diffraction patterns of the CMTFs with various tin contents. Phase identification indicates that all the films have anatase phase with tetragonal crystal structure (JCPDS Card no: 071-1167). No peaks are observed that might confirm the presence of the tin oxide (Sn_xTiO_y). It can be concluded that tin ions may occupy the interstices or ordinary lattice sites of the CMTFs when forming a tin-titanium solid solution. With increasing tin content the intensity of the (101) peak decreases gradually and the full widths at half maxima values of this peak broaden. So, the crystalline structure tends to deteriorate due to the substitution of tin. The average crystallite size of the anatase phase that estimated by Scherrer's equation [12], decreased from 25.4 to 14.7 nm as the tin content increased (Table 1). The presence of tin in TiO_2 lattice inhibits the growth of anatase nanocrystals and enhances structural defects like oxygen vacancies, dislocations and crystallite boundaries. It is possible that exceeding increase of located tin in TiO_2 lattice delays phase transition from amorphous to anatase phase.

TEM image of Sn1 is exhibited in Fig. 2 that shows homogeneous porous structure. It can be concluded that the anatase nanocrystals connect to each other to form a framework consisting of mesopores.

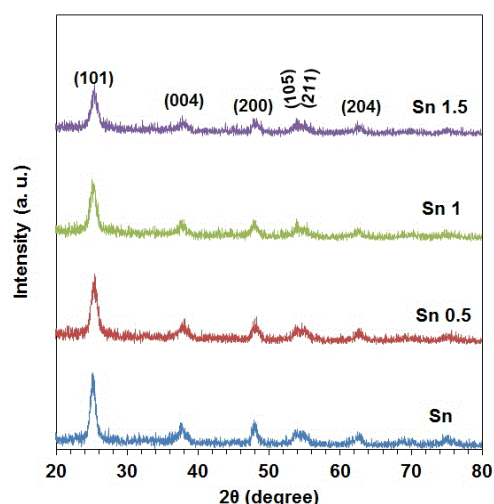


Fig. 1. GIXRD patterns of the CMTFs doped with various tin contents

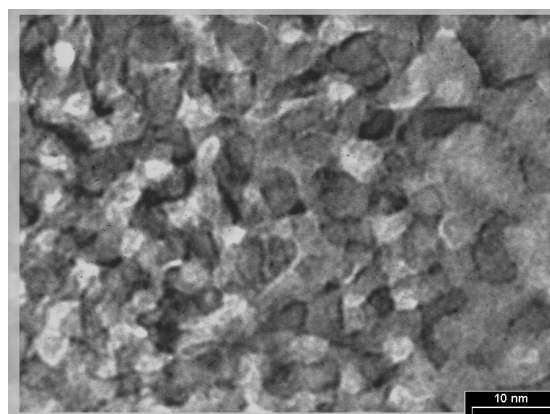


Fig. 2. TEM image of Sn1 sample

3.2. Chemical analysis

The quantitative analysis of doped CMTFs measured by AAS proves that the levels of doping values are close to the nominal values (Table 1).

Table 1. Doping content, average crystallite size, band gap, specific surface area, mean pore size, average pore size, and photovoltaic characteristics of the DSSCs

DSSC	Sn (mol%) (expected)	Sn (mol%) (AAS)	average crystallite size (nm)	Band gap (eV)	Specific surface area (m^2/g) (BET)	Mean pore size (nm) (BET)	Average pore size (nm) (BJH adsorption)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
Sn 0	0	0	25.4	3.27	102.89	17.20	13.90	8.96	0.774	0.597	4.14
Sn 0.5	0.5	0.43	23.1	3.25	114.43	15.18	12.12	9.78	0.766	0.572	4.28
Sn 1	1.0	0.91	19.5	3.22	139.42	13.43	9.22	10.76	0.759	0.631	5.15
Sn 1.5	1.5	1.39	14.7	3.18	148.43	12.75	7.06	11.35	0.753	0.662	5.65

3.3. Optical characterization

Fig. 3 illustrates absorbance spectra and difference of absorbance of the CMTFs without and with various tin contents. All the films exhibit low absorption in visible region which is enhanced with their entrance to ultraviolet region. By increasing tin contents, the absorption of the films has considerable enhancement in ultraviolet and visible regions, and the absorption edges are shifted to the longer wavelengths which are known as red-shift. The effect that the tin dopant leaves on the CMTFs could be easily noticed due to the difference of absorbance spectrum when a broad absorbance peak has been observed in ultraviolet and visible regions (Fig. 3b). This indicates that the doped films are more photoactive and mainly responsible for the electron generation in these regions. The band gap of the CMTFs that calculated by Tauc's equation [13], decreased from 3.27 to 3.18 eV as the tin content increased (Table 1). Due to presence of tin ions in TiO_2 lattice, the tin p orbital admix with TiO_2 and create new intermediate energy levels inside TiO_2 band gap. As a result of these, charge transfer transition between the tin p electrons and the valance and conduction bands of TiO_2 becomes narrower and the Fermi level of TiO_2 decreases. Therefore, the excitation of doped films occurs with lower energy radiation.

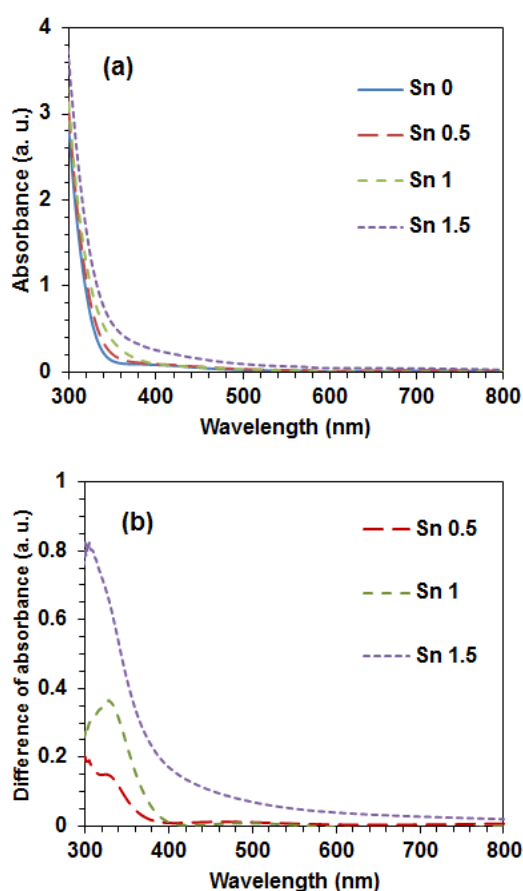


Fig. 3. (a) Absorbance spectra and, (b) difference of absorbance of the CMTFs without and with various tin contents

3.4. BET and BJH analysis

The N_2 adsorption/desorption isotherms and Barrett-Joyner-Halenda (BJH) analysis of adsorption branches of the CMTFs with various tin contents are shown in Fig. 4. All the isotherms have stepwise manner and show a type IV curve with H1 hysteresis loop that proves the CMTFs having mesoporous structure [14]. The BJH analysis shows that all the films have narrow pore size distribution in the range of 3 to 24 nm indicating CMTFs have uniform pore channels. By increasing tin content, the specific surface area increases from 102.89 to 148.43 m^2/g , while the mean pore size decreases from 17.20 to 12.75 nm (Table 1). These changes might be the result of inhibiting anatase nanocrystallites from growth and leaving behind fine pores that have larger specific surface area.

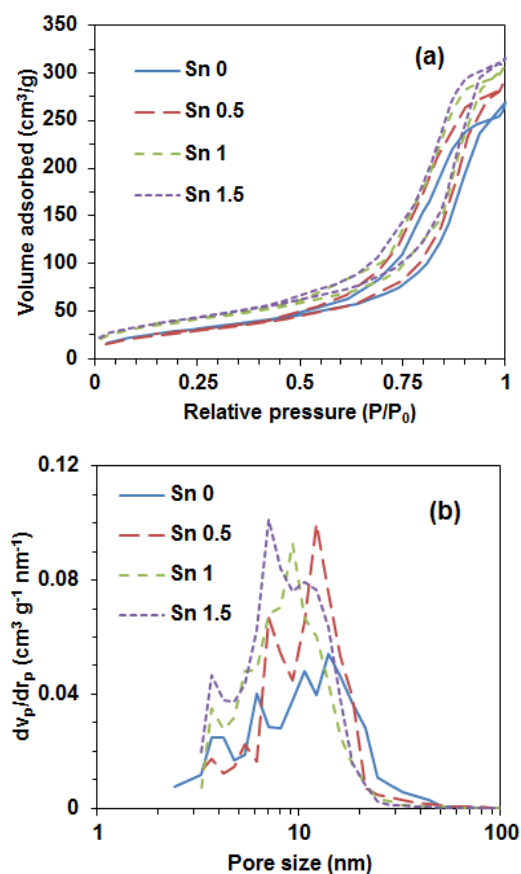


Fig. 4. (a) N_2 adsorption/desorption isotherms and, (b) BJH pore size distribution of adsorption branches of the CMTFs doped with various tin contents

3.5. Photovoltaic performance of DSSCs

Fig. 5 illustrates the photocurrent density-voltage (J - V) characteristics of the DSSCs made of CMTFs with different tin contents. It can be observed that with the increase of tin content, the short circuit current increased from 8.96 to 11.35 mA/cm^2 , while the open circuit voltage decreased from 0.774 to 0.753 V. Cells conversion

efficiency is affected by the changes of the short circuit current and increased from 4.14 to 5.65 (Table 1). Short circuit current enhancement is due to improved surficial and optical properties of the CMTFs as a result of being doped with tin. By 1.5 mol% tin doping, the specific surface area of the CMTFs has increased 44% and consequently the content of dyes which up take is incremented nearly to the same level and has caused more electrons production and photoanodes' better harvest of incident photons. Due to Fermi level decrease, driving force of electrons movement from LUMO level of dye to TiO₂ conduction band has increased and thus electron injection efficiency is significantly enhanced. Moreover, by decreasing band gap the absorption of photons with lower energy has increased. However, by the over presence of tin ions in TiO₂ lattice, density of structural defects and charge trapping centers increments which leads to increased scattering and recombination of charge carriers and as a result charge transfer efficiency is reduced which is observable in short circuit current drop in levels higher than 1 mol% tin. Open circuit voltage drop is due to Fermi level reduction because it is a function of Fermi level difference with the potential of Redox electrolyte. It can be concluded that the increase of the produced electrons as a result of specific surface area enhancement plays a determinant role in cell performance improvement. In a way that this factor with the help of electron injection increment has prevented cell efficiency drop via tin doping up to 1.5 mol%.

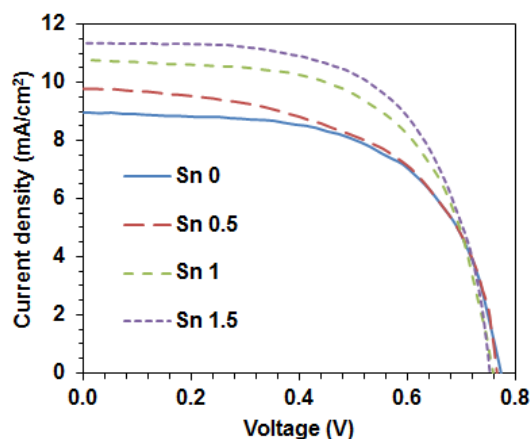


Fig. 5. Photocurrent density-voltage curves of the DSSCs made of CMTFs with different tin contents

4. Conclusions

In current research, a simple method for manufacturing DSSCs photoanode using tin doped CMTFs by means of spray pyrolysis method was introduced which has led to decreased production costs. Films evaluation as a result of doping revealed that structural variations led to deterioration but surficial and optical changes led to cell's

photovoltaic performance improvement. In such a way that by increasing tin content, on one hand structural defects density which blocked charge carrier movement increased and on the other hand by increasing specific surface area and films light absorption, the level of electrons production and injection to TiO₂ conduction band was boosted that ultimately cell efficiency was increased to 5.65% by dominance of surficial and optical alterations.

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References

- [1] J. Huo, Y. Hu, H. Jiang, X. Hou, C. Li, *Chemical Engineering Journal* **258**, 163 (2014).
- [2] Y. Zhang, Z. Xie, J. Wang, *Thin Solid Films* **518**(24), e34 (2010).
- [3] M. N. Shan, S. S. Wang, Z. Q. Bian, J. P. Liu, Y. L. Zhao, *Solar Energy Materials and Solar Cells* **93**(9), 1613 (2009).
- [4] T. Nikolay, L. Larina, O. Shevaleevskiy, B. T. Ahn, *Energy & Environmental Science* (4), 1480 (2011).
- [5] J. Liu, H. Yang, W. Tan, X. Zhou, Y. Lin, *Electrochimica Acta* **56**(1), 396 (2010).
- [6] K. P. Wang, H. Teng, *Physical Chemistry Chemical Physics* **11**, 9489 (2009).
- [7] B. Yacoubi, L. Samet, J. Bennaceur, A. Lamouchi, R. Chtourou, *Materials Science in Semiconductor Processing* **30**, 361 (2015).
- [8] S. Yun, J. Lee, J. Chung, S. Lim, *Journal of Physics and Chemistry of Solids* **71**(12), 1724 (2010).
- [9] N. Todorova, T. Giannakopoulou, T. Vaimakis, C. Trapalis, *Materials Science and Engineering B* **152**(1-3), 50 (2008).
- [10] M. Zukalová, J. Procházka, A. Zúkal, J. H. Yum, L. Kavan, *Inorganica Chimica Acta*, **361**(3), 656 (2008).
- [11] J. H. Koh, J. A. Seo, S. H. Ahn, J. H. Kim, *Thin Solid Films* **519**(1), 158 (2010).
- [12] B. D. Cullity, *Wesley Publishing Company Inc*, London, (1978).
- [13] M. Sreemany, S. Sen, *Materials Chemistry and Physics* **83**(1), 169 (2004).
- [14] T. Pauporte, J. Rathousky, *Microporous and Mesoporous Materials* **117**(1-2), 380 (2009).

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