

## Solar Cells Made From Extracts of Solutions

T. N. Patrusheva<sup>1</sup>, S. D. Kirik<sup>1</sup>, I.V. Nemtzev<sup>2</sup>, A.M. Zhyzhaev<sup>3</sup>, O.Yu. Fetisova<sup>3</sup>, A.A. Romanov<sup>1</sup> and A. I. Khol'kin<sup>4</sup>

<sup>1</sup>Siberian Federal University, pr. Svobodny, 79, Krasnoyarsk, Russia

<sup>2</sup>Krasnoyarsk Scientific Centre of the Siberian Branch of the RAS, Akademgorogok, Krasnoyarsk, Russia

<sup>3</sup>Institute of Chemistry and Chemical Technology of Siberian Branch of Russian Academy of Science, Akademgorogok, Krasnoyarsk, Russia

<sup>4</sup>Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Science, Moscow

Corresponding author Tamara Patrusheva

Dye sensitized solar cells (DSSC) have been fabricated by cost-effective extraction-pyrolysis technique. Organic extracts of Ti(IV), In(III), Sn(IV) were prepared with carboxylic acids as a extractant and after thermal decomposition were used for ITO (In-Sn-O) and TiO<sub>2</sub> films preparation. The resulting films were investigated by X-ray diffraction, transmission electron microscopy and optical spectroscopy in the visible and IR wavelengths. The obtained ITO films had homogeneous composition with grain sizes 6±2 nm. The films transmittance in the visible wave range were about 95 %. The photoanode with three-layers structure was constructed using Ti(IV) extracts with different concentrations. The first compact layer improved the adhesion with the electrical contact of the cell, the second the mesoporous layer enhanced the dye adsorption, and the third one was light-scattering layer. The films deposited from titanium extracts with a concentration to 0.25 M consist of anatase crystallite with size of 8-10 nm, whereas the use of a more concentrated extracts results the films with anatase crystallites with size of 15-20 nm.

**Key words:** extraction-pyrolysis technique, transparent conductive films, multilayer structure oa photoanode, dye sensitized solar cells

### Introduction

Solar photovoltaic cell can converted the solar radiation into the electricity for watches and calculators, traffic lights etc. There is the great practical interest to manufacturing of the solar cells on the glass for building construction in Germany and Switzerland (Solfroix) and in Australia (Dyesol).<sup>1,2</sup> Dye sensitized solar cell (DSSC) is simple, environmentally friendly and relatively cheap to fabricate.<sup>3-5</sup> DSSC have the potential to produce electricity at the low light, for example, in a partially shaded or in cloudy weather.<sup>6-7</sup> Such glass can be made in the form of blinds or are located on roofs and facades of buildings.

Solar glass is a packet in which the two glasses are covered inside with transparent conductive films as solar cell electrodes and one of the electrodes is covered by titanium dioxide and impregnated with the dye for absorption of light and there is electrolyte between the panes. Energy conversion in DSSCs begins when the photoexcited electrons of the dye are injected into the semiconducting layer and finally transported through the external circuit to the counter electrode. At the counter electrode, the electrons are returned to the hole in the dye molecule by

the redox mediators. The dye is regenerated and produces electricity.<sup>8-10</sup> The process of sunlight conversion into electricity in a photovoltaic cell similar to photosynthesis in nature, where the synthesized by the action of sunlight chlorophyll helps to oxygen release. The branched chain of channels in a sheet is delivers the water and nutrients throughout the sheet. Microchannels system in the solar cell operates in a similar manner. Photovoltaic cells are regenerated by dye injecting into the channels and simultaneous evacuation of spent dye. This process restores the efficiency of the electricity production in the solar cell.

Usually for the DSSC fabrication different techniques are used. Transparent electrodes of ITO (In-Sn-O) or FTO (F-Sn-O) or AZO (Al-Zn-O) films are obtained by vacuum deposition.<sup>11,12</sup> ITO films are traditionally obtained by vacuum sputtering targets heated to high temperatures at low substrate temperatures.<sup>13</sup> The reactive sputtering process employ large machines with uniform gas flow and a uniform distribution of gas in the chamber and with very complex processes of measurement and control systems of the gas flow to stabilize the reactive sputtering process.

One of the main methods for coating a pane of glass is vacuum gas transport technology (CVD). For TiO<sub>2</sub> films with antibacterial properties using RF process stimulated plasma-chemical vapor deposition<sup>14</sup>. For titanium dioxide with desired characteristics used the hydrothermal synthesis as well as various variations thereof, such as the microwave hydrothermal synthesis, providing a high heating rate and uniformity of reaction mixtures.<sup>15</sup> TiO<sub>2</sub> coatings is made by rolling technique.<sup>16-17</sup>

There are number of reports on the structures and roles of carboxylic acid on optoelectronic performance of DSSC.<sup>13-15</sup> Chenodeoxycholic acid (CDCA) is the most effective agent as it has a huge hydrophobic tail and a hydrophilic head (–COOH group). It efficiently reduces dye aggregation and electron recombination via the formation of a thin passivation layer on the vacant TiO<sub>2</sub> surface resulting in improvement of photon to electron conversion efficiency.<sup>18, 19</sup>

The organic solution of carboxylic salts can be the beneficial precursors for the electrodes and photoanode of solar cells. The problem of film deposition on the surface of large dimensions and complex shapes can be solved using solutions as a starting materials. The availability of raw materials and the cost of manufacturing method are important factors in the manufacture of functional materials. The choice of method is generally associated with optimal properties thin solid film for a particular use, and minimizing the manufacturing costs.

## Materials and methods

This article describes the extractive-pyrolytic method of ITO and TiO<sub>2</sub> films producing in one technological scheme, which does not require the vacuum equipment usage and is capable of applying the coating on the surface of various shapes and sizes. The self-organization processes occurring during film formation from organic solutions include the considered approach to nanotechnology. Organic extracts of Ti, In, Sn have been obtained from inorganic salts of metals. The extraction of metals was performed by cation-exchange mechanism with monocarboxylic acids, in particular  $\alpha$ -branched C<sub>5</sub>-C<sub>9</sub> carboxylic acids.<sup>20</sup> The obtained solutions of metal carboxylates were free of impurities.

The clarification of metals concentration in solutions was provided with Atomic adsorbtion method with spectrophotometer AAS-3 company CARL ZEISS JENA and Mass spectroscopy method with GC-MS on the GCD plus Hewlett Packard using a column HP-FFATi.

The working solutions were prepared by mixing extracts in the set proportions. The substrate was coated by rolling of wetting film. After pre-drying at 120 ° C and heating at 450–□500 ° C about 3 minutes the oxide film was obtained. Then the film was cooled to room temperature.. Then the film was cooled to room temperature. Cycles of coating was repeated 10-15 times to achieve a film thickness 300–500 nm.

The processes of thermal decomposition of the extracts were examined with differential scanning thermoanaltizator STA 449 F1 Jupiter from Netzsch in air. Gaseous decomposition products of metal carboxylates were determined by gas chromatography.

X-ray Diffraction patterns are obtained using X'Pert PRO diffractometer (PANalytical) with CuK $\alpha$  radiation and PIXcel detector equipped with a graphite monochromator. For scanning the substrate with the film was mounted in a standard sample position and rotated with the rate 1 turn per second. Scan range: 5 to 70 ° on a scale 2 $\theta$ , step 0.026 °,  $\Delta t$  - 50c. Morphology of TiO<sub>2</sub> films was studied by scanning probe force microscope (SZSM) Veeco MultiMode NanoScopeIIIa SPM System. The study SZSM microrelief surface and its local properties conducted using a specially prepared probes as needles made of silicon nitride. The working part of such tip has dimensions of the order of ten nanometers. The typical distance between the probe and the sample surface is 0.1-10 nm. Surface scanning is performed in tapping mode (tapping mode). Scan size was 1x1 mm<sup>2</sup>. The films were also studied with an atomic force microscope AFM (Veeco MultiMode NanoScope IIIa SPM System), transmission electron microscope (JEOL JEM-2100) and Hitachi ultra-high resolution scanning electron microscope S5500.

Optical properties studied with spectrophotometer SF-M400 and Fourier spectrometer Vertex 80 V.

### Results and discussion

The complete wetting of the substrate is necessary to achieve the films uniformity and strengthening and the binding to substrate, particularly for low energy surfaces (glass). Compared with the titanium alkoxide used in the sol-gel method the organic extracts have better wetting properties and stability of properties over time due to the non-volatility of the organic solution.

The thermal decomposition of In, Sn and Ti carboxylates showed that the initial heating (90–160°C) removed the chemically bonded water. Then the excess of the extractant is removed in the temperature range of 220 to 290°C. Process of thermal decomposition of metal carboxylates associated with exothermic maxima in the DTA curve indicated a temperature range 350–450°C. In this temperature range the decomposition of indium, tin and titanium carboxylates are virtually identical (Fig. 1).

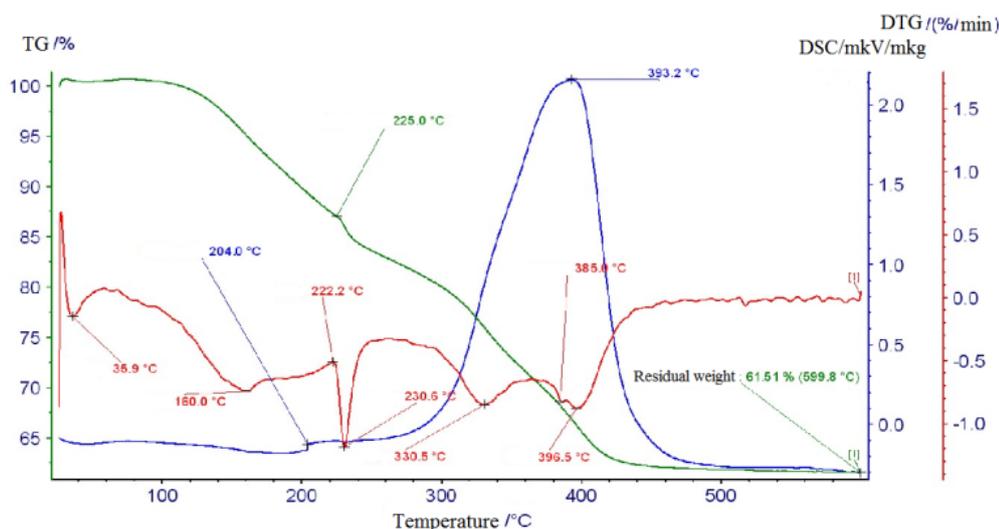


Fig. 1. Thermograms of tin carboxylates

1 - weight loss, 2 - weight loss velocity, 3 - differential scanning calorimetry

The gas-escape kinetics study showed the presence of CO<sub>2</sub> as the principal product of thermal decomposition (86–90%), along with CO (6–8%) and traces of hydrocarbons. Among the gaseous products of pyrolysis CH<sub>3</sub>COOH and acetone were also detected. In the result of

pyrolysis at 400–450 °C the organic extracts were decomposed with release of gaseous products and a solid solution of indium tin oxide was obtained.

Thickness of wetting films obtained from solutions of extracts depends on the surface tension of the solution, which is determined experimentally.<sup>21</sup> The surface tension of solution determines the disjoining pressure and thickness of wetting film.<sup>22</sup> The disjoining pressure (P) determined according to the equation:

$$P = 2\sigma/R \quad (1)$$

where: R - radius of the capillaries to measure the surface tension ( $\sigma$ ). The disjoining pressure (P) of wetting film compensates for atmospheric pressure and the itself pressure  $P_{atm}$  of wetting P(h) of the film.

$$P = P_{atm} + P_h \quad (2)$$

The own pressure of wetting film  $P_h$  depends on the thickness (h) by the hydrostatic equation:

$$P_h = h \cdot \rho \cdot g \quad (3)$$

where:  $\rho$  is density of the liquid, and g - gravity acceleration.

From the equations (1-3), we get the final expression for calculating of the wetting film thickness:

$$h = (2\sigma - RP_{atm}) / R \cdot \rho \cdot g \quad (4)$$

The oxide film thickness was evaluated taking into account the results of thermal analysis. The solution with 2 % concentration provides the continuous film after pyrolysis of the first layer with a thickness of 30 nm. The desired film thickness is achieved by applying a certain number of layers.

Optimal conditions for forming the transparent conductive film with thickness 300 nm have been found at the annealing temperature of 550 °C for 30 min.<sup>23</sup> Sheet resistance of ITO films obtained by wet technique was about 300  $\Omega$ /sq.

X-ray diffraction pattern of the ITO film (Fig. 2) show that the dominant ITO peak observed at 30.5 °2 $\theta$ . The peak observed at 35,16 ° 2 $\theta$  corresponds to indium oxide ( $In_2O_3$ ), and peaks at 51.43 °, 61.12 °2 $\theta$  belong tin oxide  $SnO_2$ . The presence of tin oxide peak in addition to ITO has confirmed that a coating of indium tin oxide composed of a mixed phase with characteristic feature of the valence change that is one of the basic requirements for electrochemical applications.

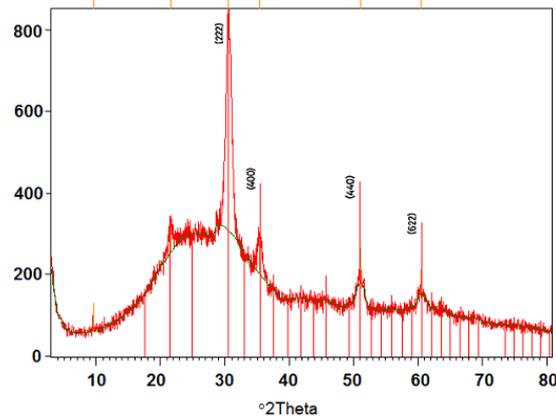


Fig. 2. XRD pattern of ITO film on glass substrate, obtained by extraction-pyrolysis method

The crystal size estimated with help of Scherer equation was about 6-10 nm.

The transmission electron microscopy image (Fig. 3) shown that the ITO film prepared by extraction-pyrolytic method has grain sizes about  $6 \pm 2$  nm (Fig. 3).

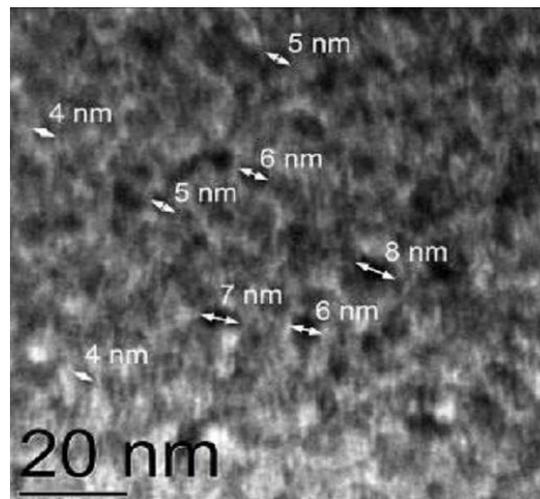


Fig. 3. The transmission electron microscopy image of ITO film obtained by extracts pyrolysis. The crystal size and uniformity of the material plays an important role in its functional activity.

The conductive oxide film should have a maximum smoothness for the application what implies, that the material should have small crystal size. The crystal grain sizes are uniform due to the solution technique usage where multiple centers of nucleation are formed and crystallization of the solid phase occurs in a narrow temperature range.

Transparent conductive oxide films have considerable optical transmittance. Fig. 4 shows the optical transmission spectra of ITO films prepared by extract pyrolysis-technique on glass and

silicon substrates for investigation of films in Visible and Infra Red region. Studies on a series of samples have shown in the visible range the films transmittance is about 90 to 95 %. The undulating nature of the spectrum is due to the dependence of the film transmission on wavelength. In the IR region ITO films reflect radiation especially after 2,5  $\mu\text{m}$ .

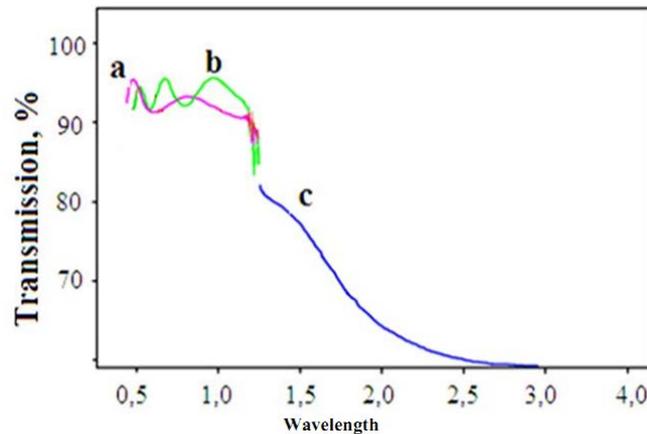


Fig. 4. The optical transmission spectra of ITO films on glass (a), quartz (b) and silicon (c)

The transparent conductive films on glass have been used as electrodes of solar cells. One of electrodes was coated by  $\text{TiO}_2$  layers.

It is advisable to use a multilayer structure of photoanode, which includes the following three layers with gradually increasing  $\text{TiO}_2$  particle size: a compact nanosized  $\text{TiO}_2$  layer to connect the ITO substrate with the mesoporous  $\text{TiO}_2$  layer and reduce the electrical loss; an mesoporous  $\text{TiO}_2$  layer or absorbing layer; and the scattering  $\text{TiO}_2$  layer with particle size 50–100 nm and with much longer optical path than the absorbing layer.

The multilayer structure of the photoanode was formed by sequentially depositing extracts solution with different concentration of metal. It is found that the concentration of the coating solution had a significant effect on the film microstructure. At higher concentrations the mechanisms of film growth changed because of the suspensions appearance and variation of distances between particles and aggregates formation. Films on a glass substrate were prepared from the 0,12, and 0,7 M solutions of the titanium extracts and their microstructure was analyzed. All of the samples were obtained by alternating the wetting and pyrolysis ten times. The resulting films had different thicknesses.

Using a dilute solution of the extract (0,12 M), we obtained continuous nanostructured films with low surface roughness (0,5–4 nm) and with 3–5 nm uniform grains (Fig. 5, a). When a more concentrated 0,7 M solution of the extract was used, in the resulting film the size of particle was  $\sim 20$  nm and the grains remained uniform. (Fig. 5, b). The concentrated titanium extracts

(0,5– 0,7M) contained liquid and solid titanium carboxylates and were suspensions, whereas the 0.12 M extract was a transparent solution. Due to this, the 0.12 M solution of the extract formed a solid nanostructured compact layer. The more concentrated extract afforded a mesoporous titanium oxide film, which retained adhesion after annealing. Based on these studies we prepared a photoanode with compact layer of a thin nanostructured TiO<sub>2</sub> film and mesoporous TiO<sub>2</sub> layer and dissipating TiO<sub>2</sub> layer from commercial powder.

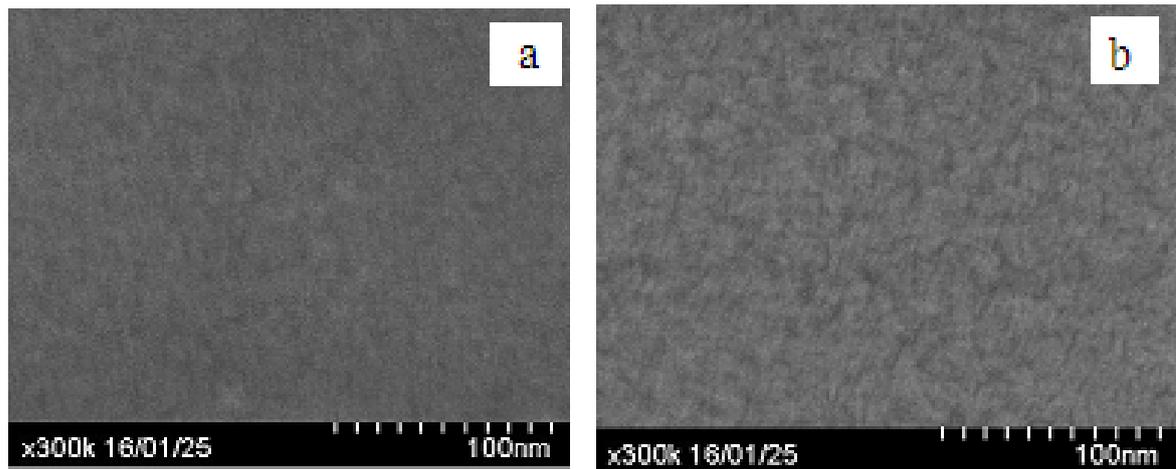


Fig. 5. SEM micrographs of the surface of the high resolution TiO<sub>2</sub> films deposited from 0, 25 M titanium extract solution (a) and 0.7 M of the titanium extract solution (b)

XRD analysis of the obtained films (Fig. 6) revealed the presence of pure anatase phase in the film prepared with 0.12 M and with 0,7 M solution of titanium extracts. Diffractogram show peaks in the position 12,4705, 25,4336, 48,1491, 54,9151, 70,3331 2 Theta and patterns are identified as TiO<sub>2</sub> anatase.

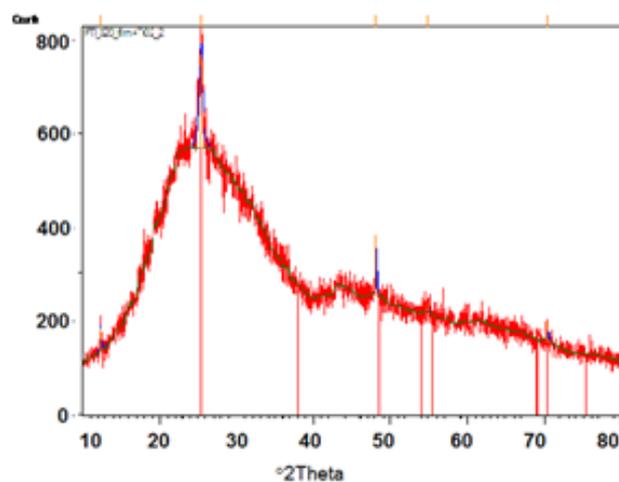


Fig. 6. XRD TiO<sub>2</sub> films, obtained with titanium extract solution

The scattering TiO<sub>2</sub> layer with particle size 50–100 nm was made from commercial TiO<sub>2</sub> powder suspended in carboxylic acids used as extractant.

The multilayer photoanode was annealed at 500°C for 30 min for crystallization of the anatase phase. The resulting films with thicknesses of 2–3 μm were adhesive and did not peel off after annealing. The dye adsorption increased with the roughness of the diffusing layer surface. The photoanode was immersed in the natural dye solution (granate, red orange, chlorophyll) for 12 h and then dried in air.

The solid electrolyte based on polyethylene glycol and the solution of the iodine pair at a ratio of 3:1 was modified by adding a propylene carbonate solution of LiClO<sub>4</sub>.

The solar cells were formed by linking the dye-impregnated photoanode with the ITO-glass counter-electrodes with the electrolyte between them. The efficiency of the solar cell was determined as the ratio of the power generated by the photocell to the power of the incident sunlight.

The efficiency of the module was calculated from  $J_{sc}$ ,  $U_{sc-ill}$ , and  $U_{sc-sh}$  obtained by the irradiating the module by the simulated solar radiation with an intensity of 50 mW/cm<sup>2</sup>. The values of  $J_{sc} = 0,6 \text{ mA/cm}^2$ ,  $U_{oc} = 300 \pm 10 \text{ mV}$ , FF=0.53, efficiency  $\eta$  was found 2,5 %.

## Conclusions

Dye sensitized solar cells (DSSC) have been prepared by extraction-pyrolysis technique. Organic extracts of Ti, In, Sn with subsequent thermal decomposition was used for ITO and TiO<sub>2</sub> films obtaining. The thermal decomposition of In, Sn and Ti carboxylates occurs at the narrow temperature region 400–450 °C. Optimal conditions for obtain the transparent conductive film with thickness 300 nm have been found at the annealing temperature of 550 °C for 30 min. Obtained ITO films were homogeneous and smooth with grain sizes  $6 \pm 2 \text{ nm}$ . The films transmittance is about 90 to 95% in the visible range of wavelength. In the IR region of spectrum ITO films reflect radiation especially after 2, 5 μm.

The photoanode three-layer structure has been created using titanium extracts with different concentrations. The photoanode consists of a compact layer that improves the adhesion and the electrical contact of the cell; a mesoporous layer that enhances the dye adsorption, and a light-scattering layer. TiO<sub>2</sub> films obtained with a dilute solution (0,12 M Ti) consist on the fine grains with a size of 5-6 nm what confirmed with XRD. TiO<sub>2</sub> films obtained with a concentrated

solution (0,7 M Ti) are mesoporous with a grain size of about 20 nm. The film obtained with commercial TiO<sub>2</sub> powder shows large grains of various sizes from 50 to 100 nm.

The photoanode of solar cell includes a transparent conductive In<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> (indium tin oxide, ITO) film on glass as electrodes and the TiO<sub>2</sub> film with different microstructure created using titanium extracts with different concentrations and sensitized with natural dye. The resulting photoanode combined with the ITO counter-electrode in the presence of quasi-solid electrolyte produce solar cell efficiency 2,5% with natural dyes.

### Acknowledgements

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### References

1. Dyesol Ltd (ASX:DYE) Half Yearly Report and Accounts ABN Newswire - Feb 29, 2016 // [http://www.dyesol.com/media/wysiwyg/Documents/top-20-lists/2016-04-26-Top\\_20\\_Shareholders.pdf](http://www.dyesol.com/media/wysiwyg/Documents/top-20-lists/2016-04-26-Top_20_Shareholders.pdf)
2. Solaronix Explores High Efficiency Perovskite Solar Cells in Partnership With EPFL LPI June 2nd, 2014 // <http://www.solaronix.com>
3. H. Hassan, Z. Abidin, F. Chowdhury, and A. Arof, *A International Journal of Photoenergy*, 2016, Article ID 3685210, 9 pages
4. V. Shanmugam, S. Manoharan, S. Anandan, and R. Murugan. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2013, 104, 35.
5. W. Yanmin. *Solar Energy Materials and Solar Cells*, 2009, 93, 1167.
6. Y.-S. Yen, T.-Y. Lin, C.-Y.Hsu et al..*Organic Electronics: Physics, Materials, Applications*, 2013, 14, 2546.
7. A. K. Arof, M. Naeem, F. Hameed et al. *Optical and Quantum Electronics*, 2014, 46, 143.
8. V. Somsongkul, C. Saekung, S. H. Thang, A. Wongchaisuwat, and M. Arunchaiya, *Chiang Mai Journal of Science*, , 2011, 38, 223.
9. J. Li, W. J. Wu, J. B. Yang, J. Tang, Y. T. Long, and J. L. Hua. *Science China Chemistry*, 2011, 54, 699.
10. S. Wooh, T.-Y. Kim, D. Song et al. *ACS Applied Materials & Interfaces*, 2015, 7, 25741.

11. [Huiyong Liu](#), [V. Avrutin](#), [N. Izyumskaya](#), [Ü. Özgür](#), [H. Morkoç](#) *Superlattices and Microstructures* 2010, 458.
12. E. Fortunato, P. Barquinha, R. Martins *Advanced Materials*, 2012, 24, 2945.
13. Xin Xu, Letao Zhang, Yang Shao, Zheyuan Chen, Yong Le, Shengdong Zhang, *IEEE Transactions on Electron Devices*, 2016, 63, 3, 1072
14. Lan-Bo Di, Xiao-Song Li, Chuan Shi, Yong Xu, De-Zhi Zhao and Ai-Min Zhu, *J. Phys. D: Appl. Phys.*, 2009. 42. 32.
15. Yu.V. Kolen'ko, B.R. Churagulov, M. Kunst, L. Mazerolles, C. Colbeau-Justin, *Appl. Catal. B: Environ.*, 2004, 54, 51.
16. P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. *Journal of Physical Chemistry B*, 2003. 107, 14336.
17. K.-M. Lee, C.-Y. Chen, S.-J. Wu, S.-C. Chen, and C.-G. Wu. *Solar Energy Materials and Solar Cells*, 2013, 108, 70.
18. C.-L. Lee, W.-H. Lee, and C.-H. Yang. *International Journal of Photoenergy*, 2016, Article ID 250397, 6 pages.
19. J. H. Yum, S. J. Moon, R. Humphry-Baker et al. *Nanotechnology*, 2008, 19, Article ID 424005.
20. A. Khol'kin and T. Patrusheva, *Extraction–Pyrolysis Method: Production of Functional Oxide Materials*. Moscow: KomKniga, 2006.
21. T. Adrianova, A. Zakharov, E. Mironov, *Reports of Conf. KSTU Ultradispersnie. motheriali.*, 1999, 1, 134.
22. Yu. Agafonov, *Colloid Journal*, 1997, 56, 469.
23. T. Patrusheva, N. Snezhko, A. Belousov, A. Ryzhenkov, Yu. Mikhlin, S. Kirik, G. Bondarenko, S. Zharkov and A. Romanov, *Journal of Applied Chemical Science International*, 2015, 3, 21.