

# Efficiency of dye sensitized solar cells with various compositions of TiO<sub>2</sub> based screen printed photoactive electrodes

Pavol Gemeiner, Milan Mikula

*Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology,  
Department of Graphic Art Technology and Applied Photochemistry,  
Radlinského 9, 821 37, Bratislava, Slovakia  
pavol.gemeiner@stuba.sk*

**Abstract:** The TiO<sub>2</sub> electrode has a key role in dye sensitized solar cell (DSSC) technology in the charge generation and charge transportation. The properties of TiO<sub>2</sub> layer affect resulting efficiency of DSSC and can be controlled by printing process and chemical composition of printing paste. TiO<sub>2</sub> pastes with different compositions of TiO<sub>2</sub> nanoparticles, ethanol, ethyl cellulose, water, acetic acid,  $\alpha$ -terpineol were prepared and screen printed onto the glass substrate with fluorine doped tin oxide (FTO). The TiO<sub>2</sub> pastes for screen printing were characterized by rheological measurements and screen printed TiO<sub>2</sub> electrodes by atomic force microscopy and UV-Vis spectroscopy. The photocurrent – voltage characteristics and efficiencies of DSSC were evaluated and compared. All prepared TiO<sub>2</sub> pastes were suitable for screen printing with ideal rheological characteristics. The highest efficiency 0.68 % and current density  $I_{sc} = 1.21 \text{ mA/cm}^2$  reached by the DSSC based on TiO<sub>2</sub> electrode with thickness 1.5  $\mu\text{m}$ , with amount of absorbed dye  $1.1 \times 10^{-8} \text{ mol/cm}^2$  and without visible cracks and particles aggregation. This TiO<sub>2</sub> electrode was prepared from the paste containing 5.4 wt. % of TiO<sub>2</sub>, 65.3 wt. % of ethanol, 1.8 wt. % of ethyl cellulose, 23 wt. % of H<sub>2</sub>O and 4.5 wt. % of CH<sub>3</sub>COOH.

**Keywords:** TiO<sub>2</sub> nanoporous electrode, dye sensitized solar cell, screen printing

## Introduction

Dye sensitized solar cells (DSSC) belong to the third generation of solar cells and due their low cost fabrication using printing technologies, low cost materials and relative high efficiency are the promising replacement for conventional silicon based solar cells (O'Regan et al. 1991). The highest achieved photon to electron conversion efficiency of DSSC, 11.5 %, is comparable to the Si cells (Chen et al. 2009, Grätzel 2009). The DSSC standard structure contains a glass substrate coated with transparent conductive oxides, the semiconductive nanoporous photoactive layer based on TiO<sub>2</sub>, a dye used as sensitizer, an electrolyte containing redox mediator and Pt counter electrode (Grätzel 2003). In DSSC technology the charge generation occurs at the semiconductor – dye interface and the charge transport is done mainly by the semiconductor – electrolyte interface. It is the opposite to conventional organic photovoltaic devices which use acceptor and donor materials to form heterojunction resulting in separation of the exciton into two carries (Nazeerudin et al. 2011). Therefore, the TiO<sub>2</sub> nanoporous semiconductor photoactive layer has crucial role in both processes, charge generation and charge transportation in DSSC. The properties of TiO<sub>2</sub> electrode as roughness, surface area and film thickness determine electronic properties of the electrode including very important

factor, the amount of absorbed dye, which leads to higher light absorbing (Rothenberger et al. 1999). These structural parameters of TiO<sub>2</sub> electrodes can be affected by printing process and particularly by properties of the printing dispersion. The screen printing, as the most widely used printing technique for TiO<sub>2</sub> photoactive electrode, provides many advantages due to low cost, speed, simplicity and possibility to print large areas (Nazeerudin et al. 2011). The main parameter of screen printing is the quality of screen printing paste. The TiO<sub>2</sub> paste often used by researchers for screen printing is standardly composed of TiO<sub>2</sub> nanoparticles (Degusa P25),  $\alpha$ -terpineol as a solvent, 10 % solution of ethyl cellulose in ethanol as a rheological agent, water and acetic acid as a aggregation blockers and adhesion enhancers (Nazeerudin et al. 2001, Ito et al. 2011). The advantage of this paste is stability and reproducibility but difficult homogenization process and the need of ethanol evaporation lead to simpler compositions. Therefore, the TiO<sub>2</sub> pastes required simpler and faster homogenization process based on alcohols as ethanol, n-butanol, 2-ethyl-1-hexanol or water (Ke Fan et al. 2010, Tsoukleris et al. 2005).

The aim of this work was to prepare TiO<sub>2</sub> pastes with different compounds of chemical substances via simple and fast homogenization process and use them for screen printing of TiO<sub>2</sub> nanoporous electrodes for DSSC. Properties as rheological

characteristics of prepared TiO<sub>2</sub> pastes, roughness, thickness and adhesion of screen printed TiO<sub>2</sub> electrodes, efficiency and photocurrent – voltage characteristics of DSSC were evaluated in correlation with the composition of prepared TiO<sub>2</sub> pastes.

## Materials and Methods

### *Preparation of TiO<sub>2</sub> pastes and screen printing process of TiO<sub>2</sub> electrodes*

TiO<sub>2</sub> pastes for screen printing were prepared via homogenization process as the mixture of TiO<sub>2</sub> nanopowder (Evonik, Aeroxide P25, ~22 nm), ethyl cellulose (Aldrich, viscosity 22 cp in toluene:ethanol 80:20), deionized water, acetic acid (>96.6 %) and  $\alpha$ -terpineol (Aldrich, >96 %). The exact chemical composition of the prepared samples is shown in Tab 1. The homogenization procedure consisted of several steps. The TiO<sub>2</sub> nanopowder was added to a mortar and stirred for 30 min with gradual addition of acetic acid (only for sample A and B), deionized water (sample A and C), ethanol and  $\alpha$ -terpineol (only for sample D). Then samples undergone homogenizations in an ultrasonic horn in 20 × 1 sec intervals. TiO<sub>2</sub> dispersion was transferred to a beaker with addition of ethyl cellulose and stirred with a magnetic stirrer for 24 hours followed by homogenization in ultrasonic bath for 20 min.

**Tab. 1.** Chemical composition of prepared TiO<sub>2</sub> pastes (wt. %).

Chemical	Sample A	Sample B	Sample C	Sample D
TiO <sub>2</sub>	5	6.5	6.5	6
Ethanol	65.7	91.6	69.2	82.8
Ethyl cellulose	1.8	1.9	1.8	2.2
H <sub>2</sub> O	23	-	23	-
CH <sub>3</sub> COOH	4.5	-	-	1
$\alpha$ -terpineol	-	-	-	7

Before printing, the FTO glasses were cleaned with ethanol and exposed to UV radiation for 45 min. Samples of TiO<sub>2</sub> pastes were screen printed (manual screen printer, polyester screen – 140 mesh, with thread diameter of 64  $\mu$ m, the distance between screen and substrate = 4 mm, polyurethane squeegee and photosensitive emulsion Kasi Fotocoat 1970) on the fluorine doped tin oxide coated glass (FTO glass, Aldrich, ~7  $\Omega$ /sq., dimension 2 × 3 cm<sup>2</sup>). After screen printing, the TiO<sub>2</sub> electrodes with the active area 1.5 cm<sup>2</sup> were dried at ambient conditions and then sintered at 450–460 °C for 30 min to remove organic compounds and to improve interconnections between nanoparticles.

### *Dye sensitized solar cells assembly*

Prepared TiO<sub>2</sub> electrodes were sensitized in 0.4 mM solution of N3 dye (Aldrich, cis-[(2,2'-bipyridyl-4,4'-carboxyl)<sub>2</sub>(NCS)<sub>2</sub>] ruthenium(II)) in ethanol for 24 hours. After emerging, the sensitized TiO<sub>2</sub> layers were cleaned with pure ethanol to remove unbound dye molecules. Platinum paste (Solaronix, Platisol T/SP) used as a catalytic layer of counter electrode was screen printed (305 mesh, thread diameter 34  $\mu$ m, distance between screen and substrate was 2 mm) onto the cleaned FTO glass and then sintered at 450 °C for 15 min. The size of screen printed Pt catalytic layers was 1 × 1.5 cm<sup>2</sup>. 18  $\mu$ l of iodine electrolyte (Solaronix, Iodolyte AN50) was added directly on the sensitized TiO<sub>2</sub> electrodes which were afterwards assembled with Pt counter electrode into a sandwich type cell and fixed with two binder clips.

### *TiO<sub>2</sub> pastes, electrodes and DSSC measurements*

Rheological properties and flow curves of prepared TiO<sub>2</sub> pastes were measured using HAAKE rotational viscometer (HAAKE VT501, cone 7.5 mm). Adhesion of screen printed TiO<sub>2</sub> electrodes were evaluated with scotch tape measurements (~2 N/cm). 3D topography, layer thickness and roughness of samples were measured by atomic force microscope (AFM, Veeco microscope DI CP-II, 5 and 100  $\mu$ m scanner, non-contact mode, tip radius 10 nm, set point = -0.039  $\mu$ m, scanning rate = 1 Hz, gain = 0.15) and obtained data were processed by the IP AutoProbeImage 2.1.15 and SPMLab Analysis software.

The amount of absorbed N3 dye at different TiO<sub>2</sub> electrodes was evaluated according Wang description (Wang et al. 2004). Samples of sensitized TiO<sub>2</sub> electrodes were immersed into a 0.1 M NaOH solution in solvent mixture water/ethanol 1:1 for 10 min which resulted in desorption of N3 dye from electrodes. Absorption of obtained solutions were measured with UV-VIS spectrophotometer (Cecil CE 3055) and amounts of absorbed dye were determined (Lambert-Beer law) using the maximum absorbance value ( $A_{max}$  at 508 nm wavelength). The value of molar absorption coefficient  $E = 1.78 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  of N3 dye at 508 nm wavelength was determined from calibration measurements (0.4 mM solution of N3 dye in the solvent consist of 0.1 M NaOH solution in solvent mixture water/ethanol 1:1) with the help of Lambert-Beer law.

Photocurrent – voltage characteristics of DSSC were measured using day-light source with the power of 880 W/m<sup>2</sup> and by the loading circuit containing two multimeters (Keithley 2000). The

value of conversion efficiency of prepared dye sensitized solar cells was measured from Eq. 1, where  $\eta$  is overall conversion efficiency and  $V_{OC}$ ,  $I_{SC}$ ,  $FF$ ,  $P_{in}$  are the open-circuit voltage, short-circuit current density, fill factor and the intensity of incident light, respectively.

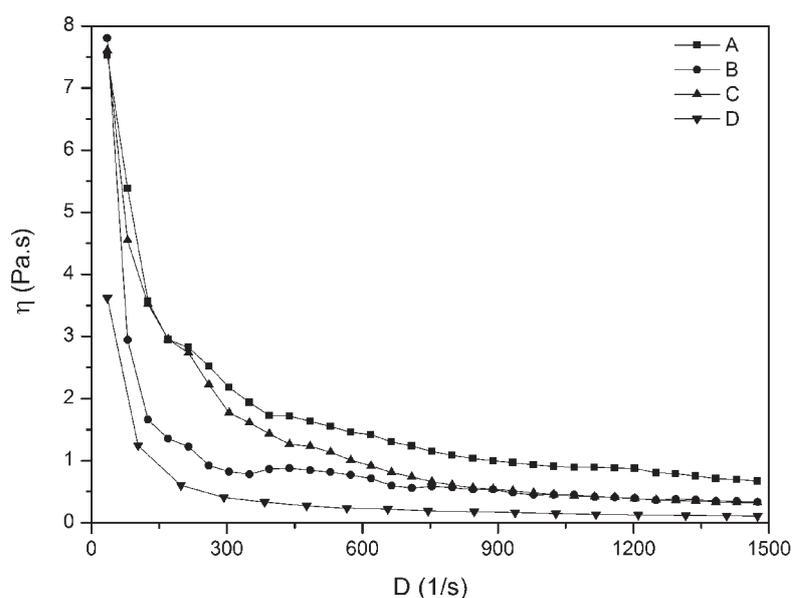
$$\eta = \frac{V_{OC} \cdot I_{SC} \cdot FF}{P_{in}} [\%] \quad (1)$$

## Results and Discussion

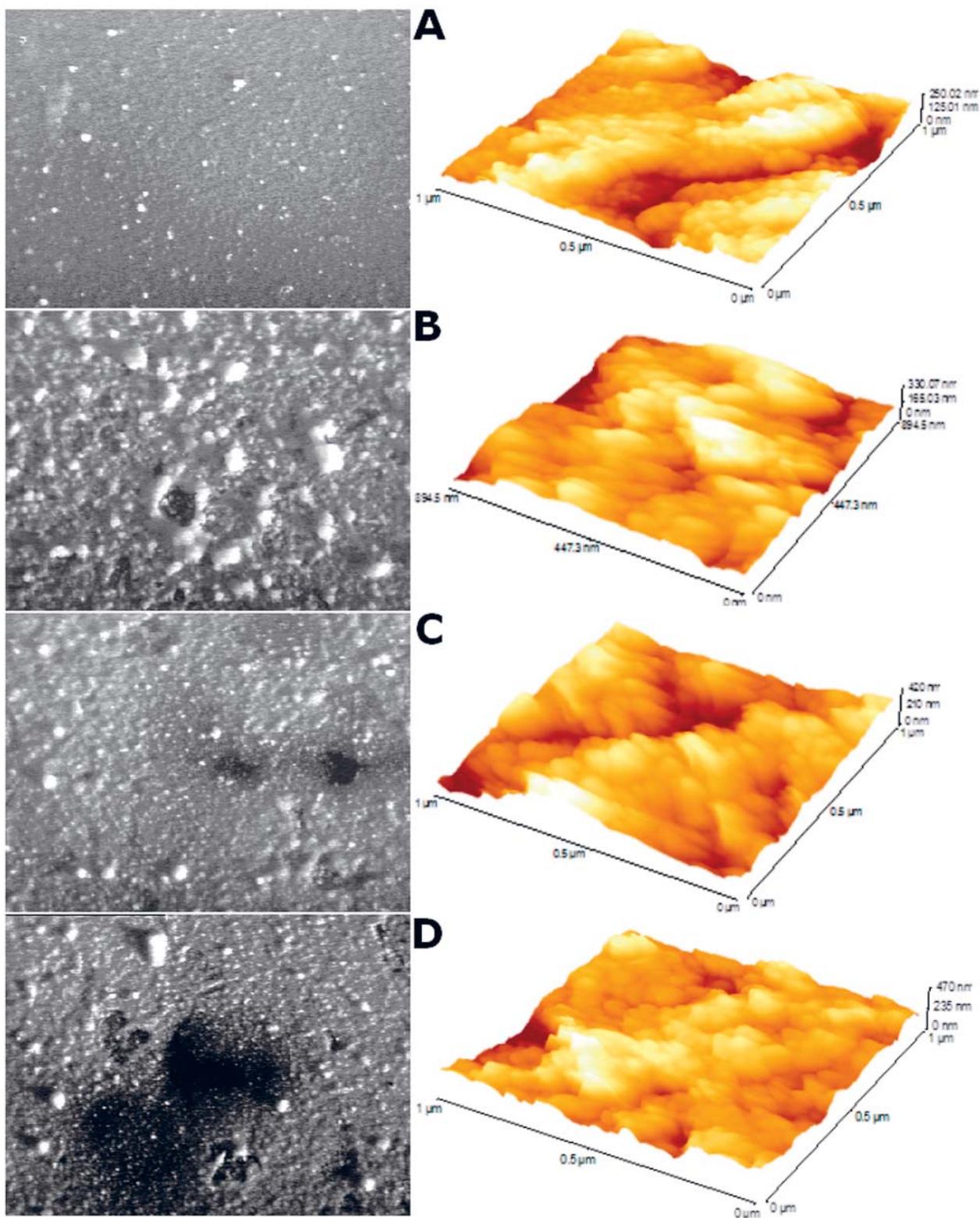
Prepared  $\text{TiO}_2$  pastes were suitable for screen printing with resulting mechanically stable  $\text{TiO}_2$  layers without significant cracks and inhomogeneities. Neither sintering at higher temperatures within 450–460 °C did not cause mechanical peeling of layers from substrate. It proves the convenient composition of all pastes, sufficient homogenization process and well set parameters of screen printing. The rheological characteristics of  $\text{TiO}_2$  pastes have optimal pseudoplastic behaviour. Viscosity decreases with increasing shear rate, typical for screen printing pastes, which corresponds with adequate amount of added ethyl cellulose (Fig. 1). The initial viscosities for samples A, B, C were within  $\eta = 7.6$ – $7.8$  Pa s and for sample D  $\eta = 3.6$  Pa s. Different rheological characteristics and lower viscosities of samples B, C and D compared to sample A could be caused by aggregation of  $\text{TiO}_2$  nanoparticles in pastes without addition of water and acetic acid. For sample D the creation of two phases of immiscible ethanol and  $\alpha$ -terpineol was apparent. This fact can lead to much lower viscosity of sample D.  $\alpha$ -terpineol should affect nanoparticles aggregation and viscosity of paste.

The  $\text{TiO}_2$  layers adhesion was evaluated via scotch tape measurements with the peeling force  $\sim 2$  N/cm. The highest adhesion has been clearly shown for sample A, in which the whole layer remained on substrate after peeling, followed by sample C with remaining  $\sim 30\%$  of layer, sample B and D which were removed completely. These differences in layer adhesion can be caused by addition of water and acetic acid to samples A and C. As Ito and Grätzel reported (Ito et al. 2007), without addition of these compounds, layers are unstable and after sintering should be mechanically peeled from substrates. The effect of water addition is in creation of hydroxyl groups on the  $\text{TiO}_2$  particles and  $\text{SnO}_2$  substrate. After dehydrogenation of these groups in sintering process the particles and substrate are linked with strong chemical bonds. At the same time, the proton  $\text{H}^+$  of acetic acid can be also adsorbed onto  $\text{TiO}_2$  nanoparticle surface, shifts the Zeta potential to positive, and keep it from aggregation (Hee-Gon Bang et al. 2012).

Thickness, roughness, 3D topography and microscopic images were taken by AFM. It is well known, that the amount of  $\text{TiO}_2$  nanoparticles in the paste affect the thickness of  $\text{TiO}_2$  layer and as well as the efficiency of DSSC. The thickness of prepared samples A, B, C and D with different content of  $\text{TiO}_2$  (Tab. 1) were 1.5, 2.5, 2.5 and 2  $\mu\text{m}$ , respectively, that corresponds with the fact mentioned above. The optical images of printed  $\text{TiO}_2$  layers were taken from optical microscope or AFM at 250 $\times$  magnification. As shown in Fig. 2, sample A had very homogeneous surface with small aggregates. The occurrence of aggregates is most significant on the surface of sample B, which was prepared without addition of water and acetic acid. Sample D had the most inhomogeneous



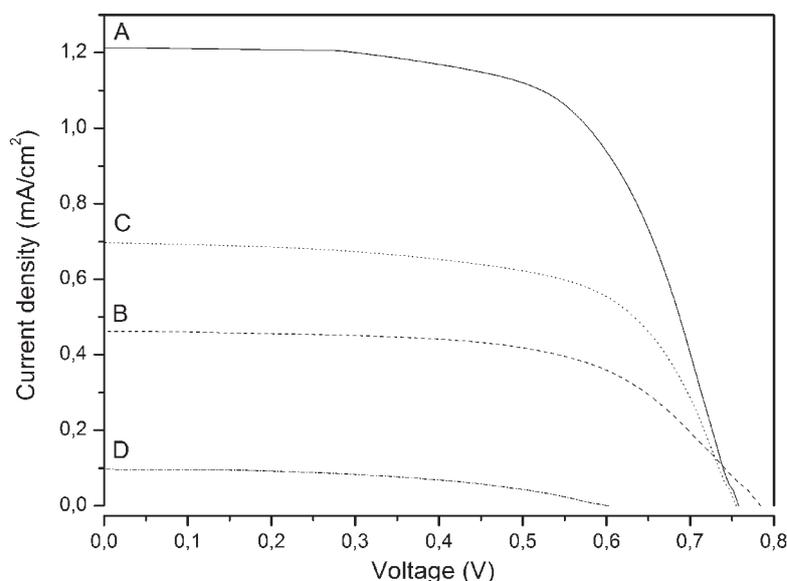
**Fig. 1.** The rheological characteristics for samples of  $\text{TiO}_2$  pastes for screen printing.



**Fig. 2.** Optical microscopy images (the left side,  $400 \times 300 \mu\text{m}^2$ ) and AFM 3D images (the right side, scans of the smoother places) of screen printed  $\text{TiO}_2$  layers.

surface. The reason is the immiscibility of ethanol and  $\alpha$ -terpineol. This fact has led after sintering to the creation of large  $\text{TiO}_2$  free areas at the places where terpineol was before. Sample C without addition of acetic acid had rougher surface with increased

occurrence of aggregates. Measured roughnesses of screen printed  $\text{TiO}_2$  layers correspond to aggregates and inhomogeneities presence. For samples A, B, C and D the measured values of roughness  $R_q$  was 44, 59, 62 and 64 nm, respectively.



**Fig. 3.** Photocurrent – voltage characteristics of dye sensitized solar cells based on different TiO<sub>2</sub> electrodes.

Fig. 3 and Tab. 2 shows the I-V characteristics and performances of prepared DSSC with screen printed samples of TiO<sub>2</sub> electrodes. The value of short-circuit current density  $I_{SC}$  (mA/cm<sup>2</sup>, at  $U = 0$  V) depends directly on charge injection and collection at TiO<sub>2</sub> electrode, on the amount of absorbed dye and layer thickness. For our samples of TiO<sub>2</sub> electrodes A, B, C and D the measured value of  $I_{SC}$  was 1.21, 0.46, 0.7 and 0.1 mA/cm<sup>2</sup>. The highest value of  $I_{SC}$  for the sample A and lowest for the sample D corresponds with differences of surface inhomogeneities, amounts of aggregates and the quantity of absorbed dye. Beneficial addition of acetic acid and water is also demonstrated here, confirmed by high  $I_{SC}$  of samples A and C. Variance between open-circuit voltages  $U_{OC}$  (V) for samples A, B and C compared to sample D indicates the poor interconnection among TiO<sub>2</sub> nanoparticles, the holes in the oxide layer and low charge injection from iodine electrolyte in the D case.

The fill factor (FF) defines ideality of solar cell, can take values between 0 and 1 and reflects electrical and electrochemical losses. Measured values of FF for our TiO<sub>2</sub> solar cells are shown in Tab. 2.

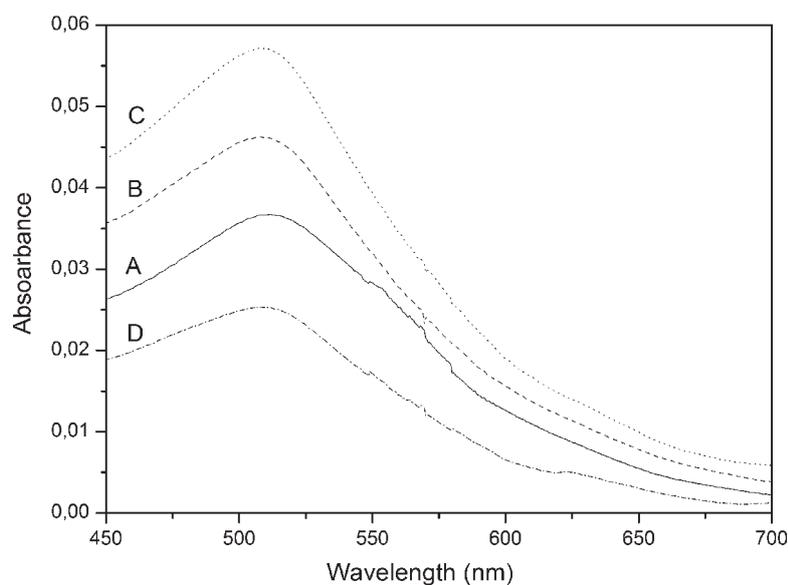
The highest efficiency  $\eta = 0.68$  % was measured for DSSC based on screen printed TiO<sub>2</sub> electrode layer of sample A followed by sample C, B and D with  $\eta = 0.38, 0.25$  and  $0.03$  %.

Higher amount of adsorbed dye (adsorbed N3 dye in mol/cm<sup>2</sup> measured from UV-VIS absorbance spectra Fig. 4) is related to thickness, roughness and homogeneity of the TiO<sub>2</sub> nanoporous electrode. However, for sample D with electrode thickness comparable to other electrodes was amount of adsorbed dye roughly half of those quantities. This can be explained by TiO<sub>2</sub> free areas on the electrode D surface, which decreases the extent of dye absorption during sensitization.

In conclusion, various pastes based on TiO<sub>2</sub> nanoparticles and different content of organics were prepared via simple and fast homogenization process. All these pastes were suitable for screen printing and forming TiO<sub>2</sub> nanoporous electrodes for DSSC. The highest efficiency  $\eta = 0.68$  %,  $I_{SC} = 1.21$  mA/cm<sup>2</sup> and  $U_{OC} = 0.76$  V was reached by DSSC based on 1.5  $\mu$ m thick TiO<sub>2</sub> electrode with roughness  $R_q = 44$  nm, containing 5.4 wt. % of TiO<sub>2</sub>, 65.3 wt. % of ethanol,

**Tab. 2.** Photovoltaic performances of DSSC based on different TiO<sub>2</sub> electrodes.

Sample	$I_{SC}$ [mA/cm <sup>2</sup> ]	$U_{OC}$ [V]	FF	$\eta$ [%]	Thickness [~ $\mu$ m]	Adsorbed N3 dye [ $\times 10^{-8}$ mol/cm <sup>2</sup> ]
A	1.21	0.76	0.65	0.68	1.5	1.10
B	0.46	0.78	0.62	0.25	2.5	1.39
C	0.70	0.75	0.64	0.38	2.5	1.70
D	0.10	0.60	0.46	0.03	2.0	0.76



**Fig. 4.** UV-VIS absorbance spectra of adsorbed N3 dye on the different samples of TiO<sub>2</sub> nanoporous layers.

1.8 wt. % of ethyl cellulose, 23 wt. % of H<sub>2</sub>O and 4.5 wt. % of CH<sub>3</sub>COOH. The amount of adsorbed N3 dye on this electrode was  $1.1 \times 10^{-8}$  mol/cm<sup>2</sup>. It was proved here that properties of TiO<sub>2</sub> electrode as thickness and amount of adsorbed dye are not the only factors which have influence on overall conversion efficiency of dye sensitized solar cell. The composition of TiO<sub>2</sub> paste could affect the homogeneity and aggregates concentration of the TiO<sub>2</sub> electrode as well. Contents of acetic acid and water in TiO<sub>2</sub> pastes significantly decreased aggregation of nanoparticles, increased adhesion of layer to substrate and short-circuit current density of DSSC.

#### **Acknowledgement**

*This work was supported by courtesy of the Slovak Grant Agency (VEGA 1/0818/13) and by the OP Research and Development of the project National Centrum of Research and Application of Renewable Sources of Energy, ITMS 26240120016, co-financed by the Fund of European Regional Development.*

#### **References**

- Grätzel M (2007) *Phil. Trans. R. Soc.* 365: 993–1005.  
 Grätzel M (2003) *J. Photochemistry and Photobiology C. Photochemistry Reviews* 4: 145–153.  
 Hee-Gon Bang, Jun-Ki Chung, Rae-Young Jung, Sang-Yeup Park (2012) *Ceramics International* 38: 511–515.  
 Chen C, Wang M, Li J, Pootrakulchote N, Alibabaei L, Ngoc-le C, Decoppet JD, Tsai J, Grätzel C, Wu C, Zakeeruddin SM, Grätzel M (2009) *ACS Nano* 3: 3103–3109.  
 Nazeerudin MK, Baranoff E, Grätzel M (2011) *Solar Energy* 85: 1172–1178.  
 Nazeeruddin MK, Péchy P, Renourd T, Zakeeruddin SM, Humphry-Baker R, Compte P (2001) *J. Am. Chem. Soc.* 123: 1613–1624.  
 Ito S, Takahashi K, Yusa S, Imamura T, Tanimoto K (2011) *International Journal of Photoenergy* 2012: 7.  
 Ito S, Chen P, Comte P, Nazeeruddin MK, Liska P, Péchy P, Grätzel M (2007) *Progress in Photovoltaics: Research and Applications* 15: 603–612.  
 Rothenberger G, Comte P, Grätzel M (1999) *Solar Energy Mater. Solar Cells* 58: 321.  
 Wang ZS, Kawauchi H, Kashima T, Arakawa H (2004) *Coord. Chem Rev* 248: 1381–1389.