

Fabrication of DSSCs with biebrich scarlet, alizarine cyanine green and evans blue dyes as new organic photosensitizers

SARITA BOSE, K.R. GENWA*

Department of Chemistry, J.N.V. University, Jodhpur, India

Dye sensitized solar cells are photoelectrochemical cells mimicking photosynthesis. They represent a new generation of solar cells which is intensively studied nowadays. This cell was fabricated using TiO₂ nanoparticles coated on FTO glass, organic dyes as photosensitizer, PEDOT:PSS as counter electrode and iodide-triiodide as electrolyte. The present work aims at the use of low cost new organic dyes viz. biebrich scarlet, alizarine cyanine green and evans blue for DSSC as an alternative to metallic dyes. In the present work, I-V characteristics, energy or power conversion efficiencies of the dyes have been studied in different solvents. The photoelectrochemical properties of the dyes were observed under 1.5 AM condition.

Keywords: *dye sensitized solar cell; TiO₂ nanoparticles; organic photosensitizers*

1. Introduction

Dye sensitized solar cells are prominent members of thin film photovoltaics family [1]. They offer the perspective of efficient and low cost fabrication and also present attractive features that facilitate market access. DSSCs are extremely efficient due to their “depth” of the nanostructure. There is a very high chance that a photon will be absorbed, and the dyes are very effective at converting it to electron. The TiO₂ nanostructures create a highly porous surface yielding an abundance of surface area, which is required for light-harvesting dyes to be easily absorbed and results in increasing cell efficiency. Power conversion efficiency for DSSCs of about 11 % [2, 3] has been achieved. Recently, the highest conversion efficiency of 18.1 % has been reported for two-terminal DSSC/silicon tandem solar cells [4]. Numerous efforts have been put to improve their efficiency. Still DSSCs are at the verge of commercialization.

Research is going on improving the efficiency and viability of the cells. One such effort is working with organic photosensitizers which offer low cost alternative to metallic dye based DSSCs. Several groups have developed metal-free organic

sensitizers to overcome the prohibitive cost of ruthenium metal complexes [5–9]. Zeng et al. [10] reported efficiency up to 10.3 % for a metal-free organic sensitizer.

A series of indoline dyes (such as D-149 and D-205) containing rhodanine-3-acetic acid as an acceptor and anchoring unit have shown very high performance ($\eta > 9\%$) [11, 12]. The indoline moiety in the series of isophorone bridged organic dyes showed remarkable power conversion efficiency as high as 7.41 % under AM 1.5 [13]. Triphenylamine [14, 15] and carbazole [16–18] derivatives have given promising results with organic dyes like hemicyanine dyes [19]. Three new D-A- π -A organic dyes (D1, D2, and D3) based on triarylamine donor N,N,4,4-tetra-p-tolyl-4H-indeno[1,2-b]thiophen-6-amine (IDTTPA) and a benzoic acid were synthesized and showed efficiency up to 5.19 % [20]. Triphenylene diamine dyes showed efficiencies in the range of 0.64 % to 0.96 % with and without ZnO compact layers [21]. The present research paper aims at producing low cost organic dyes based solar cells and comparing the results obtained for these dyes in various solvents.

1.1. Structure and working of DSSC

DSSC is a photoelectrochemical cell in which the junction is made by

*E-mail: krg2004@rediffmail.com

a semiconductor-electrolyte interface. The DSSC was fabricated using TiO_2 nanoparticles, a wide band gap semiconductor, coated on FTO glass slide having $1\text{ cm} \times 1\text{ cm}$ working area. This electrode was photosensitized by organic dyes which finally acted as an anode. Graphite-PEDOT:PSS was used for making counter electrode, i.e. cathode. The electrodes were sandwiched and a liquid iodide-triiodide as redox electrolyte was inserted to speed up the redox reaction of the cell. The structure and work of a typical DSSC is shown in Fig. 1.

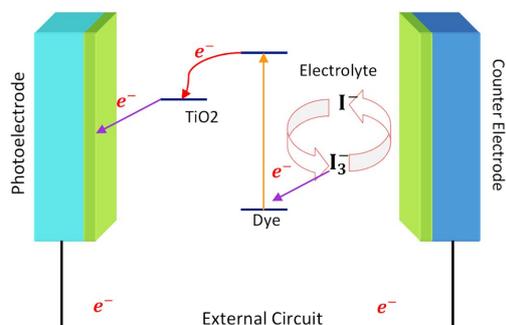


Fig. 1. Structure and working of DSSC.

2. Experimental

2.1. Materials

TiO_2 nanoparticles (anatase), acetic acid (pH 3 to 4), Triton-X100, (0.5 M) KI, (0.5 M) I_2 , ethylene glycol, ethanol, acetone, dimethylsulfoxide (DMSO), PEDOT:PSS, double distilled water and conducting FTO glass slides were used for the experiments.

2.2. Structure and description of the dyes

The TiO_2 coated FTO slides were sensitized by the organic dyes in various solvents for evaluation their photochemical properties. The properties and structures of the dyes used in this work are described below. The chemical structures are shown in Fig. 2a, Fig. 2b and Fig. 2c, respectively.

(a) Biebrich scarlet

It is a red solid powder acidic dye, readily soluble in water, acetone, DMSO and ethanol, with

molecular formula $\text{C}_{22}\text{H}_{16}\text{N}_4\text{Na}_2\text{O}_7\text{S}_2$, molecular weight 512.52 g/mol, maximum absorption $\lambda_{\text{max}} = 510\text{ nm}$.

(b) Alizarine cyanine green

It is a bluish green powder acidic dye readily soluble in water, acetone, DMSO and ethanol, with molecular formula $\text{C}_{28}\text{H}_{20}\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$, molecular weight 622.57 g/mol and maximum absorption $\lambda_{\text{max}} = 642\text{ nm}$.

(c) Evans blue

It is a deep blue powder acidic dye soluble in water and DMSO, slightly less soluble in ethanol and insoluble in acetone, with molecular formula $\text{C}_{34}\text{H}_{24}\text{N}_6\text{Na}_4\text{O}_{14}\text{S}_4$, molecular weight 960.81 g/mol and maximum absorption $\lambda_{\text{max}} = 606\text{ nm}$ to 611 nm .

2.3. Methodology

DSSC fabrication involved various important steps including selection and cleaning of conducting transparent glass slides, preparing semiconducting paste for anode, dye sensitization of the TiO_2 layer, electrolyte preparation and counter electrode fabrication. The slides were masked by scotch tape at three sides and the TiO_2 paste was then applied onto the slide using doctor blade method. The slide was allowed to dry at room temperature then sintered at $500\text{ }^\circ\text{C}$ for one hour. Sintering was done for making TiO_2 layer mesoporous. The slide was then placed in photosensitizer solution for 12 hours in dark for proper adsorption. Excess dye was washed with the same solvent used for dissolving the dye and dried. Counter electrode was prepared by applying thin graphite coating and PEDOT:PSS (mixed with DMSO in 3:1 ratio) was spin coated upon the graphite layer. It was sintered at $150\text{ }^\circ\text{C}$ for 15 min. Finally, both slides were joined together through binder clips. Electrolyte was inserted from the sides of the slide and it distributed evenly through capillary action. The complete cell was then placed under solar spectrum for I-V characterization under 1.5 AM sun condition.

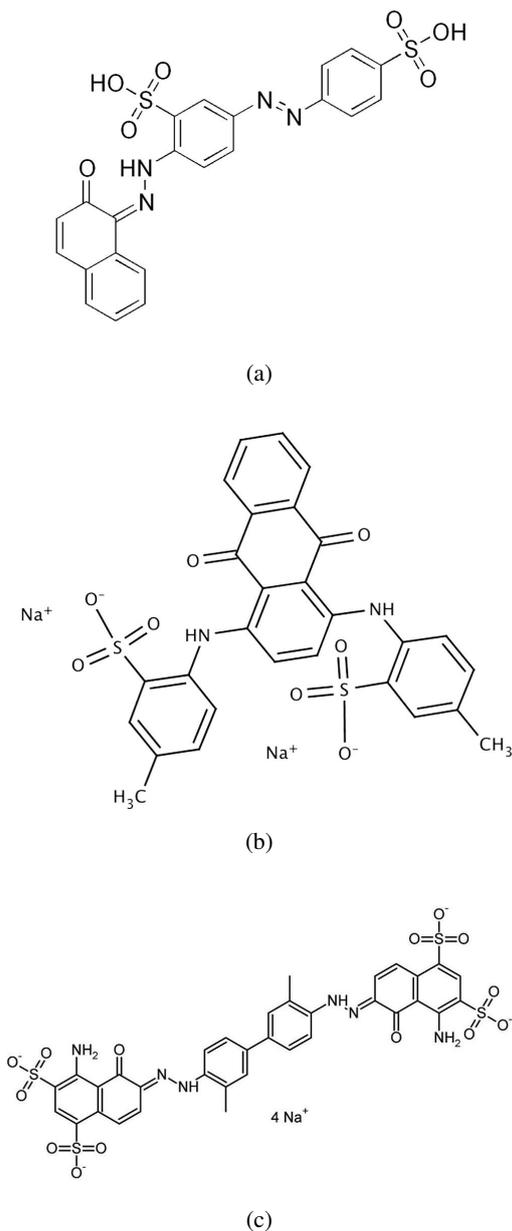


Fig. 2. Chemical structure of (a) biebrich scarlet, (b) alizarine cyanine green, and (c) evans blue.

3. Results and discussion

3.1. UV-Vis study of spectral properties of the dyes

The dyes were dissolved in various solvents viz. distilled water, ethanol, acetone and DMSO. These dyes are characterized by good absorption properties and have anchoring sites for proper adhesion on TiO₂ layer. The absorption properties of the dyes

were studied by UV-Vis spectrophotometer. Fig. 3a shows that biebrich scarlet (BS) revealed the best absorption in DMSO. Acetone and DMSO both showed splitting in the spectrum. In ethanol BS showed no splitting but a broad absorption spectrum was observed. Alizarine cyanine green (ACG) showed broad spectrum in all the solvents, with the highest absorption peak in DMSO which can be observed in Fig. 3b. Evans blue (EB) was insoluble in acetone. Fig. 3c shows that EB revealed the highest absorption in DMSO. EB was less soluble in ethanol, thus, a low absorption was observed in ethanol.

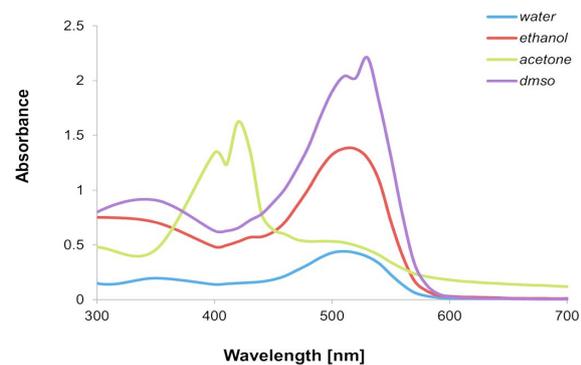
3.2. Morphological study of TiO₂ electrode

The surface morphology of TiO₂ electrode was evaluated by SEM and XRD. The SEM images show that the electrode has a typical porous structure. Porosity is the main feature of TiO₂ thin layer, which makes the adsorption of dye more effective and helps in increasing efficiency of the cell. Mesoporous structure has high surface area affecting dye loading and thus the electron transport rate is also enhanced, thereby increasing the cell performance [22]. SEM images were examined at different magnifications (2.00 K and 17.6 K) as shown in Fig. 4. The images clearly show that the TiO₂ layer is highly porous and evenly distributed. Granular porous particles of TiO₂ can be seen clearly.

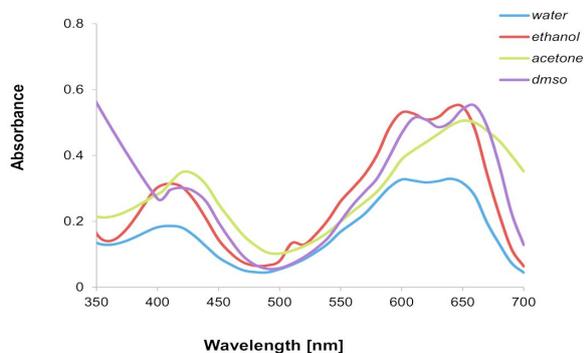
The X-ray diffraction instrument was used to collect the intensity data of the scattered signals to get the diffraction pattern of the measured sample. This pattern is normally taken as the signal versus the phase angle. Fig. 5 shows the data taken in 2θ range. XRD patterns of the TiO₂ layer exhibit strong diffraction peaks at 25° and 48° indicating TiO₂ in the anatase phase.

3.3. I-V characterization

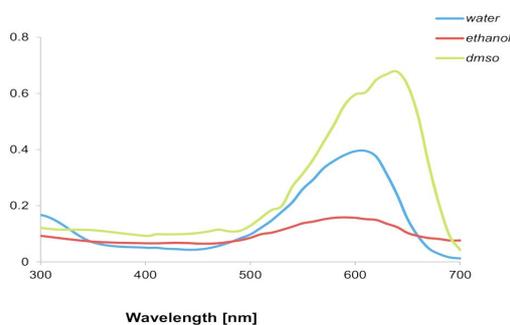
Current-voltage measurements (I-V measurements) were undertaken under solar spectrum to determine efficiencies of the solar cells. The device performances were analyzed for DSSCs sensitized with biebrich scarlet, alizarine cyanine green and evans blue. Fabricated cells were



(a)



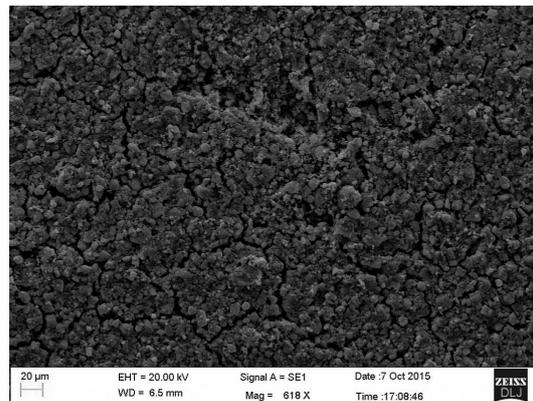
(b)



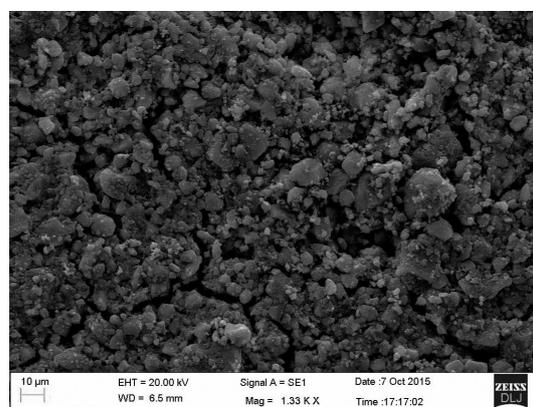
(c)

Fig. 3. Absorption spectra of (a) biebrich scarlet, (b) alizarine cyanine green, and (c) evans blue in different solvents.

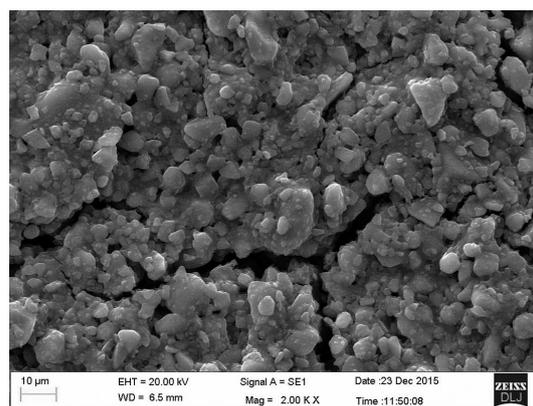
characterized using a variable load resistor in the circuit. A voltage was applied between the working and counter electrode of the solar cell and the current output was measured. The photovoltaic parameters: open circuit voltage V_{oc} , short circuit current density J_{sc} and photoelectric conversion efficiencies η of the DSSCs with active area of 1 cm^2 were



(a)



(b)



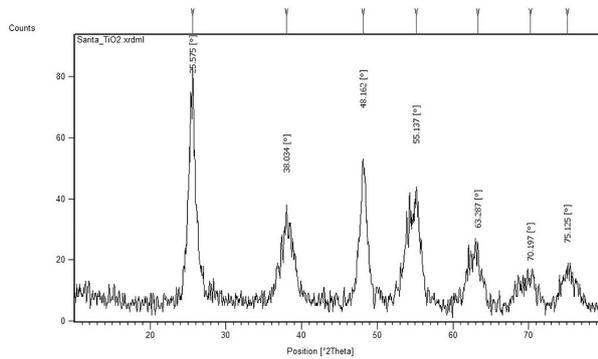
(c)

Fig. 4. SEM images of TiO_2 layer coated on FTO glass slides at different magnifications.

measured. The comparative results are summarized in Table 1a, Table 1b and Table 1c. The open circuit voltage V_{oc} and short circuit current I_{sc} of the solar cells were measured under 100 mW/cm^2 at AM 1.5 G condition.

Table 1. Photoelectrochemical parameters of the DSSCs with (a) biebrich scarlet, (b) alizarine cyanine green and (c) evans blue dyes in various solvents.

(a) biebrich scarlet				
Solvent	V_{oc} [mV]	J_{sc} [$\mu\text{A}/\text{cm}^2$]	Fill factor	η [%]
water	534	362	0.54	0.1048
acetone	560	330	0.54	0.093
DMSO	683	445	0.55	0.167
ethanol	665	387	0.53	0.1379
(b) alizarine cyanine green				
solvents	V_{oc} [mV]	J_{sc} [$\mu\text{A}/\text{cm}^2$]	Fill factor	η [%]
water	581	326	0.52	0.098
acetone	650	364	0.61	0.135
DMSO	672	338	0.56	0.178
ethanol	681	474	0.53	0.132
(c) evans blue				
Solvent	V_{oc} [mV]	J_{sc} [$\mu\text{A}/\text{cm}^2$]	Fill factor	η [%]
water	561	350	0.52	0.103
DMSO	616	427	0.56	0.148
ethanol	483	243	0.57	0.068

Fig. 5. XRD spectra of the anatase TiO_2 powder.

The typical J-V curves for DSSCs using biebrich scarlet and alizarine cyanine green dye in water, acetone, DMSO and ethanol are shown in Fig. 6a and Fig. 6b. J-V curves for the cells sensitized with evans blue dye in water, ethanol and DMSO are shown in Fig. 6c. The J-V curve shows maximum power point (PP), which corresponds to the highest value obtained by the product of voltage and current. These maximum voltage and current are represented as V_{mp} and I_{mp} , respectively.

Corresponding fill factor (FF) of the device is calculated by equation 1:

$$FF = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}} \quad (1)$$

where V_{mp} is voltage at power point, I_{mp} is current at power point, V_{oc} is open circuit voltage (highest voltage when current is zero), I_{sc} is short circuit current (highest current when voltage is zero).

The cell performance was assessed for all the cells in different solvents. The comparative performance and photoelectrochemical parameters are summarized in Table 1. Conversion efficiency (η) of the device was determined by the equation 2:

$$\eta = \frac{V_{oc}I_{sc}FF}{P_{in}} \quad (2)$$

where η is conversion efficiency of the cell, V_{oc} is open circuit voltage (highest voltage when current is zero), I_{sc} is short circuit current (highest current when voltage is zero), FF is fill factor, P_{in} is power input (in this case, it is $100 \text{ mW}/\text{cm}^2$).

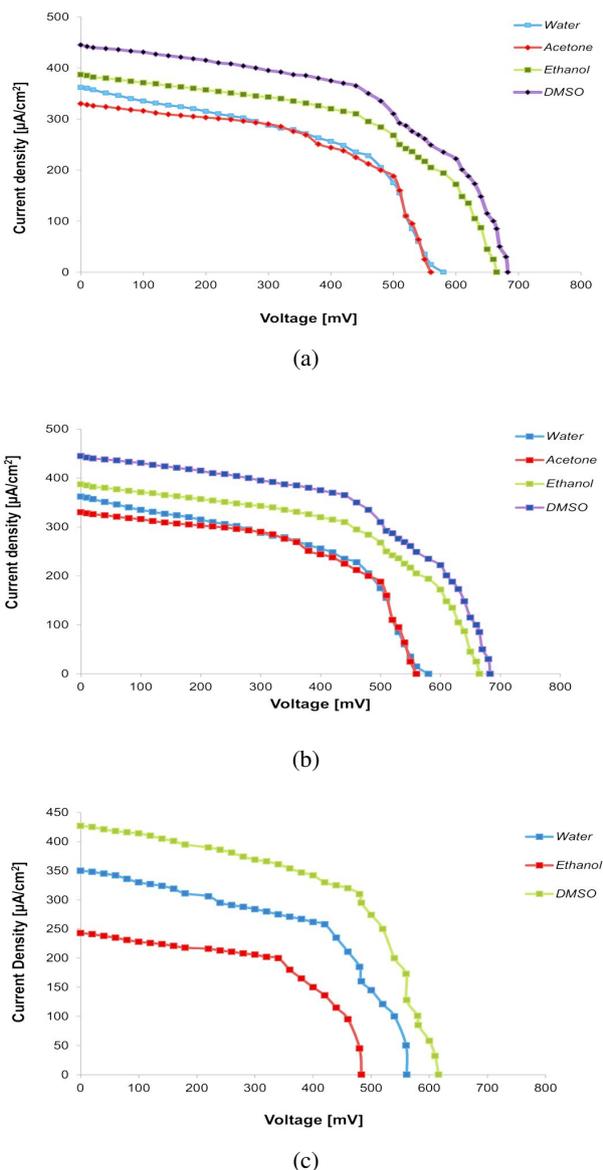


Fig. 6. J-V curves for the DSSCs sensitized with (a) biebrieh scarlet, (b) alizarine cyanine green, and (c) evans blue dye in different solvents.

The various analyses performed during the experiment showed that the new metal free organic dyes used in the research have good absorption properties and are appropriate for DSSC. These dyes are reasonably low cost and easily available. Their molecular structure reveals presence of anchoring groups for better bonding on the TiO_2 layer. Thus, the results obtained depend upon the capability of the dye to adsorb on a semiconducting layer.

The results of the Table 1a, Table 1b and Table 1c show that the values of conversion efficiencies are affected by the solvent used for the dyes. Though the values of applied voltage were good, still the dyes showed the low conversion efficiency. This might be due to low current generation by the dyes. Biebrieh scarlet showed the highest efficiency of 0.167 in DMSO with $V_{oc} = 683$ mV, $J_{sc} = 445$ $\mu\text{A}/\text{cm}^2$ and $FF = 0.55$. Its efficiency was the lowest in acetone. Alizarine cyanine green showed $V_{oc} = 672$ mV, $J_{sc} = 474$ $\mu\text{A}/\text{cm}^2$ and $FF = 0.56$ with the highest efficiency of 0.178 in DMSO. Evans blue also showed good efficiency in DMSO with $V_{oc} = 640$ mV, $J_{sc} = 368$ $\mu\text{A}/\text{cm}^2$, $FF = 0.56$ and $\eta = 0.148$.

4. Conclusions

The main motive of the research was to develop low cost DSSC using organic dyes. The new metal free organic dyes used in the research have good absorption properties. These dyes are reasonably low cost and easily available. The presence of anchoring groups for better bonding on the TiO_2 layer has not been the best characteristic of the dyes. Therefore, the structure modification of the dye may improve the efficiency of the cell. As far as high efficiency is concerned, these organic dyes are generally less efficient than metallic dyes. The result reveals that the efficiency is influenced by the structure of the dye and the solvent. Proper adsorption of the dye on titania layer also affects the efficiency of the cell. The present work involved all simple techniques used for DSSC fabrication and analysis and good results have been achieved for alizarine cyanine green and biebrieh scarlet in DMSO.

Acknowledgements

The Authors are thankful to the Head of the Department of Chemistry, the J.N.V. University, Jodhpur, and the DRDO, Jodhpur, for providing necessary facilities. One of the Authors (Sarita Bose) is grateful to the University Grant Commission, New Delhi, for providing the Junior Research Fellowship (F.1-17.1/2012-13/RGNF-2012-13-SC-Raj-19733/(SA-III).

References

- [1] DEB S.K., *Sol. Energ. Mat. Sol. C.*, 88 (2005), 1.
- [2] CHIBA Y., ISLAM A., WATANABE Y., KOMIYA R., KOIDE N., HAN L., *Jpn. J. Appl. Phys.*, 45 (2006), L638.
- [3] GAO F., WANG Y., ZHANG J., SHI D., WANG M., HUMPHRY-BAKER R., WANG P., ZAKEERUDDIN S.M., GRÄTZEL M., *Chem. Commun.*, 23 (2008), 2635.
- [4] KWON J., IM M.J., KIM C.U., WON S.H., KANG S.B., KANG S.H., CHOI I.T., KIM H.K., KIM I.H., PARK J.H., CHOI K.J., *Energ. Environ. Sci.*, 9 (2016), 3657.
- [5] CHEN R., YANG X., TIAN H., WANG X., HAGFELDT A., SUN L., *Chem. Mater.*, 19 (2007), 4007.
- [6] HARA K., HORIGUCHI T., KINOSHITA T., SAYAMA K., SUGIHARA H., ARAKAWA H., *Sol. Energ. Mat. Sol. C.*, 64 (2000), 115.
- [7] SAYAMA K., TSUKAGOSHI S., HARA K., OHGA Y., SHINPOU A., ABE Y., SUGA S., ARAKAWA H., *J. Phys. Chem. B*, 106 (2002), 1363.
- [8] HORIUCHI T., MIURA H., UCHIDA S., *J. Photoch. Photobio. A*, 164 (2004), 29.
- [9] KIM S., LEE J.K., KANG S.O., KO J., YUM J.H., FANTACCI S., ANGELIS F.D., CENSO D.D., NAZEERUDDIN MD.K., GRÄTZEL M., *J. Am. Chem. Soc.*, 128 (2006), 16701.
- [10] ZENG W., CAO Y., WANG Y., SHI Y., ZHANG M., BAI Y., WANG F., PAN C., WANG P., *Chem. Mater.*, 22 (2012), 1915.
- [11] ITO S., ZAKEERUDDIN S.M., HUMPHRY-BAKER R., LISKA P., CHARVET R., COMTE P., NAZEERUDDIN M.K., PÉCHY P., TAKATA M., MIURA H., UCHIDA S., GRÄTZEL M., *Adv. Mater.*, 18 (2006), 1202.
- [12] ITO S., MIURA H., UCHIDA S., TAKATA M., SUMIOKA K., LISKA P., COMTE P., PÉCHY P., GRÄTZEL M., *Chem. Commun.*, 41 (2008), 5194.
- [13] LIU B., ZHU W.H., ZHANG Q., WU W.J., XU M., NING Z.J., XIE Y.S., TIAN H., *Chem. Commun.*, 13 (2009), 1766.
- [14] KOZMA E., CONCINA I., BRAGA A., BORGESSE L., DEPERO L.E., VOMIERO A., SBERVEGLIERI G., CATELLANI M., *J. Mater. Chem.*, 21 (2011), 13785.
- [15] SAKONG C., KIM H.J., KIM S.H., NAMGOONG J.W., PARK J.H., RYU J.H., KIM B., KO M.J., KIM J.P.L., *New J. Chem.*, 36 (2012), 2025.
- [16] SRINIVAS K., KUMAR C.R., REDDY M.A., BHANUPRAKASH K., RAO V.J., GIRIBABU L., *Synthetic. Met.*, 161 (2011), 96.
- [17] DUAN T., FAN K., ZHONG C., PENG T., QIN V., CHEN X., *Rsc Adv.*, 2 (2012), 7081.
- [18] CHEN C., LIAO J.Y., CHI Z., XU B., ZHANG X., KUANG D.S., ZHANG Y., LIU S., XU J., *J. Mater. Chem.*, 22 (2012), 8994.
- [19] DING W.L., WANG D.M., GENG Z.Y., ZHAO X.L., XU W.B., *Dyes Pigments*, 98 (2013), 125.
- [20] LIU Z., DUAN K., GUO H., DENG Y., HUAN H., YI X., CHEN H., TAN S., *Dyes Pigments*, 140 (2017), 312.
- [21] ERTEN-ELA S., CAGATAY CAKIR A., *Energ. Source. Part A*, 37 (2015), 807.
- [22] MEHMOOD U., RAHMAN S.U., HARRABI K., HUSSEIN I.A., REDDY B.V.S., *Adv. Mater. Sci. Eng.*, 2014 (2014).

Received 2017-09-27

Accepted 2018-06-15