Performance improvement of dye-sensitized solar cell by introducing $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 film as an efficient blocking layer

Yiying Qin^{a,d}, Zhiqiang Hu^{a*}, Boon Han Lim^{a,b}, Bin Yang^a, Kok-Keong Chong^b, Wei Sea Chang^c, Putao Zhang^a, Haitao Zhang^a

ABSTRACT:

Luminescence mediums: samarium ion and yttrium ion, were introduced to expand the photo-response region of TiO_2 by means of the down-conversion effect to convert ultraviolet light into visible light, offering a unique method to enhance the photovoltaic performance of dye-sensitized solar cells (DSSCs). Their crystal structures, optical properties as well as photovoltaic performance were investigated systematically. The result indicates that the DSSCs doped with a total molar ratio of 4 mol% of Sm^{3+} and Y^{3+} show an overall power conversion efficiency of 4.09%, which is equivalent to improvements of 17.52% and 16.2% as compared to the no blocking layer DSSCs and pure TiO_2 blocking layer DSSCs respectively. The improvement in conversion efficiency is attributed to the dual effects including down-conversion of ultraviolet light and reduction of electron-hole recombination rate.

^a *Institute of New Energy Material, Dalian Polytechnic University, Dalian 116034, China;*

^b *Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Bandar Sungai Long, 43000 Kajang, Selangor, Malaysia*

^c *School of Engineering, Monash University Malaysia, Bandar Sunway, Selangor 47500, Malaysia*

^d *Kunshang Innovation Institute of Nanjing University*

**Author to whom correspondence should be addressed.*

E-mail: hzq@dlpu.edu.cn. Tel: +86-41186332256, Fax: +86-41186332256;

Keywords: dye-sensitized solar cell; down-conversion; $\text{Sm}^{3+}/\text{Y}^{3+}:\text{TiO}_2$; blocking layer; recombination rate; co-doped TiO_2 ; samarium; yttrium;

1. Introduction

Since the breakthrough of achieving power conversion efficiency as high as 7.9% by Regan and Gratzel in 1991, dye-sensitized solar cells (DSSCs) have attracted worldwide interest owing to the various advantages including low production cost, reasonably high efficiency, flexible substrate and adaptable to simple roll-printing technique for module production [1]. Generally, the major components of DSSCs consist of an electrolyte containing a redox mediator, a counter electrode capable of regenerating the redox mediator, and a working photoelectrode made from semiconductor film i.e., usually TiO_2 with a sensitizer adsorbed onto the surface of the semiconductor. To date, considerable strategies have been employed to develop high power conversion efficiency of DSSCs through modification and optimization on the three aforementioned components. Light-harvesting ability is one of the key factors to determine the photovoltaic performance. Optimization of light-harvesting efficiency can be performed via two approaches as follows: (1) introducing light scattering materials with larger size sub microstructure (in the diameter range of 200 nm - 400 nm) on the top layer of transparent TiO_2 film to manage incident light more efficiently through increasing optical path inside the photoanode; and (2) widening the spectral-response range of incident light fallen onto photoanode. Many sensitizers were developed to modify transparent TiO_2 films and have realized some breakthroughs in photovoltaic performance [2]. To widen the light absorption range of a solar cell, Roose et al. [3] has compiled various kinds of dopants on TiO_2 for DSSCs application done by numbers of researchers globally.

It is well known that rare-earth (RE) compounds can efficiently convert incident light from either near-infrared or ultraviolet spectral range to visible range owing to their specific 4f electron structure and unique properties. To increase light absorption range of a solar cell, RE compounds are doped in DSSCs acting as either up-conversion [4-8] or down-conversion luminescent medium [3, 9-15] to extend the spectral-response range of photo-absorber. Numerous studies have demonstrated that introducing dual dopants from RE group (i.e. Yb^{3+} , Er^{3+} , Ho^{3+} etc.) into TiO_2 electrode can further enhance the power conversion efficiency [5-6, 8, 16-19].

On the other hand, charge recombination process between photo-generated electrons and the oxidized species (such as dye cations or I_3^- in the redox electrolyte)

is a major factor to cause the loss of photocurrent, and subsequently resulting in a serious decrease in the photovoltaic performance of DSSCs [20-21]. As a result, it is vital to introduce an effective compact or blocking layer onto fluorine doped tin oxide (FTO) coated glass for effectively suppressing the electron recombination. Sun et al. [22] created an In-doped TiO_2 compact layer to block the electron recombination and achieved a performance improvement of 11.9%. Usai et al. [23] also found that yttrium-doped BiVO_4 induces the higher photocatalytic activities, a clear evidence of the lower charge carriers recombination in heterostructured yttrium-doped systems.

Recently, we have carried out detailed study on the performance of Sm-doped TiO_2 substrate by varying the dopant concentration and amount of P25 used [24-26]. In addition, a few research works on RE photoluminescence have found that Yttrium (Y) can improve the photo-catalytic activity of TiO_2 nanosheets film [27]; can sensitize other materials in co-doping conditions [28-31]; and can strengthen the luminescence of Sm with peaks at visible light region [32]. Specifically, Zhao et al. [31] carried out a detailed comparison of single doping (Eu^{3+}) and dual-doping (Eu^{3+} and Y^{3+}) of TiO_2 with same amount of total molar percentage of rare earth materials and the result has concluded that Y^{3+} can act as catalyst to Eu^{3+} in co-doping situation. Therefore, dual dopants of Sm and Y not only can further enhance the down-conversion effect, it can also play another important role in reducing recombination rate. For this purpose, $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 film as photoanode has been introduced in our study to improve the power conversion efficiency of DSSCs in both aspects including light harvesting ability and minimizing recombination rate. Fig. 1 illustrates the down-conversion mechanism of a DSSC with co-doped TiO_2 blocking layer.

2. Experiment

2.1 Materials

All reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. The reagents were analytical grade and can be used immediately without further purification.

2.2 Preparation of $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 conversion film and $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 powder

In a typical procedure applied for the synthesis of material, a mixture of samarium nitrate ($\text{Sm}(\text{NO}_3)_3$) and yttrium oxide (Y_2O_3) in a molar ratio of 1:1.5 was dissolved in 0.2 mL of nitric acid in a solution with total doping molar of 4 mol%. The role of samarium nitrate is to supply samarium ion. Other material such as samarium oxide can be used to accomplish the task too.

Then, 2 mL of deionized water, 6.0 mL of ethanol and 3.0 mL of glacial acetic acid were added subsequently to form solution A. Following that, 5 mL butyl titanate was dissolved in 12 mL ethanol for 30 min to form solution B. Then, solution A was added dropwise into solution B and mixed thoroughly with magnetic stirrer. After magnetic stirring for 6 hours, homogeneous sol was formed. The obtained sol was spin-coated on a FTO substrate. The substrate was dried at 150°C for 30 min and subsequently annealed at 500°C for 3 hours to obtain FTO substrate with $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 compact blocking layer. In addition, the residue of the sol was aged to form a gel. The gel was dried thoroughly at 80°C , followed by calcination at 500°C for 3 hours to obtain powder form of $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 . The powder was then grinded for photo-luminescence measurement purpose. For a comparison, a FTO substrate with pure TiO_2 compact blocking layer and pure TiO_2 powder were prepared by using the same methods.

2.3 Synthesis of DSSCs based on down-conversion blocking layer

Transparent TiO_2 paste was obtained by mixing 0.7 g of TiO_2 nanoparticles (P25, Germany), 2 mL of deionized water, 0.5 mL of glacial acetic acid and 0.1 mL of Triton X-100. The paste was coated on substrate with an area of 0.25 cm^2 by screen-printing technique. FTO substrates with three types of substrates were used in this study: (1) substrate without any blocking layer, (2) substrate with pure TiO_2 blocking layer and (3) substrate with $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 blocking layer, which were labelled as FTO, FTO/ TiO_2 and FTO/RE-doped TiO_2 substrates respectively. The photoanodes were cooled down to room temperature after being dried thoroughly at 80°C , followed by calcination at 500°C for 30 min.

Dye sensitization was carried out by the immersing film electrodes in N719 ethanol solution, which is in a sealed vessel at room temperature for 12 h. The electrodes were washed with ethanol to obtain the photoanode. The transparent Platinum (Pt) counter electrode, photoanode and liquid electrolyte (LiI/I₂) were assembled into a sandwich-type solar cell for characterization and measurement.

2.4 Characterization and measurements

The phase of the product was identified by X-ray powder diffraction (XRD, D/Max-3B), using Cu K α radiation ($\lambda=1.5405$ Å) to scan over a range of 2θ from 10° to 70° at room temperature. X-ray energy-dispersive spectroscopy (EDS, OXFORD INCA, X-Max50) were carried out to investigate the phase structure and compositions of the samples. Fluorescence properties of the samples were measured by fluorescence spectroscopy (LS55, Perkin-Elmer) in the spectral region between 350 and 700 nm. Transmittance characteristics of the blocking layers were measured by UV-Vis spectrophotometer (Lambda35, Perkin-Elmer). Current density-voltage characteristic of the DSSC were investigated under the illumination of AM1.5G simulated sunlight at irradiance of 100 mW/cm^2 , by using a solar simulator (SSA50) and a Keithley 2400 digital ohmmeter. The monochromatic incident photo-to-current efficiency (IPCE) of the DSSCs was characterized by spectrometer (SM-25).

3. Results and discussion

3.1 X-ray diffraction patterns

Fig. 2(a) shows the XRD patterns of 4 mol% Sm³⁺/Y³⁺ co-doped TiO₂ and pure TiO₂. Despite the two samples showing the same crystal structure, the Sm³⁺/Y³⁺ co-doped TiO₂ gives a broad diffraction peaks as compared to the undoped sample. This is due to the grain refining of the doped powders. The diffraction peaks at $2\theta = 25.3^\circ, 37.9^\circ, 48.1^\circ, 54.0^\circ, 55.2^\circ, 62.8^\circ$ and 68.9° correspond to the orientation of (101), (004), (200), (105), (211), (204) and (116), respectively, where all the peaks can be indexed to the pure anatase TiO₂ (PDF#21-1272). No other oxide hydrates

were detected. In addition, to confirm the presence of Sm^{3+} and Y^{3+} ions in TiO_2 , the co-doped sample was analysed using EDS. The EDS result shows (refer to Fig. 2(b)) several peaks corresponding to the existence of Sm, Y, Ti, Pt, C and O. The platinum (Pt) peak is caused by the operation of the spray platinum on the powder samples to prevent electrical discharging during EDS. The carbon element is attributed to the carbon conductive adhesive tape that was used to stick the sample on holder for preventing electrical discharge. The weight percentage and atomic percentage of the elements are listed in Table 1. The atomic percentage ratio of Sm^{3+} and Y^{3+} ions is 0.69: 2, which is equivalent to molar ratio of 1:1.58 for the quantity of samarium nitrate and yttrium oxide used. On the other hand, the weight percentage ratio of the two ions is 4.05:6.92, which is equivalent to molar ratio of 1:1.44. The two evaluations show that the doped ions are inline with the molar ratio of samarium nitrate and yttrium oxide used.

Table 1 The weight percentage and atomic percentage of elements of co-doped TiO_2 blocking layer as analysed under EDS

Element	Weight%	Atomic%
C K	9.05	19.34
O K	34.57	55.46
Ti K	40.82	21.87
Y L	6.92	2.00
Sm L	4.05	0.69
Pt M	4.46	0.59
Totals	100.00	

3.2 Photoluminescence (PL) properties of $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2

The fluorescence spectra of TiO_2 blocking layer with 4 mol% of Sm, Y-dopant were measured to quantify the effect of modification with RE compounds, and it is shown in Fig. 3(a). In the excitation spectra of Fig. 3(a) (left spectrum), the ultraviolet peak centred at 389 nm is contributed by the absorption of TiO_2 composite due to $^6\text{H}_{5/2} \rightarrow ^6\text{P}_{3/2}$ transition in Sm^{3+} . For the emission spectra of Fig. 3(a) (right spectrum), the luminescence peaks at 586 nm excited with UV light at 395 nm is assigned to the electronic transitions of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$. However, the PL is quite weak and only one transition can be clearly seen, which can be resulted from the very thin layer of

blocking layer. In order to further prove of the down-conversion effect, we measured the fluorescence spectra of the $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 powders prepared by sol-gel method. As shown in the excitation spectra of Fig. 3(b) (left spectrum), the excitation spectrum exhibits two peaks positioned at 395 nm and 473 nm, which corresponds to the ${}^6\text{H}_{5/2} \rightarrow {}^6\text{P}_{3/2}$ transition and ${}^6\text{H}_{5/2} \rightarrow {}^6\text{I}_{13/2}$ transition, respectively. The peak at 395 nm is assigned to the anatase host absorption, and it has confirmed that energy was transferred from TiO_2 host to Sm^{3+} ions, while the weaker peak that 473 nm can be caused by the direct excitation of Sm^{3+} [10]. On the other hand, for the emission spectra of Fig. 3(b) (right spectrum), the luminescence peaks at 568 nm and 600 nm excited with UV light at 395 nm are assigned to the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$ and ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ *f-f* electronic transitions of the Sm^{3+} in the $4f^5$ configuration, respectively. However, the transition of ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ is not so clear. The down-conversion mechanism of our device can be illustrated in the electronic transition diagram as shown in Fig. 3(c). The possible down-conversion luminescence mechanism points out that Sm^{3+} ions in the ${}^6\text{H}_{5/2}$ ground state are excited to the ${}^6\text{P}_{3/2}$ excited state by absorbing photons with wavelength 395 nm, followed by radiationless deactivation into the ${}^4\text{G}_{5/2}$, which are the initial levels of the emission ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$ or ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$. These results are in good agreement with the previous studies [9-10, 33-34], which only involved single dopant. The popular sensitizers such as N719 has relatively high absorption ability in visible region [2, 35-36]. Obviously, the luminescence at 570 nm can be reabsorbed by the dye N719 via a down-conversion of the $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 in order to optimize the sunlight harvesting ability of DSSCs.

There are two observations in the PL spectra of Fig. 3(b). The first observation is that the pure TiO_2 exhibits similar peaks at the same region. This occurrence of peaks was explained by Liqiang et al. [37] where these peaks are attributed to excitonic PL, which are mainly resulted from surface oxygen vacancies and defects of TiO_2 nanoparticles. The second observation is that a slightly peak shifts can be seen by comparing the spectra between Fig. 3(a) and Fig. 3(b). The shift of peaks is because of different methods were adopted in preparing the test samples, i.e., spin-coating the test sample on a substrate and by grinding the test sample into powder. These two methods can create slight different in the structure and particle size.

3.3 Transmittance spectra

Fig. 4 shows the UV-vis transmittance spectra of the bare FTO, FTO/TiO₂ and FTO/RE-doped TiO₂ substrates. It is clearly shown that the transmittance of substrates with RE-doped TiO₂ down-conversion blocking layer or FTO/TiO₂ are lower than that of without blocking layer (FTO) in the visible light region. However, the transmittances of FTO/TiO₂ and FTO/RE-doped TiO₂ substrates at 550 nm are both higher than 75%, which are considered sufficiently high to be employed for DSSCs [22, 38]. Comparing with the FTO/TiO₂ substrate, the FTO/RE-doped TiO₂ film has an additional advantage to absorb ultraviolet light by down-converting it to visible light, and hence the FTO/RE-doped TiO₂ DC film has shown a considerable increase of the light transmittance in the spectral range between 500 and 800 nm. The high transmittance of the RE-doped TiO₂ substrates promote high optical absorption of dye N719 to increase the short-circuit photocurrent density (J_{sc}) of DSSC.

3.4 Photovoltaic properties

To study the effect of blocking layer, the electrical characteristics of three DSSCs samples with bare FTO, FTO/TiO₂ and FTO/RE-doped TiO₂ substrate were measured under solar simulator. Fig. 5 shows the photocurrent density-voltage (J - V) curves of the three different samples of DSSCs under AM1.5G simulated sunlight with intensity of 100 mW/cm². Short circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and overall power conversion efficiency (η) of these test samples of DSSCs, are listed in Table 2. The measured photovoltaic performance (J_{sc} and η) of the DSSCs with bare FTO, FTO/TiO₂ and FTO/RE-doped TiO₂ substrates are (9.10 mA/cm², 3.48%), (9.67 mA/cm², 3.52%) and (11.12 mA/cm², 4.09%) respectively. The slight increment of both J_{sc} and η by introducing pure TiO₂ blocking layer to DSSC is justified as the retardation of unfavourable charge recombination process with redox species [22]. RE-doped TiO₂ blocking layer has the highest values for both J_{sc} and η among the three substrates in which the measured result shows an increment of 17.5% and 16.2% in power conversion efficiency as compared to that of the DSSCs with bare FTO and FTO/TiO₂ blocking layer respectively. The improvement of photovoltaic performance via inserting the RE-doped TiO₂ blocking layer can be

categorized into two major reasons: the down-conversion of UV light to visible light and the retardation of electron-hole recombination process with the electrolyte charge.

Single doping of Sm^{3+} was conducted on the photoanode by Qin et al. [24], whilst co-doping Sm^{3+} and Y^{3+} were carried out on the blocking layer in this article. Even though the performance improvements are around 16% in both articles, it does not indicate that Y^{3+} did not help in performance improvement. In fact, blocking layer is quite thin comparing to the photoanode layer. The amount of down-convertible photons would be less in blocking layer as compared to photoanode layer as discussed by Qin et al. [24]. In this case, co-doping of Y^{3+} plays a role as catalyst to dopant Sm^{3+} . With the combined effect of co-doping, it allows the DSSC to have 16.2% of improvement in power conversion efficiency although the blocking layer is very thin. This result also inline with the conclusion of Y^{3+} and Eu^{3+} co-doping to TiO_2 , drawn by Zhao et al. [31].

Table 2 Photoelectric properties of the dye sensitized solar cells based on different substrates.

Sample	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	$\eta/\%$
FTO	0.709	9.10	0.54	3.48
FTO/ TiO_2	0.717	9.67	0.51	3.52
FTO/RE-doped TiO_2	0.723	11.12	0.51	4.09

3.5 Incident photon to current efficiency (IPCE)

The incident photon to current efficiency (IPCE) is defined as the number of photon-generated electrons in the external circuit of solar cell per incident photon. Fig. 6 shows that the IPCE of DSSCs with pure TiO_2 and RE-doped TiO_2 acting as blocking layers for wavelength in the range between 300 nm and 400 nm. It has clearly shown that the DSSC with a RE-doped TiO_2 blocking layer has a higher IPCE as compared to that of the DSSC with pure TiO_2 blocking layer. Since the RE-doped involves down-conversion from ultra-violet range to visible range of sunlight, the IPCE graph has verified that there are more electrons generated in the range of 300-400 nm by the RE-doped solar cells as compared with the pure TiO_2 . The

significant improvement in IPCE has indicated that RE-doped TiO₂ blocking layer can increase percentage in sunlight conversion in low wavelength and hence enhance power conversion efficiency to 4.09% as shown in [Table 2](#).

4. Conclusions

In summary, down-conversion doping materials samarium and yttrium were introduced into TiO₂ blocking layer to optimize the performance of DSSCs. The measurement results have indicated that the photocurrent density and power conversion efficiency of the fabricated DSSC based on RE-doped TiO₂ DC blocking layer were increased by 22.19% and 17.52% as compared to that of pure P25 electrode (bare FTO). The increment in photovoltaic performance is ascribed to the down-conversion effect of RE-doped TiO₂ and retardation of the electron-hole recombination process or reduction of dark current. Hence, the strategy of introducing down-conversion rare earth compounds to DSSCs has exhibited a promising result by obtaining high power conversion efficiency.

Acknowledgements

We would like to thank the support from National High Technology Research and Development Program 863 (No. 2006AA05Z417), Construction Project of Science and Technology Platform of Dalian (2010-354), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (No. 2013-70), Shanghai Pujiang Program (No. 13PJ1403300), “Shu Guang” project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation (No. 13SG55), Innovation Program of Shanghai Municipal Education Commission (No. 13ZZ138), National Natural Science Foundation of China (NSFC) (No. 61376009), Science and Technology Commission of Shanghai Municipality (No. 14YF1410500), Shanghai Young Teacher Supporting Foundation (No. ZZEGD14011), the Opening Project of State Key Laboratory of High Performance Ceramics and Superfine Microstructure (SKL201313SIC), and State

Key Laboratory for Modification of Chemical Fibers and Polymer Materials,
Donghua University (LK1221).

References

- [1] B. O'Regan, M. Grätzel, A low cost high efficiency solar cells based on dye-sensitized colloidal TiO₂ films, *Nature* 353 (1991) 737-740.
- [2] Md. K. Nazeeruddin, E. Baranoff, M. Graetzel, Dye-sensitized solar cells: A brief overview, *Solar Energy* 85 (2011) 1172-1178
- [3] B. Roose, S. Pathak and U. Steiner, Doping of TiO₂ for sensitized solar cells. *Chem. Soc. Rev.* 44 (2015) 8326-8349.
- [4] J. Yu; Y. Yang, R. Fan, P. Wang, Y. Dong, Enhanced photovoltaic performance of dye-sensitized solar cells using a new photoelectrode material: upconversion YbF₃-Ho/TiO₂ nanoheterostructures, *Nanoscale* 8 (2016) 4173-4180.
- [5] P. Du, J. H. Lim, S. H. Kim, J. S. Yu, Facile synthesis of Gd₂O₃:Ho³⁺/Yb³⁺ nanoparticles: an efficient upconverting material for enhanced photovoltaic performance of dye-sensitized solar cells, *Opt. Mat. Exp.* 6 (2016) 1896-1904.
- [6] J. Wang, J. Lin, J. Wu, M. Huang, Z. Lan, Y. Chen, S. Tang, L. Fan, Y. Huang, Application of Yb³⁺,Er³⁺-doped yttrium oxyfluoride nanocrystals in dye-sensitized solar cells, *Electrochim. Acta* 70 (2012) 131-135.
- [7] T. Liu, X. Bai, C. Miao, Q. Dai, W. Xu, Y. Yu, Q. Chen, H. Song, Yb₂O₃/Au Upconversion Nanocomposites with Broad-Band Excitation for Solar Cells, *J. Phys. Chem. C* 118 (2014) 3258-3265.
- [8] N. Yao, J. Huang, K. Fu, X. Deng, M. Ding, M. Shao, X. Xu, Enhanced light harvesting of dye-sensitized solar cells with up/down conversion materials, *Electrochim. Acta* 154 (2015) 273-277.
- [9] L. Wei, Y. Yang, X. Xia, R. Fan, T. Su, Y. Shi, J. Yu, L. Li, Y. Jiang, Band edge movement in dye sensitized Sm-doped TiO₂ solar cells: a study by variable temperature spectroelectrochemistry. *RSC Adv.* 5 (2015) 70512-70521.
- [10] H. Hafez, M. Saif, M.S.A. Abdel-Mottaleb, Down-converting lanthanide doped TiO₂ photoelectrodes enhancement of dye-sensitized solar cells. *J. Power Source* 196 (2011) 5792-5796.
- [11] S. Chen J. Lin, J. Wu, Facile synthesis of Y₂O₃:Dy³⁺ nanorods and its application in dye-sensitized solar cells, *Appl. Surf. Sci.* 293 (2014) 202-206.

- [12] M. Zahedifar, Z. Chamanzadeh, S.M. H. Mashkani, Synthesis of $\text{LaVO}_4\text{:Dy}^{3+}$ luminescent nanostructure and optimization of its performance as down-converter in dye-sensitized solar cells, *J. Lumin.* 135 (2013) 66-73.
- [13] Q. Li, J. Lin, J. Wu, Z. Lan, J. Wang, Y. Wang, F. Peng, M. Huang, Y. Xiao, Preparation of $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ downconversion luminescent material and its application in dye-sensitized solar cells, *Chinese Sci. Bull.* 56 28-29 (2011) 3114-3118.
- [14] W.B. Dai, Y.F. Lei, P. Li, L.F. Xu, Enhancement of photovoltaic performance of TiO_2 -based dye-sensitized solar cells by doping $\text{Ca}_3\text{La}_{3(1-x)}\text{Eu}_{3x}(\text{BO}_3)_5$, *J. Mater. Chem. A* 3 (2015) 4875-4883.
- [15] P. Xiang, W. Ma, T. Xiao, L. Jiang, X. Tan, T. Shu, Ta-doped hierarchical TiO_2 spheres for dye-sensitized solar cells, *J. Alloys Compd.* 656 (2015) 45-50.
- [16] Y. Wang, Y. Zhu, X. Yang, J. Shen, X. Li, S. Qian, C. Li, Performance optimization in dye-sensitized solar cells with $\beta\text{-NaYF}_4\text{:Yb}^{3+},\text{Er}^{3+}@ \text{SiO}_2@ \text{TiO}_2$ mesoporous microspheres as multi-functional photoanodes, *Electrochim. Acta* 211 (2016) 92-100.
- [17] M. Luoshan, M. Li, X. Liu, K. Guo, L. Bai, Y. Zhu, B. Sun, X. Zhao, Performance optimization in dye-sensitized solar cells with $\beta\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$, and graphene multi-functional layer hybrid composite photoanodes, *J. Power Sources* 287 (2015) 231-236.
- [18] Q. Li, J. Lin, J. Wu, Z. Lan, Y. Wang, F. Peng, M. Huang, Enhancing photovoltaic performance of dye-sensitized solar cell by rare-earth doped oxide of $\text{Lu}_2\text{O}_3\text{:}(\text{Tm}^{3+}, \text{Yb}^{3+})$, *Electrochim. Acta* 56 (2011) 4980-4984.
- [19] A.R. Tanyi, A.I. Rafieh, P. Ekaneyaka, A.L. Tan, D.J. Young, Z. Zheng, C. Vijila, G.S. Subramanian, R.L.N. Chandrakanthi, Enhanced efficiency of dye-sensitized solar cells based on Mg and La co-doped TiO_2 photoanodes, *Electrochim. Acta* 178 (2015) 240-248.
- [20] C. Zhang, S. Chen, H. Tian, Y. Huang, Z. Huo, S. Dai, F. Kong, Y. Sui, Experimental investigation of back electron transfer and band edge shift in dyed TiO_2 electrodes, *J. Phys. Chem. C* 115 (2011) 8653-8657.
- [21] H. Yu, S. Zhang, H. Zhao, G. Will, P. Liu, An efficient and low-cost TiO_2 compact layer for performance improvement of dye-sensitized solar cells, *Electrochim. Acta* 54 (2009) 1319-1324.
- [22] X. Sun, Q. Zhang, Y. Liu, N. Huang, P. Sun, T. Peng, T. Peng, X.Z. Zhao, Photovoltaic performance improvement of dye-sensitized solar cells through introducing In-doped TiO_2 film at conducting glass and mesoporous TiO_2 interface as an efficient compact layer, *Electrochim. Acta* 129 (2014) 276-282.

- [23] S. Usai, S. Obregón, A.I. Becerro, G. Colón, Monoclinic-tetragonal heterostructured BiVO₄ by Yttrium doping with improved photocatalytic activity, *J. Phys. Chem. C* 117 (2013) 24479–24484.
- [24] Y. Qin, Z. Hu, B. H. Lim, W. S. Chang, K.K. Chong, P. Zhang, H. Zhang, Sol-hydrothermal synthesis of TiO₂:Sm³⁺ nanoparticles and their enhanced photovoltaic properties, *J Alloys Compd.* 686 (2016) 803-809.
- [25] Y.Y. Qin, Z.Q. Hu, P.T. Zhang, H.S. Hao, M.Z. Nie, G.S. Liu, Synthesis and properties of Sm³⁺-doped TiO₂ down-conversion photoanode for dye-sensitized solar cells. *Chin. J. Lumin.* 36 (2015) 868-874.
- [26] Y.C. Cao, Research on the optical properties of Sm³⁺, Eu³⁺ doped nano TiO₂ prepared by sol-gel method. Master degree thesis, 2013, University Technology of Kunming.
- [27] Q. Zhang, Y. Fu, Y. Wu, Y.-N. Zhang, T. Zuo, Low-cost Y-doped TiO₂ nanosheets film with highly reactive {001} facets from CRT waste and enhanced photocatalytic removal of Cr(VI) and methyl orange, *ACS Sustainable Chem. and Eng.* 4 (2016) 1794-1803.
- [28] Y. Zhao, Y. Zhao, F. Bai, Synthesis, characterization and fluorescence properties of rare earth, *Spectrosc. Spect. Anal.* 29 (2009) 1929-1932.
- [29] X. Zhan, J. Yu, Q. Huang, Investigation on enhanced photoluminescence of Er³⁺/Y³⁺/Yb³⁺ co-doped alumina powders, *J. Fuzhou Uni.* 40 (2012) 531-534.
- [30] X. An, Y. Zhao, J. Bao, Y. Li, L. Wang, J. Ye, Synthesis and fluorescence properties of rare earth (La³⁺ Gd³⁺ Y³⁺ and Tb³⁺) complexes with crown ethers and p- phthalic acid, *Chinese Rare Earths* 27 (2006) 5-9.
- [31] S.Q. Zhao, M. Guo, M. Zhang, X. Wang, S. Chang, Synthesis and photocatalytic properties of TiO₂ nanopowders codoped with Eu³⁺ and Y³⁺ ions, *J. Uni. Sci. and Tech. Beijing*, 32 3 (2010) 355-359.
- [32] H. Wang, M. Xue, Y. Wang, P. Chen, Synthesis of rare earth tribasic complexes with Sm and characterization of fluorescence properties, *Chem. Ind. Times* 23 (2009) 42-43.
- [33] D.J. Park, T. Sekino, S. Tsukuda, A. Hayashi, T. Kusunose and S. Tanaka, Photoluminescence of samarium-doped TiO₂ nanotubes. *J. Solid State Chem.* 184 (2011) 2695-2700.
- [34] L. Hu, H. Song, G. Pan, B. Yan, R. Qin, Q. Dai, L. Fan, S. Li and X. Bai, Photoluminescence properties of samarium-doped TiO₂ semiconductor nanocrystalline powders. *J. Lumin.* 127 (2007) 371-376.
- [35] M. Grätzel, Photoelectrochemical cells, *Nature* 414 (2001) 338-344.
- [36] N. Ahmad-Ludin, N. Abdul-Karim, M.A. Mat-Teridi, M.A. Ibrahim, S. Sepeai, K. Sopian, M.Y. Sulaiman, Nilofar Asim, Absorption spectrum of N719 and SQ1 dye on TiO₂ surface of

dye-sensitized solar cell in Latest Trends in Renewable Energy and Environmental Informatics, Proceedings of the 7th International Conference on Renewable, Kuala Lumpur, Malaysia April 2-4, 2013 Energy Sources (RES '13), Editors: A. Zaharim and K. Sopian, WSEAS Press, 255 – 258.

- [37] J. Liqiang, Q. Yichun, W. Baiqi, L. Shudan, J. Baojiang, Y. Libin, F. Wei, F. Honggang, S. Jiazhong, Review of photoluminescence performance of nano-sized semiconductor materials and its relationship with photocatalytic activity, Sol. Energ. Mat. Sol. C., 90 (2006) 1773-1787.
- [38] S. Lee, J.H. Noh, H.S. Han, D.K. Yim, D.H. Kim, J.K. Lee, J.Y. Kim, H.S. Jung, K.S. Hong, Nb-doped TiO₂: a new compact layer material for TiO₂ dye-sensitized solar cells, J. Phys. Chem. B 113 (2009) 6878-6882.

Figure captions

Fig. 1: Schematic illustration of the DSSCs with an improved light harvesting ability by introducing down-conversion blocking layer of $\text{TiO}_2: \text{Sm}^{3+}/\text{Y}^{3+}$.

Fig. 2: (a) XRD patterns of pure and $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 products; (b) EDS spectrum of $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 product.

Fig. 3: (a) Fluorescence spectral range of $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 product with different total number of moles, (b) spectral range of $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 blocking layer, (c) schematic illustration for the DC process of $\text{Sm}^{3+}/\text{Y}^{3+}$ co-doped TiO_2 product.

Fig. 4: Transmittance spectral range of DSSCs with different blocking layers.

Fig. 5: J - V curves of DSSCs based on FTO, FTO/ TiO_2 and FTO/RE-doped TiO_2 substrates.

Fig. 6: Incident photon to current efficiency (IPCE) of DSSCs with pure TiO_2 and RE-doped TiO_2 blocking layer in ultraviolet region.

Table captions

Table 1: The weight percentage and atomic percentage of elements of co-doped TiO₂ blocking layer as analysed under EDS.

Table 2 Photoelectric properties of the dye-sensitized solar cells based on different substrates.

Tables 1

Element	Weight%	Atomic%
C K	9.05	19.34
O K	34.57	55.46
Ti K	40.82	21.87
Y L	6.92	2.00
Sm L	4.05	0.69
Pt M	4.46	0.59
Totals	100.00	

Tables 2

Sample	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	$\eta/\%$
FTO	0.709	9.10	0.54	3.48
FTO/TiO ₂	0.717	9.67	0.51	3.52
FTO/RE-doped TiO ₂	0.723	11.12	0.51	4.09

Figures 1

Figure 2(a)

Figure 2(b)

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 4

Figure 5

Figure 6