Article ID: 1000-324X(2011)07-0774-05 **DOI:** 10.3724/SP.J.1077.2011.11015

Tandem Dye-sensitized Solar Cell Based on Metal Mesh

HUANG Yi-Min, LIU Zhi-Yong, WANG Xiao-Qi, LU Yu-Ming, CAI Chuan-Bing

(Physics Department, Shanghai University, Shanghai 200444, China)

Abstract: A newly structured tandem dye-sensitized solar cell (tandem DSC) based on stainless mesh was introduced, in which the electrode constituted a first TiO_2 film on TCO and a second TiO_2 film on stainless mesh. Negative interaction between different dyes in this structure is less than that by normal method of cocktail-dyes dipping. The application of stainless mesh here reduces the loss of incident light, solves the problem of electronic connection between two different TiO_2 films, as well as improves electron transport and collection. This tandem cell achieved a power conversion efficiency of 1.96% with short circuit current density of 8.4mA/cm^2. Compared with normal mono-layer DSC with similar cell thickness, efficiency was improved about 62% by this tandem structure. Electrochemical impedance spectroscope (EIS) was used to analyze the electron transport in tandem DSC, and an equivalent circuit for tandem DSC was also proposed here. Meanwhile, the increased cell thickness and electron recombination on the surface of the stainless mesh have obvious influence on the photovoltaic performance.

Key words: tandem; dye-sensitized solar cell; metal mesh

With the increasing concern on the issue of energy and global environment, especially on the low-carbon economy, dye-sensitized solar cell with a present highest efficiency up to 12%[1-3], as the third generation of solar cell, is drawing attentions from the whole world.

During the past decade, there have been various kinds of investigations to achieve high energy conversion efficiency. Among the wide-ranging new concepts and methods, tandem could be taken into consideration as a practicable mean to improve J_{sc}, thereby increasing the efficiency η, in the spirit of boarding the total range of spectral response by the application of two different but complementary dyes. However, accompany with its prosperity, tandem DSC is confronted with some challenges. Firstly, maintaining a maximum transparency which would ensure higher light absorption rate requires as few pieces of electrodes as possible. The common two-pieces structure of tandem DSC[4] posed a strict requirement on the transparency of TCO, which would increased the cost of DSC. Secondly, common method of simply dipping TiO_2-coated substrate in one dye solution then another (DSC-cocktail) often bring a loss to J_{sc}, due to negative interaction between different dyes[5]. Thirdly, there are few reports on convenient and separate staining of respective dyes on a two-TiO_2-layers in one-piece structure. The problem left here is how to handle the bad connection between the two separate TiO_2 layers, which would impact the electrons transfer in TiO_2 layers, thus reduce the collection rate of excited electrons. Though the compressing method[6] could be a potential way to solve connective problem, it is still not practical in tandem DSC. Meanwhile, Fan *et al*[7] used conductive mesh to fabricate DSC. However, there are few reports on tandem DSCs based on metal mesh. Only Kenshiro Uzaki *et al*[8] reported a tandem DSC consisting of floating electrode. However, their tandem DSC was still a series and two-pieces-like structure, thus facing the above mentioned first challenge of light harvesting.

In this paper, a new tandem construction based on metal mesh was put forward. We compared the performance of tandem cell with single cells, and further studied the factors that may mainly impact the performance of tandem DSC.

1 Experimental

A porous TiO_2 film onto a fluorine-doped tin oxide (FTO) glass substrate was prepared using reported method[9]. FTO glass was purchased from Dalian Hepta-Chroma SolarTech Co., Ltd.. TiO_2 paste was supplied by Institute of Plasma Physics, Chinese Academy of Sciences.

Received date: 2011-01-04; **Modified date:** 2011-02-25; **Published online:** 2011-03-30
Foundation item: National Natural Science Foundation of China (50702033, 10774098); Project of Science and Technology Commission of Shanghai Municipality (0752nm017, 08521101502)
Biography: HUANG Yi-Min(1986–), female, candidate of master. E-mail: adowntour@gmail.com
Corresponding author: LIU Zhi-Yong, lecturer. E-mail: zyliu@shu.edu.cn

Stainless mesh was purchased from Anping Anxin Wire Mesh Co., Ltd., with line size of about 30 μm, thickness of 86 μm, and porosity less than 2%. The thickness of the TiO_2 film on FTO glass substrate was about 8 μm. The areas of TiO_2 film on FTO and on stainless mesh were both 0.5 cm×0.5 cm. The two parts of TiO_2 films were totally overlapped when in tandem structure. A platinum-coated FTO glass was used as the counter electrode. A dye solution [N719] was prepared in 1:1 acetonitrile and tert-butyl alcohol solvents. A dye solution (0.2mmol/L) of Ruthenium 620-1H3TBA[N749] was prepared in 1:1 acetonitrile and tert-butyl alcohol solvents. The electrode was immersed in the dye solution for 12h to adsorb the dye onto the TiO_2 surface. 0.1 mol/L LiI, 0.08 mol/L I_2, 0.5 mol/L 4-tert-butyl pyridine, and 0.6 mol/L 2-dimethyl-3-propylimidazolium iodide in acetonitrile constitute the electrolyte used here. The current-voltage characteristics were measured using the previously reported method[9] with a solar simulator (AM1.5, 100mW/cm^2, SAN-EI XES-151S). The electrochemical impedance spectra were measured with an impedance analyzer. EIS spectra were recorded over a frequency range of 10^{-2}–10^5Hz. The applied bias voltages were set at the open-circuit voltages (V_{oc}) of the DSCs respectively.

2 Results and discussion

2.1 Structure of tandem cell and working principle

Figure 1(a) demonstrated the new construction of tandem DSC. A conductive and flexible mesh was introduced into DSC's working electrode. The tandem cell's anode constituted a normal first TiO_2 layer (stained with dye N719)on TCO, and a second TiO_2 layer(stained with dye N749)on stainless mesh. The first TiO_2 layer on TCO was closer to the source of illumination. The area of TiO_2 layer on stainless mesh was totally overlapped with the first TiO_2 layer on TCO, and another end of stainless mesh was connected with TCO. A platinum-coated FTO glass was used as the counter electrode here. Figure 1(b) showed the flow of electron transport in the tandem cell. The excited electrons on the first TiO_2 layer were collected by TCO; while the excited electrons on the second TiO_2 layer probably were collected by their attached stainless mesh and transferred directly through the mesh to external circuit for the higher conductivity of stainless mesh than TiO_2 layer. The advantages of this construction lie in that: without part of light loss caused by semi-electrode, the incident light can be given a better play. The stainless mesh played a vital role here as a frame to support the second TiO_2 layer, which conveniently separated staining of two respective dyes on two separate TiO_2 layers, as well as functioned as a better electron collector for the second TiO_2 layer. It also resolved the above mentioned problems of connection between the two TiO_2 layers, successfully collecting the excited electrons on both the first and second TiO_2 layer. The stainless mesh chosen here is due to its advantages of low cost, low thickness, good tolerance to high sintered temperatures, allowing the electrolyte filled in the entire cell thus few problems for I^-/I_3^- redox couple transportation in this device, as well as the capability to realize flexible DSCs based on it.

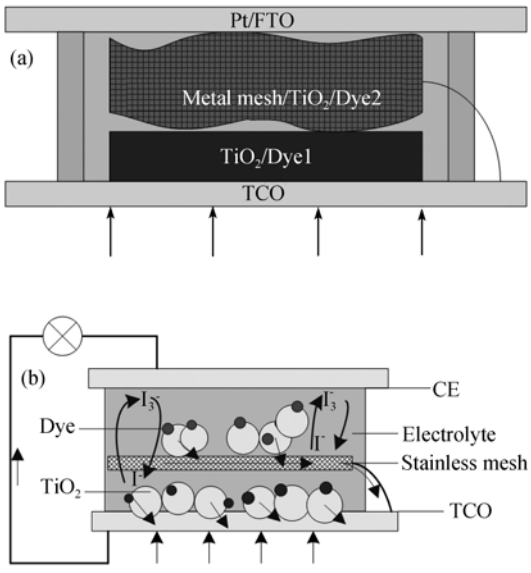

Fig. 1 Schematics (a) and working principle (b) of tandem cell

2.2 Photovoltaic performance of tandem cell

Two single cells (Cell Sin1, Cell Sin2) were prepared as reference cells for the Cell Tan. The electrode of Cell Sin1 was 8μm-thick TiO_2 film on FTO, and that for Cell Sin2 was TiO_2 film on stainless mesh, while the electrode of Cell Tan was 8μm-thick TiO_2 film on FTO and a second TiO_2 film on stainless mesh. The counter electrode and electrolyte used in these cells were identical. Table 1 and Figure 2 concluded the details of *I-V* performances and structure of those cells. V_{oc} of Cell Tan was lower than that of Cell Sin1, while much higher than V_{oc} of Cell Sin2. Due to the parallel structure, the V_{oc} of this tandem DSC is limited by the V_{oc} value of Cell Sin2. Therefore, it was important to improve the V_{oc} of Cell Sin2, though 0.396 V was comparable to the result of Fan *et al*[7]. The J_{sc} of Cell

Table 1 *I-V* performances of Cell Tan, Sin1 and Sin2

Cell	J_{sc}/(mA·cm^{-2})	V_{oc}/V	*FF*	η
Sin1	8.388	0.725	0.539	3.28%
Sin1’	5.457	0.706	0.313	1.21%
Sin2	3.090	0.396	0.329	0.40%
Tan	8.425	0.544	0.429	1.96%

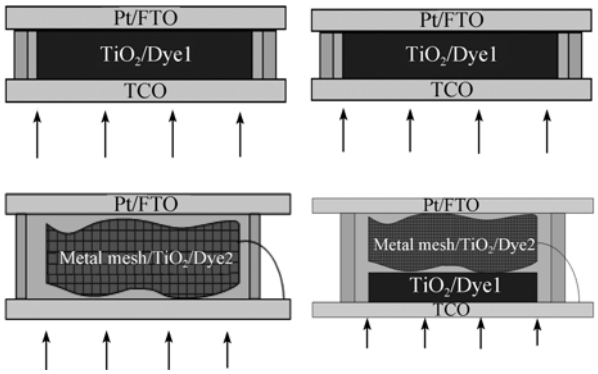

Fig. 2 Structure of different cells
(a) Sin1, 25μm spacer; (b) Sin1', 120μm spacer; (c) Sin2; (d) Tan

Tan was a little higher than that of Cell Sin1, but was lower than the summation of J_{sc} of Cell Sin1 and Cell Sin2. This behavior maybe due to the low complementary degree between dye N719 and N749, or more dark current caused by the increased thickness of the tandem structure. Because charge carriers for the excited electrons on first TiO_2 layer have to go through holes of mesh to reach the counter electrode, as shown in Fig. 1(b). On the matter of *FF*, even with a lower sheet resistance (R_h), due to stainless mesh application, the increased Nernstian diffusion resistance within electrolyte (R_3) may result in the increased total internal resistance of Cell Tan, thus a low *FF*. The efficiency of Cell Tan was yet not higher compared with Sin1, which may be caused by the thickness of the tandem structure and the low efficiency achieved by the second layer based on stainless mesh. Considering that the increased thickness of cell due to tandem construction would bring higher electrolyte diffusion resistance (R_3), and at the same time may bring more recombination, here Cell Sin1' (which had similar thickness with Cell Tan and same structure as Cell Sin1) was applied to compare with Cell Tan. Both J_{sc} and efficiency of Cell Tan were higher than that of Cell Sin1', which verified the advantage of this tandem structure. Compared with normal mono-layer DSC (Sin1') with similar cell thickness, efficiency was improved about 62% by this tandem structure.

Figure 3(a) compares the photovoltaic performances of Cell Tan, Cell Sin1 and Cell Sin2. Figure 3(b) illustrates the electrochemical impedance spectroscopy (EIS) of these cells. From Bode phase plots which suggesting the electron lifetime[10], listing from left to right, were Cell Tan, Cell Sin2, Cell Sin1, respectively. The relation between electron lifetime and mid-frequency peak in EIS was: $\tau_n=1/2\pi f_{mid}$[11]. Both Cell Tan and Cell Sin2 showed longer electron lifetime than that of Cell Sin1. And R_h corresponds to the sheet resistance of DSC, Cell Sin2 (13 Ω) and Cell Tan (16 Ω), both containing stainless mesh, performed smaller R_h than Cell Sin1 (33 Ω) as shown in the

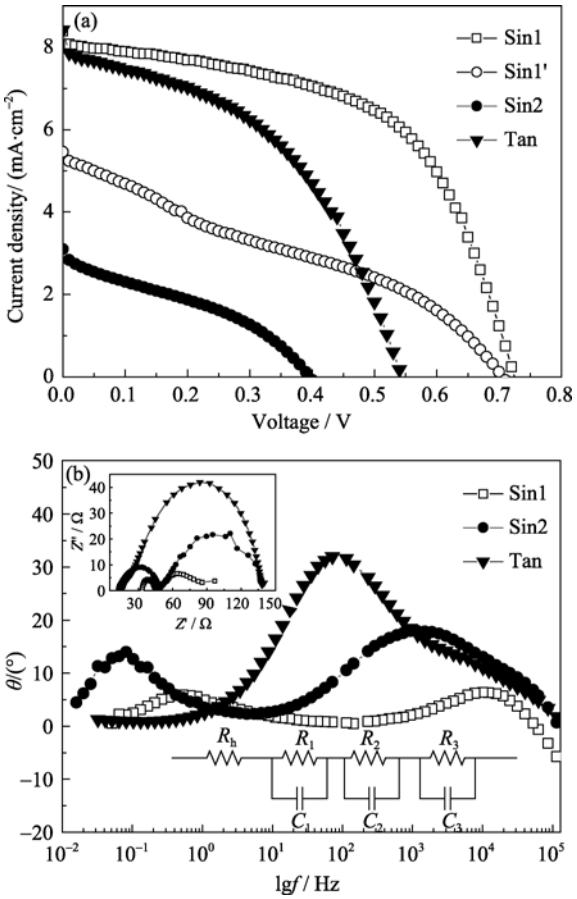

Fig. 3 (a) *I-V* performances of Cell Tan, Sin1 and Sin2; (b) EIS and equivalent circuit for Cell Tan, Sin1 and Sin2 in dark

inset of Fig. 3(b), which was consisitent with the smaller resistance caused by stainless mesh, indicating a better conductive property of stainless mesh applied in DSC.

Compared with the TiO_2 film on FTO glass substrate, the TiO_2 film on stainless mesh bearded more cracks, as shown in Fig.4, which may result in more negative recombination between the excited electrons and electrolyte. It has been reported that the different thermal expansion coefficients[8] of stainless mesh and the TiO_2 film were actually responsible for the cracks. When the samples were heated up, the thermal stress inside the TiO_2 film on

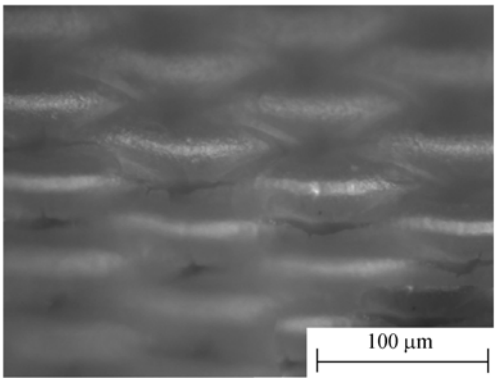

Fig. 4 Metallographic image of TiO_2 films on stainless mesh

stainless mesh increased. And if the thermal stress was not reduced well and was concentrated in some position of the film, it would suddenly release at the stress limitation and broke the film. Metallographic microscope with mini heating platform allowed us to observe the surface of TiO_2 film and the formation of cracks during the whole sintering processes. Experiments results showed that a scheme of a 30 min stop at 70℃ with a later slower heating up at the speed of 1℃/min, compared with the normal sintering process, can reduce the size of cracks and weaken recombination.

The low efficiency of tandem cell maybe caused partly by recombination, therefore we compared performances of Cell S1 (based on stainless mesh without surface treatment) and Cell S2 (based on Al-deposited stainless mesh). Figure 5(a), (b) (c) show SEM of surface of stainless mesh and Al-deposited stainless mesh. Cell S1 had higher efficiency than Cell S2, as shown in Fig. 5(d), which can be explained by the work function of Al(4.28 eV) and steel(4.5 eV). It could be easier for electrons on Al-treated stainless mesh transiting to the energy level of I^-/I_3^- in electrolyte, thus more recombination and less J_{sc} than Cell S1. More efforts are necessary to weaken recombination reaction, such as a dense TiO_2 isolation layer deposited on the stainless mesh.

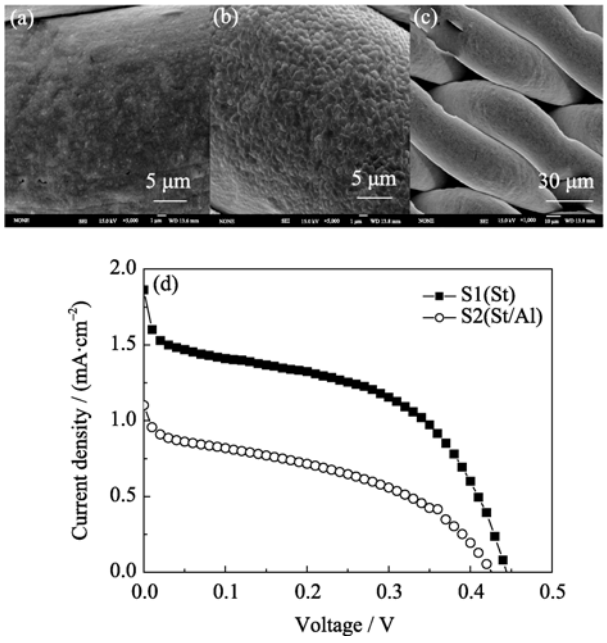

Fig. 5 (a) SEM image of the surface of stainless mesh; (b), (c) SEM images of Al-deposited stainless mesh; (d) *I-V* performances of Cell S1 and S2

3 Conclusions

The new structure of tandem dye-sensitized solar cell put forward in this paper, supplied a potential solution to some challenges of tandem DSC. The efficiency achieved by this tandem construction is 1.96%, with a relative low *FF* and J_{sc}, which can be respectively explained by the increased thickness of electrolyte and recombination. More efforts are necessary to study effective surface treatment for stainless mesh, in order to reduce recombination. In conclusion, this new tandem construction, with its own advantages, could not only offer some sort of enlightenment to tandem DSC design, but also can be developed for fabricating the flexible dye-sensitized solar cells.

References:

[1] O'Regan B, Grätzel M. A low-cost, high- efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature*, 1991, **353:** 737–740.

[2] Grätzel M. Solar energy conversion by dye-sensitized photovoltaic cells. *Inorg. Chem.*, 2005, **44(20):** 6841–6851.

[3] Ogura R Y, Nakane S, Morooka M, *et al*, High-performance dye-sensitized solar cell with a multiple dye system. *Appl. Phys. Lett.,* 2009, **94(7):** 073308–1–3.

[4] Dürr M, Bamedi A, Yasuda A, *et al*. Tandem dye- sensitized solar cell for improved power conversion efficiencies. *Appl. Phys. Lett.*, 2004, **84(17):** 3397–3399.

[5] Inakazu Fumi, Yusuke Noma, Yuhei Ogomi, *et al*. Dye-sensitized solar cells consisting of dye-bilayer structure stained with two dyes for harvesting light of wide rang of wavelength. *Appl. Phys. Lett.*, 2008, **93(9):** 093304–1–3.

[6] Lindström Henrik, Holmberg Anna, Magnusson Eva, *et al*. A new method to make dye-sensitized nanocrystalline solar cells at room temperature. *Journal of Photochemistry and Photobiology A: Chemistry*, 2001, **145(1/2):** 107–112.

[7] Fan Xing, Wang Fuzhi, Chu Zengze, *et al*. Conductive mesh based flexible dye-sensitized solar cells. *Appl. Phys. Lett.*, 2007, **90(7):** 073501–1–3.

[8] Uzaki Kenshiro, Pandey Shyam S, Hayase Shuzi, *et al*. Tandem dye-sensitized solar cells consisting of floating electrode in one cell. *Journal of Photochemistry and Photobiology A*, 2010, **216(2/3):** 104–109.

[9] Wang X Q, Cai C B, Wang Y F, *et al*. Transistorlike behavior in photoconductor based on dye-sensitized solar cell. *Appl. Phys. Lett.*, 2009, **95(1):** 011112–1–3.

[10] Wang Qing, Moser Jacques-E, Grätzel Michael, *et al*. Electrochemical impedance spectroscopic analysis of dye-sensitized solar cells. *J. Phys. Chem. B*, 2005, **109(31):** 14945–14953.

[11] Kern R, Sastrawan R, Ferber J, *et al*. Modeling and interpretation of electrical impedance spectra of dye solar cells operated under open-circuit conditions. *Electrochimica Acta*, 2002, **47(26):** 4213–4225.

基于金属网的叠层染料敏化太阳能电池

黄毅敏, 刘志勇, 王晓祺, 鲁玉明, 蔡传兵

(上海大学 物理系, 上海 200444)

摘 要: 本文提出了一种新型染料敏化太阳能电池的叠层结构设计, 其中光阳极由导电玻璃上的第一层 TiO_2 纳米薄膜和不锈钢网上的第二层 TiO_2 纳米薄膜组成, 不同染料间的负反应相比混染共敏方式少. 此结构中引入的金属网, 减少了导电玻璃的使用片数, 从而减少入射光的损失; 同时也解决了两层不同 TiO_2 薄膜间的电连接性问题, 并提高电子传输和收集效率. 此叠层电池的光电转换效率达 1.96%, 短路电流为 8.4mA/cm^2, 相比相同电池厚度的单层电池, 效率提高约 62%. 通过阻抗谱分析了叠层电池内部的电子传输, 给出叠层电池的等效电路图. 此外, 还发现电池厚度的增加及电子在不锈钢网表面的复合对光电性能有显著影响.

关 键 词: 叠层; 染料敏化太阳能电池; 金属网

中图分类号: TM914 **文献标识码:** A