



Alternating assembly structure of the same dye and modification material in quasi-solid state dye-sensitized solar cell

Beibei Ma, Rui Gao, Liduo Wang*, Fen Luo, Chun Zhan, Jiaoli Li, Yong Qiu*

Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

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ABSTRACT

Only one sort of dye and a dye-modification material is used to form an alternating assembly structure in dye-sensitized solar cell. The alternating assembly can increase the adsorption of dye sensitizer, prohibit the aggregation of the dye, and retard the recombination reaction. These effects are investigated by ultraviolet–visible spectrum, Fourier transform infrared spectrum, transient photovoltages, current density–voltage characteristics and dark current measurements. The photon–electron conversion efficiency of the cell with alternating assembly structure rise by 16%, from 3.86% to 4.49% under AM 1.5 irradiation. And the stability of the cell is also improved.

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1. Introduction

Since the dye-sensitized solar cell (DSC) was first reported by Grätzel in 1991 [1], investigations have focused on both the efficiency [2,3] and stability [4–7] of the cells for their future practical service. As one of the pioneer of the Ru polypyridine complex sensitizer, cis-(SCN)₂ bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium dye (N3-dye) is always considered as a mature sensitizer, which had been developed adequately, and a record conversion efficiency of 11% was achieved in cells using N3-dye in 2004 [8]. However, little work has focused on the adsorption of the sensitizer on TiO₂ films. There is a general agreement that sensitizer can be adsorbed on the surface of TiO₂ films as more as possible after several hours soaking, therefore, the TiO₂ film is often soaked in a 3×10^{-4} M solution of the N3-dye in dry ethanol over 12 h only once since such protocol was first reported [9]. And it seems that the N3-dye has been adequately utilized, since the incident photon to current conversion efficiency (IPCE) of N3-dye has reached a plateau of approximately 80% at around 530 nm [10]. In some reports, it took less than 10 min to anchor the dye onto nanocrystalline TiO₂ electrodes at high temperature, but the work was still with the purpose of saturated adsorption of N3-dye by once soaking [11]. Nevertheless, more N3-dye molecules adsorbed on the metal oxide films still can further enhance the photon utilization efficiency in this field, therefore,

more N3-dye molecules adsorbed on the films is significant for DSC.

On the other hand, the increasing of N3-dye molecules adsorbed on the films is not entirely the same as the increasing of the adsorption of N3-dye. In fact, it is well known that, only the N3-dye molecules adsorbed on the TiO₂ films in monolayer can work as sensitizer [12], and dye coverage on the TiO₂ surface has not achieved a closely packed monolayer, even at saturation [13,14]. The time dipping ZnO films in the N3-dye solution was much shorter than that for TiO₂ films, as ZnO may react with N3-dye, which can destroy the films [15]. Though the TiO₂ films have better stability than ZnO films in N3-dye solution, there may be also some problems with the TiO₂ electrodes with over-saturation adsorption of N3-dye. Bernard Wenger et al. reported that the slow component of the electron injection from the electronically excited dye molecule into the conduction band of TiO₂ semiconductor in DSC arises from the aggregated state of the dye, which may cause the reductive quenching of N3 derivatives [16]. But little attention has been paid to investigate the correlation between these phenomena and the performance of the corresponding solar cell.

To enhance the spectrum response over a wide wavelength region, in recent years many researchers have devoted themselves to exploring methods for multi-layer sensitized TiO₂ electrode with different dyes since 1997 [17]. To compare with the tandem structure [18–20], multi-layer sensitization has more advantages on wide wavelength photosensitization, because some photon may lose in the interlayer between the top cell and the bottom cell, and what's more, the technology of multi-layer sensitization is simple and convenient. However, though at least two sorts of dye sensitiz-

* Corresponding authors. Tel.: +86 10 62788802; fax: +86 10 62795137.

E-mail addresses: chldwang@mail.tsinghua.edu.cn (L. Wang), qiuy@mail.tsinghua.edu.cn (Y. Qiu).

ers were used in multi-layer dye sensitization and the light capture efficiency of the cells has been greatly ameliorated [21–23], the increase in photon–electron conversion efficiency was not remarkable compared with single dye sensitizing in the last decade [24]. And more important is that the mechanisms of multi-layer dye sensitized solar cell are still ambiguous. By far, no research is reported on sensitizing repeatedly with one dye.

Al_2O_3 has been considered as a modification material of TiO_2 photoanode because the former has a large band gap, which can be used to form insulating barrier at the TiO_2 /dye interface and also as the physical separation of injected electrons from the oxidized dye/redox couple in the electrolyte [25,26]. Because this effect and the alkaline of Al_2O_3 , Clifford et al. [27] employed the deposition of a secondary Al_2O_3 layer to absorb a secondary dye for multi-layer dye sensitization. The previous method to sensitize the nanocrystalline TiO_2 films with two or three different dyes is to adsorb different dyes onto the TiO_2 films layer by layer by dipping the films in different solution sequentially [22,28]. Because this method suffers from the problems on competitive adsorption of different dye sensitizer, the secondary metal oxide layer is considered as a good idea for multi-layer sensitization. Although much work has been done to study Al_2O_3 as a modification material of the TiO_2 /dye interface, little attention has been paid to the dye/electrolyte or TiO_2 /electrolyte interface. And the excellent performance of Al_2O_3 in multi-layer dye sensitized solar cell is also just ascribed to the physical separation both on the TiO_2 /dye interface and the interface of different dyes. Further study of the carrier layer in multi-layer dye sensitized solar cell is needed. With this purpose, it is an appropriate strategy to study an alternating assembly structure with only one sort of dye and Al_2O_3 .

It was observed in our recent study that Al_2O_3 can act as a dye-modification material in DSC, the Al_2O_3 postmodification can result in higher conversion efficiency and a better stability of solar cell [29]. This result suggests that Al_2O_3 used in multi-layer dye sensitized solar cell may take effect as dye-modification of Al_2O_3 .

In this work, an alternating assembly structure with only one sort of dye (N3-dye) and Al_2O_3 as dye-modification material is used in multi-layer dye-sensitized solar cell. This alternating assembly structure can increase the adsorption of dye sensitizer, while prohibiting the aggregation of the dye at the same time. The Al_2O_3 postmodification in the alternating assembly structure can also retard the recombination reaction of the electrons on the TiO_2 surface. An increasing of conversion efficiency is achieved by using this alternating assembly structure.

2. Experimental

Porous TiO_2 films were prepared using TiO_2 colloid dispersion, which was spread on completely cleaned fluorine-doped tin oxide (FTO) glass substrates. A thin compact TiO_2 film was deposited on the FTO glass substrates before depositing the porous layer. The freshly spread films were then thermo-treated at 450°C for 30 min.

N3-dye was purchased from Solaronix Company. Dye sensitization was carried out by soaking the nanoporous TiO_2 films in a 3×10^{-4} M solution of N3 in absolute ethanol.

After the sensitization, a quasi-solid state polymer electrolyte containing 0.0383 g P25 TiO_2 powder, 0.1 g LiI, 0.019 g I_2 ,

Table 1
Alternating assembly structure on the nanoporous TiO_2 films.

Sample number	Structure
N3-dye only	N3-dye
One circle	$\text{Al}_2\text{O}_3/(\text{N3}/\text{Al}_2\text{O}_3)_1$
Three circles	$\text{Al}_2\text{O}_3/(\text{N3}/\text{Al}_2\text{O}_3)_3$
Five circles	$\text{Al}_2\text{O}_3/(\text{N3}/\text{Al}_2\text{O}_3)_5$

0.264 g, poly(ethylene oxide) (PEO, Mw = 2,000,000) and 44 μl 4-tertbutylpyridine in 1:1 acetone–propylene carbonate was spread on the sensitized TiO_2 film by spin-coating to form a hole conducting layer, then a platinum-coated ITO glass counter-electrode was added. To prepare the platinum counter electrode, 100 μl solution of H_2PtCl_6 (7.5 mM) in 2-propanol was deposited onto the ITO glass and the electrode was then sintered at 380°C for 15 min.

Modification by Al_2O_3 was performed as follows: the sensitized nanoporous TiO_2 electrode was dipped into a solution of $\text{Al}(\text{OC}_3\text{H}_7)_3$ for 30 s, then rinsed with deionized water and hydrolyzed in air for 1 h.

The ultraviolet–visible (UV–vis) reflectance absorption spectra were measured with Hitachi U-3010 spectroscopy, and the Fourier transform infrared (FTIR) spectra with PE FTIR-2000.

The current–voltage (I – V) characteristics and dark current measurements were taken by using a Keithley 4200 semiconductor analyzer with a 0.25 cm^2 active area. There were three parallel groups of comparison for each set of I – V tests. Data from the group with median efficiency was presented in the paper. The employed light intensities were $30\text{ mW}/\text{cm}^2$ and $100\text{ mW}/\text{cm}^2$, AM 1.5. The transient photovoltages of DSC for electron recombination lifetime testing were studied by probing the cells with a weak laser pulse at 532 nm, which was generated by a frequency-doubled Nd:YAG laser (pulse duration of 15 ns). The transient photovoltage signal was tested under the open-circuit condition and recorded using a TDS220 oscilloscope (Tektronix) in the time scale of second [30].

3. Results and discussion

3.1. The alternating assembly structure used in DSC

The structure sketch of the alternating assembly structure after the nanoporous TiO_2 films and the corresponding sample number was shown in Table 1. The modification and sensitization process was repeated several times in the alternating assembly. A layer of N3-dye and a layer of Al_2O_3 modification were recorded as one circle of the alternating assembly, except in the first circle the adsorption of dye was 12 h with the purpose to consistent with the ordinary cell, while in the other circles the adsorption of dye was only 20 min. And to exert the function of Al_2O_3 better, an Al_2O_3 layer before the first alternating assembly circle was added in the cells with alternating assembly structure.

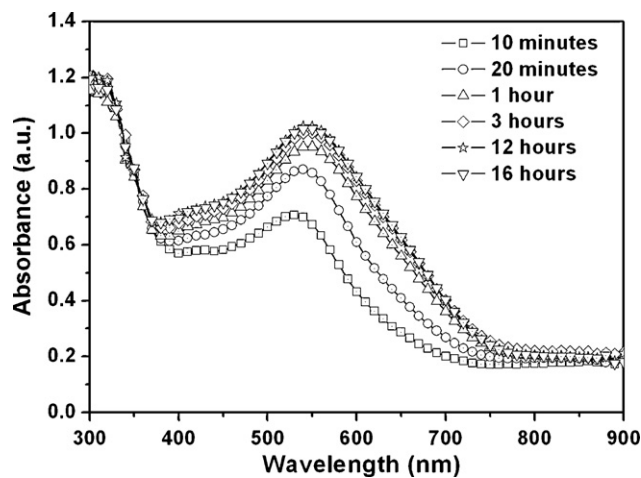


Fig. 1. UV–vis absorption spectra of N3-dye on TiO_2 films with different adsorption time.

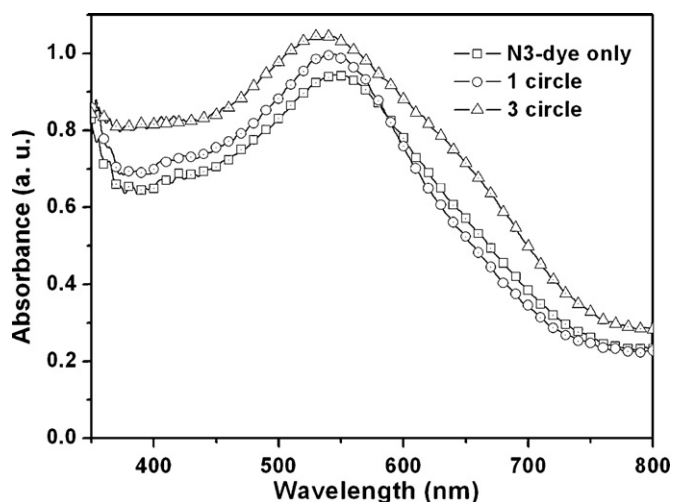


Fig. 2. UV-vis absorption spectra of TiO₂ films with different circles alternating assembly structure.

3.2. Increasing the adsorption of N3-dye

Since dye coverage on the TiO₂ surface has not achieved a close-packed monolayer, even at the condition of saturation absorption. When soaking the TiO₂ films in N3-dye solution, the adsorption of N3-dye becomes saturation after several hours. Longer adsorption cannot achieve more adsorption, as shown in the UV-vis absorption spectra of the dye-sensitized TiO₂ films with different adsorption time of dye in Fig. 1.

But as observed in UV-vis absorption spectra in Fig. 2, though the TiO₂ films have been soaked in N3-dye solution for 12 h in the first circle, the adsorption of N3-dye of three circles alternating assembly still increased significantly. This result suggests that after a new metal oxide layer is covered on the film, such as Al₂O₃, the adsorption of N3-dye can be raised by anchoring the dye molecule onto the new carrier layer.

3.3. Prohibiting the dye aggregation

As mentioned in the introduction part, the over-saturation adsorption of N3-dye would suffer from the problem of dye aggregates. The report of X-ray analysis of a single crystal of N3 showed the interaction between the sensitizer molecules, which resulted from the hydrogen bonding. The structural models of sensitizer

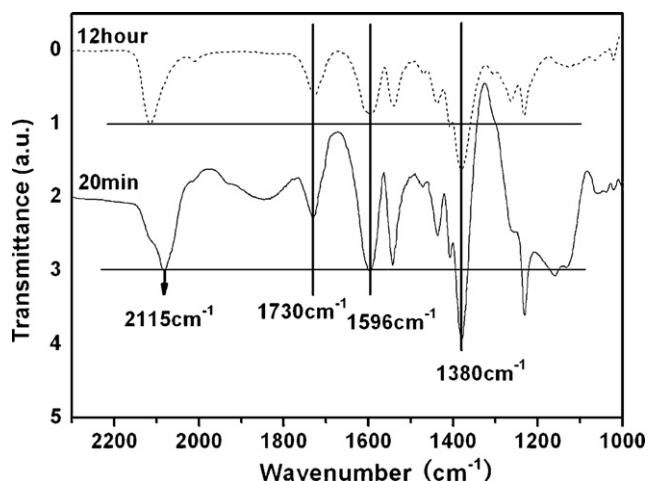


Fig. 3. FTIR spectrum of N3-dye on TiO₂ films with different adsorption time.

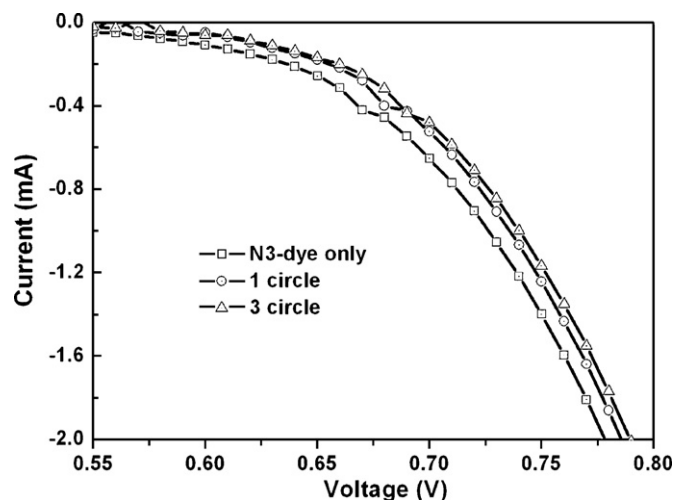


Fig. 4. Dark currents of cells with different circles alternating assembly structure.

molecules anchoring to the TiO₂ anatase surface also showed that there are two or three free carboxylic groups, which were not in contact with the surface, when the N3-dye molecular was absorbed on TiO₂ films [31]. And these free carboxylic groups may cause the H-bonding aggregates, which reduced the performance of DSC. If the interpretation is correct, the aggregates should be suppressed when the ratio of free carboxylic groups to the dye molecular decreased.

In our recent study [29], the Al₂O₃ coating in situ deprotonated N3 on TiO₂ films can also prohibit the N3-dye aggregation, because it can react with the free carboxylic groups of N3-dye.

And because the slow component of electron injection can be actually suppressed by diluting the N3-dye solution [16], the dye aggregates under an un-saturated adsorption condition, such as shortening the adsorption time in the alternating assembly, may also be able to avoid the N3-dye aggregation.

This speculation was confirmed by FTIR spectroscopy. Fig. 3 was the FTIR spectra for dye-absorbed TiO₂ films treated in dye solution for 20 min and 12 h, respectively. The spectra were normalized by the peak at 2115 cm⁻¹, which came from the group SCN⁻ and the ratio of SCN⁻ to dye molecule was considered as a constant. It is obviously observed that the peak of -COOH at 1730 cm⁻¹ was

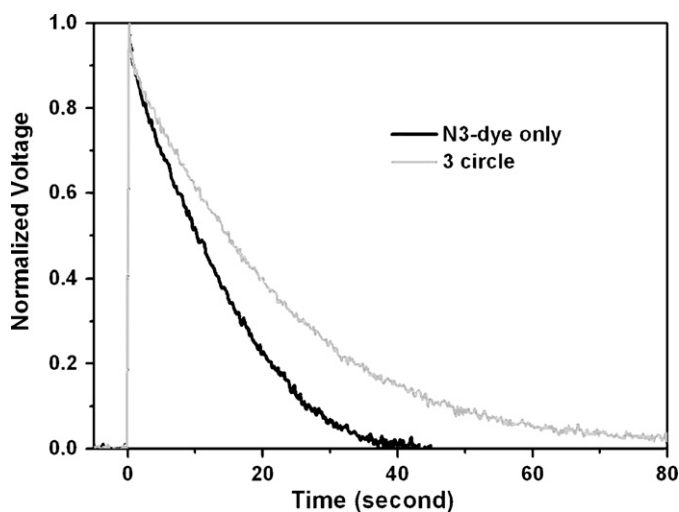


Fig. 5. Normalized transient photovoltage spectra for cells with different circles alternating assembly structure.

Table 2

Dark current value of cells with different circles alternating assembly structure at voltage of 0.8 V.

Sample	Dark current value at 0.8 V voltage (mA)
N3-dye only	2.60
One circle	2.40
Three circles	2.30

weakened, while the peak of COO^- at 1596 and 1380 cm^{-1} were enhanced sharply. The dye aggregates may cause the reduction of short-circuit current of DSC.

Therefore, to repeat short-time adsorption of N3-dye and the Al_2O_3 modification after the first adsorption of N3-dye can hopefully prohibit all the N3-dye aggregation, and then enhance the conversion efficiency of cells.

3.4. Retarding the recombination reaction

As Al_2O_3 was used to be a modification material of TiO_2 photoanode since the layer of Al_2O_3 can form insulating barrier at the TiO_2/dye interface because of its higher band gap comparing with TiO_2 , and at the same time as physical separation of injected electrons from the oxidized dye/redox couple in the electrolyte. The

Table 3

Parameters of DSC with different circles alternating assembly structure (the room temperature is 20°C).

Light intensity (mW/cm^2)	Sample	I_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
30	N3-dye only	4.76	0.67	67.3	7.15
	One circle	4.70	0.68	69.2	7.32
	Three circles	5.02	0.68	68.6	7.75
	Five circles	4.87	0.67	69.5	7.56
100	N3-dye only	9.47	0.70	58.3	3.86
	One circle	11.23	0.71	56.0	4.46
	Three circles	11.45	0.69	56.9	4.49
	Five circles	10.60	0.69	59.4	4.34

Al_2O_3 layer has no influence on the electron injection of the cells, but can retard the recombination reaction. This effect of Al_2O_3 layers in the alternating assembly structure can be proved by the dark current measurements and the transient photovoltage measurements, as shown in Figs. 4 and 5.

The dark current curves in Fig. 4 showed that the dark current onset shifted to a larger potential with the increase of the circle number. To observe more clearly, the dark current values of different circles alternating assembly structure at the same potential were presented in Table 2, the dark current values at the same potential decreased while increasing the number of alternating assembly circles from 0 to 3. This observation indicated that the Al_2O_3 retarded the charge recombination. Therefore, the photovoltage was enhanced and the dark current was reduced.

The photovoltage transient measurements carried out under the open-circuit condition denoted the recombination rate of the injected electrons and the electrolytes. Fig. 5 showed the normalized transient photovoltage curves of the dye-sensitized solar cells with and without three circles alternating assembly under the open-circuit condition with a weak laser pulse at 532 nm . As shown in Fig. 5, the decay was slower in cell with three circles alternating assembly structure, and the half-life time increased from 10.3 s to 15.0 s , which was consistent with the dark current measurements and indicates that the Al_2O_3 layer can retard the recombination between the injected electrons and the electrolytes.

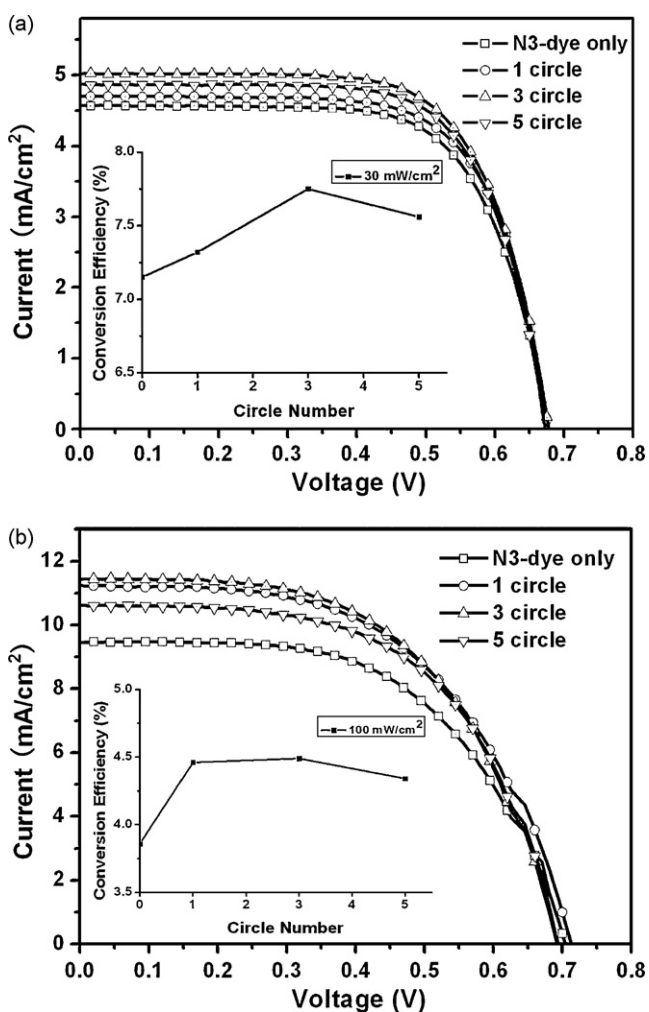


Fig. 6. Performance of the DSC with different circles alternating assembly structure. (a) Under $30\text{ mW}/\text{cm}^2$ light intensity. (b) Under $100\text{ mW}/\text{cm}^2$ light intensity (the insert figure shown the conversion efficiency comparison with different circles alternating assembly structure in DSC).

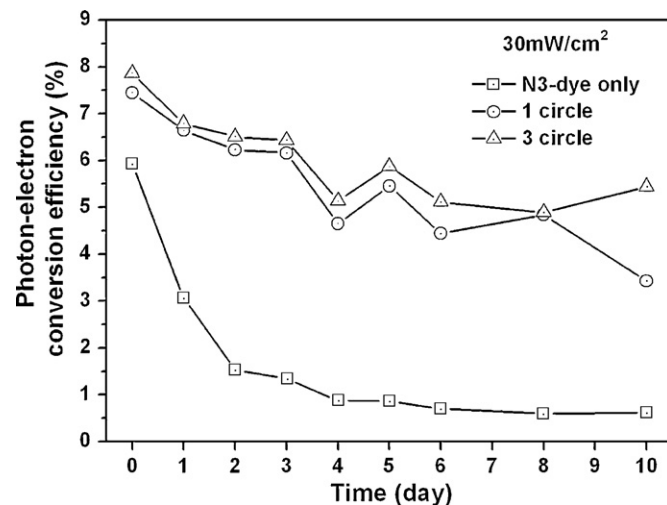


Fig. 7. Performance of the cells with different circles alternating assembly structure during 10 days testing.

3.5. Enhanced performance of DSC with alternating assembly

The performance of the solar cells with different circles alternating assembly was shown in Fig. 6 and Table 3.

It can be observed that when the DSC have three circles alternating assembly structure, the photon–electron conversion efficiency raised from 3.86% to 4.49% by 16% under 100 mW/cm² light intensity. This improvement is more significant than using the Al₂O₃ as a core-shell structured material, as shown in the supporting information. The conversion efficiency decrease for the cell with five circles alternating assembly may be caused by the excessive thickness of Al₂O₃ as an insulating barrier.

We also tested the cells over a ten-day period to check the stability without encapsulation under ambient conditions at the temperature of 20 °C and humidity of 14%. Fig. 7 gave the data of the photon–electron conversion efficiencies over the 10 days. The cells with alternating assembly structure showed better stability under 30 mW/cm² illumination.

To be brief, the DSC with alternating assembly structure performed better both at the conversion efficiencies and stability than the ordinary cells.

4. Conclusion

In summary, the alternating assembly of the same dye and a dye-modification can form a new metal oxide layer to increase the dye adsorption, while prohibiting the N3-dye aggregation at the same time by repeating the progress of un-saturated adsorption of N3-dye and the Al₂O₃ dye-modification, the Al₂O₃ layers can also depress the recombination reaction of injected electrons. The photon–electron conversion efficiency of the cell with three circles alternating assembly structure of N3-dye/Al₂O₃ raised from 3.86% to 4.49% by 16% under AM 1.5 irradiation. Further attempts to achieve multi-layer sensitization with different dyes showed that, there are at least five problems should be considered in the multi-layer dyes sensitization of DSC: (1) different regions of the visible spectrum; (2) adsorption of dyes and the dye aggregation in adsorption progress; (3) energy level matching between TiO₂ and the dye, and that between different dyes; (4) electron injection and recombination reaction in the multiple structure; (5) the stability of the multi-layer sensitized solar cell. There into an intermediate carrier material such as Al₂O₃ can be used to deal with the second, the forth and the fifth problem, which has been developed in this paper. For the first time, it is revealed that the intermediate carrier material is one of the most important factors for multi-layer sensitized solar cell. This paper has made a basic research of intermediate carrier material for the multi-layers dyes sensitization. Further studies about optimizing the multi-layer dyes sensitization are ongoing under the guidance of this work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.11.004.

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