OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 2, February 2009, p. 101 - 105

Improved performance of dye-sensitized solar cell by using a coral-like TiO_2 film

S.-Q. FAN, R.-J. CAO*, Y.-X. XI, M. GAO, M.-D. WANG, G. WANG, C.-W. KIM[a], J.-J. KIM[a], C. BAIK[a]

Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, P. R. China
[a]Department of Chemistry, Korea University, Jochiwon, Seochang 208, Chungnam 339-700, Republic of Korea

A coral-like TiO_2 film with peculiar morphology was reported in this study. It was composed of submicrometer-sized aggregates of nanocrystalline TiO_2 particles and submicrometer-sized micropores. Dye-sensitized solar cells (DSSCs) were assembled based on these TiO_2 films. Because of the superior light scattering property and the nature of high electron diffusion coefficient of the coral-like TiO_2 electrode, the solar cell presented a red-shifted IPCE spectrum, output a higher photocurrent (15.24 mA cm^{-2}) and an improved power conversion efficiency (8.57%), compared with that made from commonly-used TiO_2 film. This finding is evident to break through the traditional concept which thinks the aggregation should be avoided in TiO_2 films for DSSCs. Therefore, it is necessary to redefine the optimal TiO_2 architecture in this field.

(Received January 28, 2009; accepted February 13, 2009)

Keywords: Coral-like TiO_2 film, Light scattering, Dye-sensitized solar cell

1. Introduction

Dye-sensitized solar cells (DSSCs) are considered to be a promising alternative to conventional solid-state junction solar cells due to their low-cost, environmental friendlyness and high power conversion efficiency [1,2]. To date, the most studied and most efficient device comprises a ~10μm thick mesoporous nanocrystalline TiO_2 film covered with ruthenium-based molecular dye, a I^-/I_3^- redox electrolyte, and a platinized conducting glass counterelectrode.

The photocurrent is one of key parameters of DSSC device and is chiefly determined by the light harvesting efficiency (LHE), charge injection and charge collection [2]. Light harvesting efficiency can be enhanced by increasing dye load amount, equivalent optical path of the TiO_2 film and molar extinction coefficient of the dye. The way to increase TiO_2 film thickness larger than 10 μm is beneficial for increasing dye adsorption amount and extending optical path, while it not only influences adversely on the electrolyte diffusion in the pores and electron transport on TiO_2 film, but also increases the charge recombination at TiO_2/electrolyte interface through augmenting the recombination centers on TiO_2 surface [2]. While the improvement of the light scattering of TiO_2 film was proved to be effective in obtaining an optimal device out put performance due to an increase in optical path [3,4]. In previous works, three kinds of effective scattering centers, including large particles [5,6], scattering spherical voids in nanocrystalline TiO_2 films by sacrificing polystyrene (PS) spheres [7], and highly ordered TiO_2 nanotube arrays [8] have been introduced.

In this study, we reported a new-typed TiO_2 film which can provide scattering centers by itself because it is formed by submicrometer-sized aggregates of nanocrystalline TiO_2 particles and submicrometer-sized pores. Both aggregates and pores of this size are expected to possess light scattering in the visible region. This kind of TiO_2 films are like coral reefs comprising lots of coral polyps, and thus denoted as "***coral-like***" films herein. The microstructure, optical property of the ***coral-like*** film and the photovoltaic performance of the assembled DSSC were investigated.

2. Experimental

2.1 Fabrication of coral-like TiO_2 powder

TiO_2 powder used to fabricate ***coral-like*** TiO_2 films was synthesized as follows. 10 mmol titanium isopropoxide (Aldrich) was dissolved in 100 mL ethanol.

25 mL tetrabutylammonium hydroxide (0.8 M) aqueous solution was then added slowly to ethanol solution. The mixture was stirred for 30 min to obtain a clear solution, and transferred to and autoclave. The temperature of the autoclave was raised to 240 °C at a rate of 5 °C/min, and held at this temperature for 6 h. The white precipitate obtained was washed several times with ethanol and are named as ***coral-like*** TiO_2 powder.

2.2 Fabrication of TiO_2 films

For fabricate ***coral-like*** TiO_2 films, firstly, 12 g coral-like TiO_2 powder was dispersed in 15 g distilled water with 0.1 g TX-10 as additive and ground in a mortar to obtain a homogenous paste. Then the paste was coated on the FTO glass (TEC-8, LOF) by doctor blade technology. After dried at room temperature, they were sintered at 500 °C for 30 min. Then they were soaked in a 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min and subsequently sintered at 500 °C for 30 min again to get the final TiO_2 films.

For comparison, the commonly-used TiO_2 paste (13 nm, T/SP, solaronix) in DSC field was also used to fabricate TiO_2 films by the same doctor blade technique. Because nano-TiO_2 particles are well dispersed in the T/SP paste, the prepared TiO_2 film was semi-transparent and thus referred to as ***SP-trans*** TiO_2 film. If this T/SP TiO_2 paste was dried and sintered at 450 °C for 30 min, an aggregated TiO_2 powder retaining the original nanocrystalline size (13 nm) can be obtained. TiO_2 films fabricated from this aggregated powder according to the same preparation method for ***coral-like*** TiO_2 film was opaque and were thus named as ***SP-op*** TiO_2 films.

2.3 Preparation of solar cells

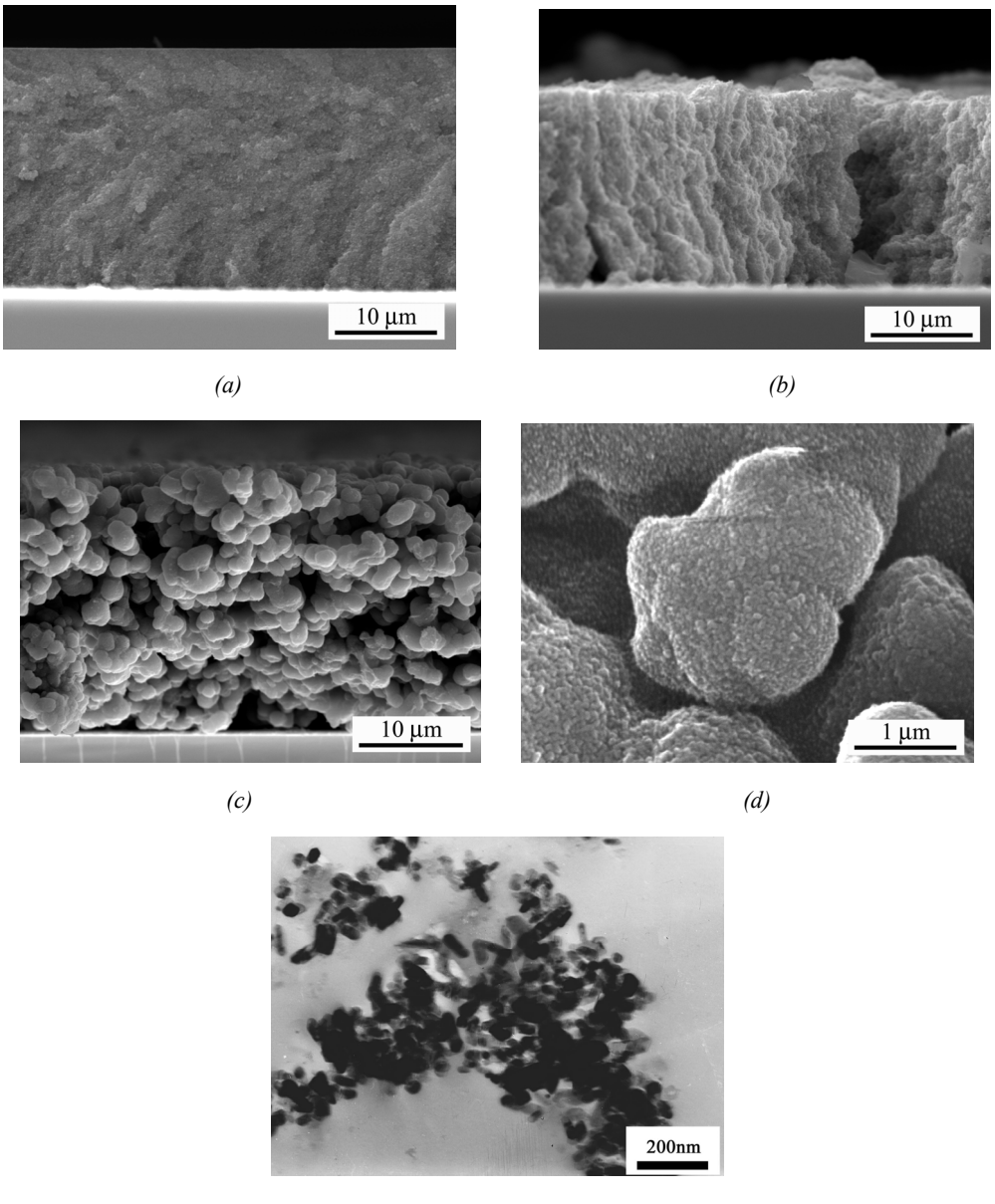
Three kinds of TiO_2 films were subsequently dipped in a 0.3 mM solution of N719 dye (solaronix, Switzerland) in ethanol overnight. Finally TiO_2 electrodes were employed to assemble a sandwich-type cell together with an electrolyte containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI, Solaronix), 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile, and a Pt counterelectrode, according to a procedure reported elsewhere [2].

2.4 Measurements

The coral-like TiO_2 powder was analyzed using transmission electron microscope (TEM, JEM200CX). The cross-sectional morphology of TiO_2 films were measured by scanning electron microscope (SEM, Quanta200). The porous microstructure of TiO_2 films was investigated through BET measurement using a nitrogen adsorption-deadsorption apparatus (Coulter SA 3100 plus, Beckman Coulter). The transmittance spectra of TiO_2 films were measured by a UV-vis spectrophotometer (UV-2450, Shimazu). The dye adsorption amount on TiO_2 films was examined by desorbing dye molecules from the film using 0.01 M NaOH ethanol solution and then measuring UV-Vis spectrum of the solution. The incident photo-current conversion efficiency (IPCE) spectra for the cells were tested on an IPCE measuring system (PV measurements). The photovoltaic performance of the cells were measured using an AM 1.5 Oriel solar simulator equipped with a 1000W xenon light source, whose intensity (100 mW/cm^2) was calibrated by using KG5 filtered Si reference solar cell. The electron diffusion coefficient was measured by the stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV) [9].

3. Results and discussion

Fig. 1 (a-d) shows the cross-sectional morphology of TiO_2 films prepared using ***coral-like*** TiO_2 powder and commonly-used T/SP powder. As can be seen, the transparent ***SP-trans*** film (Fig.1a) was compact and uniform in the micrometer-sized scale. The opaque ***SP-op*** film (Fig.1b) presented a coarse outlook with micrometer-sized pores and irregular agglomerates of nano-TiO_2. However, the morphology of the ***coral-like*** film (Fig.1c) was quite different with the films prepared by SP powders. It was composed of large particles with the diameter of less than 2 μm and micropores in the submicrometer scale. Both particles and micropores can be differentiated from one to one. The large particles were not solid, but the agglomerates of TiO_2 nanocrystals (Fig.1d). The stacking of TiO_2 nanocrystals within a large particle can produce smaller micropores with a mean pore size of 22 nm (Table 1), as determined from N_2 adsorption measurement. The TiO_2 nanocrystals were proved to be a mixture of spherical and columnar particles from the TEM image (Fig.1e), and had a mean size of 29 nm from the BET estimation (Table 1). This size was higher than that of T/SP TiO_2 nanocrystals (12-13 nm), which thus lead to a relatively lower specific surface area of the film. As a result, the dye adsorption amount of the ***coral-like*** film was nearly half of that of the transparent *SP-trans* film (Table 1).



(a) *(b)* *(c)* *(d)* *(e)*

*Fig. 1. SEM cross-sectional views of **SP-trans** (a) and **SP-op** (b) TiO_2 films, **coral-like** TiO_2 films at low magnification (c) and at high magnification (d), and TEM image of coral-like TiO_2 powder (e).*

Table 1. Porous microstructure of TiO_2 films and dye load amount.

TiO_2 films	Specific surface area ($m^2\ g^{-1}$)	d_{BET} [a] (nm)	Average pore size (nm)	Dye load amount (mol cm^{-2} μm^{-1})
Coral-like	51	29	22	5.4×10^{-9}
SP-trans	120	12	15	8.6×10^{-9}
SP-op	105	13	35	5.1×10^{-9}

[a] d_{BET} is calculated using the specific surface area $A = 6/d\rho$ with the assumption of monodisperse, spherical particles, and $\rho = 3.90$ g cm^{-3}.

Although the coral-like TiO_2 film had a lower dye load amount, it can present a dramatic light scattering performance. Fig.2 shows the transmitted spectra of 10-μm-thick TiO_2 films prepared on FTO glass using T/SP powder and ***coral-like*** powder. The transmittance of the ***SP-trans*** TiO_2 film was 10-60% in the visible region, which accorded with its semitransparent appearance. The opaque ***SP-op*** film demonstrated a very low transmittance of less than 1%, suggesting that most incident light can be scattered. As for the ***coral-like*** TiO_2 film, the transmittance was even close to zero. It clearly indicates that the ***coral-like*** film has better light scattering capacity. According to the previous reports, when 400 nm diameter TiO_2 particles [5] were added to the films or 200-400 nm pores were formed in the films [7] can produce

considerable light scattering effect. Therefore, the submicrometer-sized aggregates and micropores in the ***coral-like*** TiO_2 films were believed to be the main factors endowing the films with excellent light scattering performance (as illustrated in Fig.3).

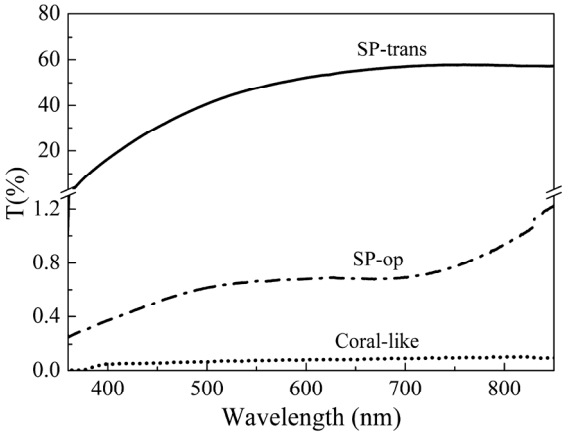


*Fig. 2. Transmittance of 10-μm-thick **SP-trans**, **SP-op** and **coral-like** TiO_2 films.*

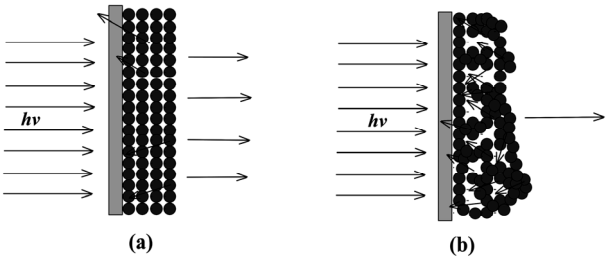


*Fig. 3. Scheme of light scattering of **SP-trans** TiO_2 film (a) and **coral-like** TiO_2 film (b).*

These ***coral-like*** TiO_2 films with superior light scattering can also yield desirable performance of the solar cells. Fig.4 shows the IPCE action spectra. Compared with the solar cell based on the transparent ***SP-trans*** TiO_2 film, that composed of the ***coral-like*** TiO_2 film exhibited an IPCE spectrum with the upper limit red-shifted ~30 nm. At the same time, the IPCE value at longer-wavelength region got raised significantly. For example, it rose from 20% to 40% at 700 nm. The IPCE red-shift phenomenon can be ascribed to the extended optical path by the light scattering, just as mentioned elsewhere [2]. As a result, the short-circuit current density (J_{SC}) and power conversion efficiency (η) of the solar cells with ***coral-like*** films were higher than those with semitransparent ***SP-trans*** films. As shown in Table 2, the J_{SC} was improved from 13.59 mA cm^{-2} to 15.24 mA cm^{-2}, and η was enhanced from 8.10% to 8.57%. Considering the dye adsorption amount of ***coral-like*** TiO_2 films, which was only half of the amount of ***SP-trans*** films, the importance of the light scattering effect on the light harvesting and the cell performance can be recognized.

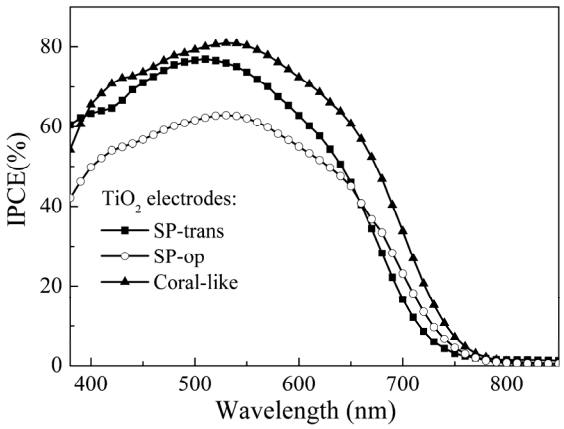


*Fig. 4. IPCE spectra of DSSCs based on the **SP-trans** (solid square), **SP-op** (circle) and **coral-like** (solid triangle) TiO_2 films.*

Table 2. Performance data of DSSCs based on 10μm-thick TiO_2 films.

TiO_2 films	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
Coral-like	15.24 ± 0.40	0.74 ± 0.01	75.8 ± 0.8	8.57 ± 0.09
SP-trans	13.59 ± 0.22	0.78 ± 0.01	76.5 ± 1.0	8.10 ± 0.05
SP-op	10.87 ± 0.51	0.72± 0.03	75.0 ± 0.5	5.97 ± 0.23

J_{SC}: short-circuit current density; V_{OC}: open-circuit voltage; FF: fill factor; η: energy conversion efficiency.

However, light scattering property was not the only factor influencing the solar cell performance. The opaque ***SP-op*** TiO_2 films had a similar light scattering performance with the ***coral-like*** TiO_2 films, but their solar cells yielded lower IPCE values (Fig.4), J_{SC} and η (Table 2). This difference can not be ascribed to the dye load amount, which was equivalent for the two kinds of films (Table 1). In order to clarify the underlying factor, we

measured other parameters of the solar cells and found a dramatic difference in the electron diffusion coefficient (D_n) of the electrodes. As displayed in Fig.5, the ***coral-like*** TiO_2 electrode and the ***SP-trans*** electrode had the same D_n, which was almost two times larger than that of opaque ***SP-op*** electrodes. For the TiO_2 films fabricated from the same nanocrystalline TiO_2 powder [10], the D_n of the film is determined by the porosity. Higher porosity leads to lower D_n due to the decrease in the connection among nano-TiO_2 particles. Therefore, the opaque ***SP-op*** film presented a comparatively lower D_n than the transparent ***SP-trans*** film due to its more porous structure. This is the main reason why to avoid aggregation as possible as we can in fabricating TiO_2 films for DSSC [2]. However, this concept was not feasible to explain the ***coral-like*** films because they had a much higher D_n even though their porosity was as high as that of opaque ***SP-op*** films. The nature of the ***coral-like*** TiO_2 powder including the particle shape, surface status, and aggregation form was expected to contribute to the high D_n of the film, although the detailed reasons need to investigate fully in the future. However, the relationship between the microstructure of ***coral-like*** TiO_2 film and the photovoltaic performance of the solar cells have proved that the optimal architecture of TiO_2 films should be re-considered against the traditional concepts for obtaining more efficient solar cells. A film whose structure can yield an excellent light scattering capacity and maintain a high electron diffusion coefficient is preferred.

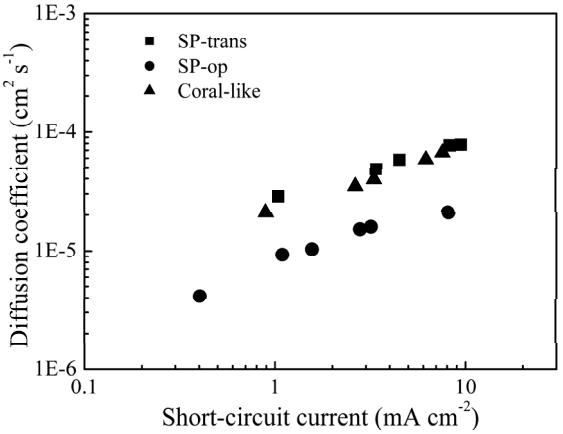


*Fig. 5. The electron diffusion coefficient of the electrodes based on the **SP-trans** (square), **SP-op** (circle) and **coral-like** (triangle) TiO_2 films..*

4. Conclusions

In summary, we presented a ***coral-like*** TiO_2 film which showed a superior light scattering property because of the existent aggregate units of nano-TiO_2 particles and micropores in the film. Compared with the ***SP-op*** TiO_2 film (made from commonly-used TiO_2 powder) which had similar light scattering property because of the aggregation, the ***coral-like*** film retained a high level for the electron diffusion coefficient due to the nature of the powder. Because of these two properties, the assembled solar cells based on ***coral-like*** TiO_2 films demonstrated an improved performance.

Acknowledgments

This work was supported by Natural Science Fund of Xi'an Jiaotong University and the BK21 Project of Korea.

References

[1] B. O'Regan, M. Grätzel, Nature **353**, 737 (1991).
[2] M. K. Nazeeruddin, I. Kay, A. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. **115**, 6382 (1993).
[3] A. Usami, Sol. Energy Mater. Sol. Cells **64**, 73 (2000).
[4] S. Hore, C. Vetter, R. Kern, H. Smit, A. Hinsch, Sol. Energy Mater. Sol. Cells **90**, 1176 (2006).
[5] A.G. Agrios, I. Cesar, P. Comte, M. K. Nazeeruddin, M. Gratzel, Chem. Mater. **18**, 5395 (2006).
[6] L. Yang, Y. Lin,, J. Jia, X. Xiao, X. Li, X. Zhou, J. Power Sources **182**, 370 (2008).
[7] S. Hore, P. Nitz, C. Vetter, C. Prahl, M. Niggemann, R. Kern, Chem. Commun. 2011 (2005).
[8] K. Zhu, N. R. Neale, A. Miedaner, A. J. Frank, Nano Lett. **7**, 69 (2007).
[9] S. Nakade, T. Kanzaki, Y. Wada, S. Yanagida, Langmuir **21**, 10803 (2005).
[10] K. D. Benkstein, N. Kopidakis, J. van de Lagemaat, A. J. Frank, J. Phys. Chem. B **107**, 7759 (2003).

*Corresponding author : fsq@mail.xjtu.edu.cn