A Composite Photoanode Based on P25/TiO₂ Nanotube Arrays/Flower-Like TiO₂ for High-Efficiency Dye-Sensitized Solar Cells

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Abstract In this work, a three-layer TiO₂ composite film consisting of flower-like TiO₂ (Flo-TiO₂) as overlayer, TiO₂ nanotube arrays as interlayer and TiO₂ nanoparticle (P25) as underlayer was fabricated as the photoelectrode of dye-sensitized solar cells (DSSCs). Due to the introduction of Flo-TiO₂, the three-layer composite film has strong light-scattering ability. Then, we have investigated and compared the photoelectric conversion properties of DSSCs based on three-layer structure (P25/TNT arrays/Flo-TiO₂) photoelectrode and double-layer film (P25/TNT arrays) photoelectrode. It is found that DSSCs based on three-layer structure exhibit a high power conversion efficiency of 6.48% compared with the DSSCs composed of double-layer film (5.11%).

KEY WORDS: Dye-sensitized solar cells (DSSCs); Flower-like TiO₂; Composite films; Photoanodes; Photoelectric conversion performances

1 Introduction

With the development of society and economy, energy problem becomes one of the major problems that human being must confront. As one kind of the third-generation solar cells, dye-sensitized solar cells (DSSCs) have attracted significant attention due to its advantages of low cost, ease of fabrication to large area and potential of high conversion efficiency in last two decades [1–4]. In general,

DSSCs consist of dye-sensitized nanocrystalline TiO₂ film photoanode, redox electrolyte and counter electrode [5, 6]. As the main part of the DSSCs, TiO₂ photoanode has a significant impact on the capture rate of light, the efficiency of electron injection and collection, and unwanted electron recombination [7]. In order to get high-efficiency DSSCs, extensive research on the photoanode has been performed to facilitate electron transport and retard electron recombination [8, 9].

The conventional TiO₂ photoelectrode made of anatase TiO₂ nanocrystals (10–50 nm) can provide large surface area for dye adsorption. However, the photoelectrode with this structure could not effectively utilize the incident light due to the existence of surface defects and grain boundaries [10, 11]. Recently, different kinds of one-dimensional (1D) TiO₂ structures have been successively synthesized and applied on the DSSCs, such as nanotubes [12], nanorods [13] and nanowires [14]. Compared with other TiO₂ structures, TiO₂ nanotube arrays (TNT arrays) have the properties of highly ordered and vertically aligned [15]. According to the report, the photoanode based on TNT arrays can greatly promote the electron transport and

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transfer, which leads to the enhancement of converting efficiency for DSSCs [16]. There are plenty of ways to synthesize the TNT arrays, such as hydrothermal [17], sol-gel [18] and electrochemical anodization [19–21]. Among these methods, electrochemical anodization has the advantages of simple equipment and easy process, and the morphology of TNT arrays can be controlled by appropriately changing the anodization voltage and time. However, the performances of DSSCs based on TNT arrays were restricted due to the limitation of specific surface areas [22].

In general, a high-efficiency photoelectrode should possess high specific surface area, rapid electron transport and outstanding light-scattering properties [23], but these factors are always incompatible with one another. To solve this problem, many researchers begin to study composite films made up of different TiO_2 nanostructures to combine their specific advantages [24, 25]. For example, Wang *et al.* [26] reported that a double-layer structure with nanoparticles as underlayer and large particles as overlayer was designed and investigated, and the conversion efficiency of 10.2% was achieved. Zhang *et al.* also reported that a TiO_2 photoelectrode based on the composite film of TiO_2 nanoparticles and TiO_2 hollow spheres was fabricated and showed high conversion efficiency [27]. It can be seen from these studies that developing scattering layer is a reliable and available way to attain high-efficiency DSSCs [28–30].

In this paper, we fabricated a three-layer TiO_2 composite film consisting of flower-like TiO_2 as overlayer, TNT arrays as interlayer and P25 nanoparticle as underlayer of the photoelectrode of DSSCs. The flower-like TiO_2 as overlayer enhanced the ability of the light scattering. The existence of TiO_2 nanotube arrays provides fast transport paths and facilitates electron transport [31]. The P25 nanoparticle as underlayer of the photoelectrode can offer good contact between TiO_2 nanotube arrays and FTO glass. Therefore, two kinds of TiO_2 composite films (P25/TNT double-layer film and P25/TNT/Flo- TiO_2 three-layer film) are designed for dye-sensitized solar cells, and their performances of many aspects were investigated.

2 Experimental

2.1 Preparation of the TiO_2 Nanotube Arrays

TiO_2 nanotube arrays (TNT arrays) films were prepared by two-step anodization of Ti foils (0.25 mm thickness, 99.7% purity) in an electrolyte solution and a Pt foil as the counter electrode via a DC power source [32]. Before anodization, the Ti foils were first polished by sandpaper and degreased by chemical polishing solution (deionized water:hydrogen

nitrate:hydrofluoric acid = 5:4:1 volume ratio). Then, the Ti foil was dipped into the ethylene glycol electrolyte solution containing 0.5 wt% NH_4F and 3 vol% deionized water. And the first anodization was carried out, while voltage 50 V was applied for 19 h. Following the anodic oxidation, the as-anodized TNT arrays/Ti substrate was rinsed with a large amount of ethanol.

2.2 Preparation of P25/TNT Composite Film

In order to separate TiO_2 nanotube arrays (TNT arrays) films from the Ti substrate, firstly, the as-anodized TNT arrays/Ti substrate was annealed in an air furnace at 450 °C for 30 min. The resulting films were then re-anodized in the same electrolyte solution at the corresponding potentials (50 V) for 1 h. After this process, the crystallized TiO_2 nanotube arrays films were separated from the Ti substrate, which could be easily transferred by tweezers. To form the composite film, we deposited P25 nanoparticle paste onto FTO glass as underlayer by using doctor-blade technique. Then, the free-standing TNT arrays films were transferred onto the P25 immediately. After being heated to 450 °C through a programmed sintering process, double-layer composite films with the TNT arrays as the overlayer film and P25 nanoparticle as the underlayer were obtained.

2.3 Preparation of Flower-Like TiO_2

The flower-like TiO_2 was synthesized by a hydrothermal treatment with a precursor solution containing 7 mL hydrochloric acid and 15 mL tetrabutyl titanate (TBT) under magnetic stirring [33]. The white precipitates of flower-like TiO_2 were collected by sealing the mixture at 180 °C for 48 h in 100 mL Teflon-lined autoclave. After being dried in an oven at 80 °C for 12 h and calcined at 500 °C for 30 min, the white samples of flower-like TiO_2 were obtained. In order to prepare flower-like TiO_2 paste, terpeneol and ethyl cellulose gel were mixed in ethanol solution using a rotary evaporator. Finally, the viscous paste of flower-like TiO_2 was obtained.

2.4 Fabrication of DSSCs Substance

For preparation the three-layer composite film, the as-prepared flower-like TiO_2 paste was deposited onto the annealed P25/TNT film by using doctor-blade technique to form the overlayer of photoelectrode. After being annealed for 30 min at 500 °C in an air furnace through a programmed sintering process, the three-layer composite films were obtained.

In order to get the DSSCs, the as-prepared two kinds of TiO_2 composite films (P25/TNT double-layer film and P25/TNT/Flo- TiO_2 three-layer film) were immersed into a

0.3 mmol/L ethanol solution of N719 at room temperature for 24 h. Then, the dye-sensitized photoanodes were separated by scotch tape spacer in three edges, and the sandwich-type DSSCs (active area 4 mm × 4 mm) were obtained by placing a Pt counter electrode on the photoanode. Finally, the electrolyte (0.5 mol/L LiI, 0.05 mol/L I₂, 0.5 mol/L 4-tert-butylpyridine and 0.3 mol/L 1,2-dimethyl-3-propylimidazolium iodide (DMPII) in dry acetonitrile) was injected into the open cell from the edge without scotch tape and the assembled cells were tested immediately.

2.5 Characterization and Measurements

The crystalline phase purity of the samples was characterized by X-ray powder diffraction (XRD, MAX-RB RU-200B, Japan). The morphologies and sizes of prepared products were measured by scanning electron microscopy (SEM, JSM-IT300, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). UV-Vis spectrophotometer (UV3600, Shimadzu, Japan) was used to characterize the diffused reflectance spectra and the surface concentration of N719 of as-prepared samples. It is important to study the photovoltaic parameters of the DSSCs, including open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF) and conversion efficiency (η). The current–voltage (I – V) characteristics were performed under AM 1.5G illumination provided by a solar light simulator (Oriol Sol3A, Newport Corporation, USA) at 100 mW cm^{−2} intensity. The active area of DSSCs was 0.16 cm² (4 mm × 4 mm). Under 100 mW cm^{−2} light illumination condition, the electrochemical impedance spectroscopy (EIS) was measured with an electrochemical workstation (IM6, Germany) with the frequency range from 0.1 Hz to 100 kHz.

3 Results and Discussion

3.1 Phase Structures and Morphology

Figure 1 shows the XRD patterns of the TiO₂ nanotube arrays (TNT arrays) and flower-like TiO₂. Evidently, after annealing process at 450 °C for 30 min, the diffraction peaks of as-prepared TNT arrays are anatase, which is consistent with the pure anatase phase of TiO₂ (JCPDS card No. 21-1272). Figure 1b shows the XRD patterns of flower-like TiO₂ after the calcination, and all the diffraction peaks were indexed to the standard rutile phase of TiO₂ (JCPDS card No. 21-1276). Above all, the XRD patterns show that the P25/TNT/Flo-TiO₂ three-layer photoelectrodes are composed of two different crystallizations of TiO₂. Research indicates that photoelectrodes consisting of different phase have both excellent photoelectric properties of anatase and

Fig. 1 XRD patterns of TiO₂ nanotube (TNT) arrays *a* and flower-like TiO₂ *b*

outstanding light reflection ability of rutile and achieve higher conversion efficiency [34–36].

Figure 2 shows typical SEM images of as-prepared TNT arrays film. It can be seen that the closely packed highly ordered nanotube arrays which open on the top but close on the bottom are obtained after two-step anodization process. The average pore diameter and wall thickness of TNT arrays are about 97.8 and 19.6 nm (Fig. 2a, b). As we know, TNT arrays film can provide vertical transport pathway to facilitate electron transport and suppress electron recombination. The SEM image of cross section of double-layer film containing TNT arrays and P25 film is shown in Fig. 2d. As the underlayer of photoelectrode, P25 nanoparticle (ca. 13 μm) can increase the contact area between the TNT arrays film and FTO glass and promote the collection of electrons.

The three-layer TiO₂ composite films were fabricated by depositing flower-like TiO₂ paste onto the annealed P25/TNT film (see Sect. 2). The whole fabrication procedure of P25/TNT double-layer film and P25/TNT/Flo-TiO₂ three-layer film is shown in Fig. 3. The flower-like TiO₂ was prepared by hydrothermal method, which can be seen from the SEM image (Fig. 4a). In order to further observe the microstructure of the samples, the TEM technique was adopted. The TEM image of the flower-like TiO₂ nanostructure which agrees with the results of SEM is shown in Fig. 4b. It is shown that flower-like TiO₂ nanostructure is made up of nanorods (Fig. 4c) around a point, and the size of flower structure is about 400 nm. Figure 4d shows the cross-sectional SEM image of P25/TNT/Flo-TiO₂ three-layer film, from which the flower-like TiO₂ overlayer (ca. 11 μm in thickness), TNT arrays interlayer (ca. 30 μm in thickness) and P25 nanoparticles underlayer (ca. 13 μm in thickness) can be clearly observed. It is worth mentioning

Fig. 2 SEM images of TiO_2 nanotube arrays in top view **a**, in bottom view **b**, in cross-sectional view **c** and cross-sectional SEM image of P25/TNT composite film **d**

Fig. 3 Schematic illustrating the fabrication process of P25/TNT double-layer film and P25/TNT/Flo- TiO_2 three-layer film

that the light-scattering capacity of DSSCs is improved due to the introduction of flower-like TiO_2 .

3.2 UV-Visible Reflectance Spectra and Dye Adsorption Measurements

The diffuse reflection spectra of two kinds of photoanodes are shown in Fig. 5. Obviously, the diffuse reflection capacity of

P25/TNT/Flo- TiO_2 three-layer film is higher than that of P25/TNT double-layer composite film ranging from 400 to 800 nm, suggesting that flower-like TiO_2 has excellent light-scattering capability. Firstly, flower-like TiO_2 nanostructure is made up of nanorods (Fig. 4) around a point, so light scattering occurs between flowers and the number of incident light is greatly increased. Secondly, the top of P25/TNT double-layer film is open owing to the unique structure of TNT arrays, inducing that some of the transmitted light is wasted directly. Moreover, rutile TiO_2 has higher refractive index than anatase TiO_2 , which is beneficial to the utilization of light [37]. As a result, the ability of light scattering and the utilization of sunlight are increased obviously [38]. In order to obtain the dye-adsorbed amount of two TiO_2 photoanodes, the dye-sensitized photoanodes were desorbed in 0.1 mol/L NaOH solution in a mixed solution (water:ethanol = 1:1, volume ratio) and then measured on UV-Vis spectrophotometer (UV3600). The value of dye adsorption is listed in Table 1 [39]. Obviously, the flower-like TiO_2 film as the overlayer possesses a large surface area for dye adsorption compared to low-dimensional TiO_2 , so the three-layer composite films offer both high light-harvesting efficiency and large dye uptake.

Fig. 4 SEM image of the surface of flower-like TiO_2 **a**, TEM image of flower-like TiO_2 **b**, the selected area TEM image of flower-like TiO_2 **c** and cross-sectional SEM image of three-layer composite film **d**

Fig. 5 Diffused reflectance spectra of DSSCs based on P25/TNT double-layer film and P25/TNT/Flo- TiO_2 three-layer composite film

3.3 Photovoltaic Performances of DSSCs

The dark current–voltage characteristics of DSSCs for two kinds of TiO_2 photoanodes are shown in Fig. 6a. As can be

seen, compared to the P25/TNT film photoelectrode, P25/TNT/Flo- TiO_2 three-layer structure photoelectrode produces a lower dark current at the same potential above 0.6 V. The dark current is used to illustrate the charge recombination, which is related to the reduction of I_3^- ions by the electrons on the conduction band. The dark current measurement indicates that after introducing flower-like TiO_2 as the scattering layer, the three-layer structure film DSSCs has a slower photoelectrons recombination rate.

The photovoltaic characteristics of two kinds TiO_2 DSSCs under illumination are shown in Fig. 6b. The corresponding photovoltaic parameters which can be obtained from the I – V curves are summarized in Table 1. As noted in Table 1, DSSCs based on P25/TNT/Flo- TiO_2 three-layer composite film attain a short-circuit current density (J_{sc}) of 16.07 mA cm^{-2} and a higher conversion efficiency (η) of 6.48%. Meanwhile, DSSCs based on P25/TNT arrays double-layer composite film only get a short-circuit current density (J_{sc}) of 13.72 mA cm^{-2} and a conversion efficiency (η) of 5.11%. Evidently, the remarkable enhancement of η for three-layer film compared to the double-layer film is mainly attributed to the improvement of J_{sc} and V_{oc} . The enhanced J_{sc} of three-layer film can be understood as a

Table 1 Comparison of the photovoltaic performances and absorbed dye amount of DSSCs made from P25/TNT/Flo-TiO₂ three-layer composite film and P25/TNT double-layer composite film

Photoanode	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	H (%)	Absorbed dye amount ($\times 10^{-8}$ mol cm ⁻²)
Three-layer	16.07	0.65	0.62	6.48	5.45
P25/TNT	13.72	0.63	0.59	5.11	4.43

Fig. 6 I - V performance of the DSSCs based on P25/TNT/Flo-TiO₂ three-layer composite film and P25/TNT double-layer film in the dark **a** and under AM 1.5 illuminations **b**

result of improved light-scattering capability from flower-like TiO₂ and fast electron transport by TNT arrays. Also, the V_{oc} of the DSSC is increased from 0.63 V for the double-layer film to 0.65 V for the three-layer film, which is mainly due to effective photocurrent generation and photoelectron collection within photoanode, and longer electron lifetime (see following EIS). As a result, after introducing flower-like TiO₂ as the scattering layer in DSSCs, the photoelectric conversion efficiency of P25/TNT/Flo-TiO₂ DSSCs increases.

Lots of researches have shown that a high-efficiency DSSCs should possess high light-harvesting efficiency, fast electron transport, long electron lifetime, low electron recombination rate and large surface area. The thicker film ensures photoelectrode to have a large enough surface to adsorb the dye molecules. However, the continued increase in thickness will slow down the transmission of electrons and impede the diffusion of electrolyte, which leads to the reduction in conversion efficiency. Therefore, it should be noted that higher efficiency might be obtained with further optimization of the conditions of DSSCs, such as film thickness, electrolyte solution and counter electrode [40].

3.4 EIS Analysis

EIS was carried out to study electron transport in the DSSCs. EIS is an excellent tool for characterizing interfacial charge-transfer processes in DSSCs. The Nyquist

plots of the DSSCs for P25/TNT double-layer composite film and P25/TNT/Flo-TiO₂ three-layer film are shown in Fig. 7a. It can be seen that the Nyquist plots exhibit two semicircles at frequency range from 0.1 Hz to 100 kHz, which represent two different charge transport processes. The equivalent circuit consists of R_s , R_{ct} and R_w , which can be obtained using Z-view software. The resistance R_s is associated with the contact situation between the FTO and TiO₂ films. The resistances R_{ct} and R_w are related to the charge-transfer resistance at redox electrolyte/Pt counter electrode interfaces and the TiO₂/electrolyte interfaces, respectively. As shown in Table 2, the R_s resistance of three-layer film is close to the double-layer composite film, which is relatively low. This means that two kinds of structures both display a good contact between TNT arrays films and FTO conducting glass. Meanwhile, the DSSCs based on P25/TNT/Flo-TiO₂ three-layer film possess slightly lower values for R_{ct} and R_w resistance, suggesting that more efficient electron transports occur at both of TiO₂/electrolyte interface and the redox electrolyte/Pt counter electrode interface. The results can be ascribed to the fact that flower-like TiO₂ as the scattering layer significantly enhances the intensity of light scattering and the utilization of light.

Figure 7b shows the Bode phase plots of EIS spectra. The electron lifetime (τ_e) can be calculated from the equation ($\tau_e = 1/2\pi f_{max}$) [41]. In this formula, f_{max} is the frequency peak in the low frequency of Bode phase plots.

Fig. 7 EIS spectra of the DSSCs based on P25/TNT/Flo-TiO₂ three-layer composite film and P25/TNT double-layer film: **a** Nyquist plots and **b** Bode phase plots

Table 2 Parameters obtained by fitting the impedance spectra of DSSCs using the equivalent circuit in Fig. 7(a)

Samples	R_s (Ω)	R_{ct} (Ω)	R_w (Ω)	τ_e (ms)
P25/TNT	26.14	33.26	42.20	45.87
Three-layer	27.05	32.33	33.39	131.58

As listed in Table 2, the three-layer film DSSCs obtain longer electron lifetime (τ_e) compared to the double-layer film, which is attributed to the existence of light diffusion in flower-like TiO₂. Therefore, the great light-scattering capability of flower-like TiO₂ can excite more electrons and improve the efficiency of light harvesting and thus leads to enhanced conversion efficiency.

In general, the research and development of DSSCs were mainly focused on the composite photoanodes which were composed of various TiO₂ structures, such as TNPs/TNTs photoanode [42] and P25/TNT/TiO₂-HB composite film [43]. The composite photoanode structure possessed the lowest charge-transfer resistances and the longest electron lifetime and achieved the higher conversion efficiency [44]. Hence, it could be concluded that facilitating the charge transport rate and increasing electron lifetime are an effective way to enhance the efficiency of DSSCs.

4 Conclusion

A three-layer composite film consisting of flower-like TiO₂ as overlayer, TNT arrays as interlayer and P25 as underlayer was successfully fabricated. After investigating and comparing the photovoltaic properties of two kinds of DSSCs, we know that the flower-like TiO₂ can adsorb dye molecules effectively and enhance light-scattering

capability of DSSCs. Therefore, the conversion efficiency (η) of DSSCs based on P25/TNT/Flo-TiO₂ three-layer composite film was enhanced and reached up to 6.48%. Thus, the fabrication of three-layer composite film opens up an alternative avenue for fabricating low-cost and high-performance DSSCs.

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References

- [1] B.O. Regan, M. Grätzel, *Nature* **353**, 737 (1991)
- [2] M. Grätzel, *Nature* **414**, 338 (2001)
- [3] F. Sauvage, J.D. Decoppet, M. Zhang, S.M. Zakeeruddin, P. Comte, M. Nazeeruddin, P. Wang, M. Grätzel, *J. Am. Chem. Soc.* **133**, 9304 (2011)
- [4] J.H. Wu, Z. Lan, J.M. Lin, M.L. Huang, S.C. Hao, T. Sato, S. Yin, *Adv. Mater.* **19**, 4006 (2007)
- [5] J. Sheng, L.H. Hu, S.Y. Xu, W.Q. Liu, L. Mo, H.J. Tian, S.Y. Dai, *J. Mater. Chem.* **21**, 5457 (2011)
- [6] G.T. Dai, L. Zhao, S.M. Wang, J.H. Hu, B.H. Dong, H.B. Lu, J. Li, *J. Alloys Compd.* **539**, 264 (2012)
- [7] J. Lagemaat, N.G. Park, A.J. Frank, *J. Phys. Chem. B* **104**, 2044 (2000)
- [8] A. Kay, M. Grätzel, *Chem. Mater.* **14**, 2930 (2002)
- [9] H. Xu, X. Tao, D.T. Wang, Y.Z. Zheng, J.F. Chen, *Electrochim. Acta* **55**, 2280 (2010)
- [10] W.Q. Wu, J.Y. Liao, H.Y. Chen, X.Y. Yu, C.Y. Su, D.B. Kuang, *J. Mater. Chem.* **22**, 18057 (2012)
- [11] X. Xin, J. Wang, W. Han, M. Ye, Z. Lin, *Nanoscale* **4**, 964 (2012)
- [12] L. Zhao, J.G. Yu, J.J. Fan, P.C. Zhai, S.M. Wang, *Electrochem. Commun.* **11**, 2052 (2009)
- [13] B. Liu, E.S. Aydil, *J. Am. Chem. Soc.* **131**, 3985 (2009)
- [14] X.J. Feng, K. Shankar, O.K. Varghese, M. Paulose, T.J. Latempa, C.A. Grimes, *Nano Lett.* **8**, 3781 (2008)

- [15] S.P. Albu, A. Ghicov, J.M. Macak, R. Hahn, P. Schmuki, *Nano Lett.* **5**, 1286 (2007)
- [16] J.H. Hu, L. Zhao, Y.P. Yang, H. Liao, S.M. Wang, X.D. Sun, J.J. Cheng, B.H. Dong, *Int. J. Photoenergy* **2**, 244 (2014)
- [17] S. Sreekantan, L.C. Wei, *J. Alloys Compd.* **490**, 436 (2010)
- [18] T. Maiyalagan, B. Viswanathan, U.V. Varadaraju, *Mater. Sci.* **29**, 705 (2006)
- [19] D. Gong, C.A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, E.C. Dickey, *J. Mater. Res.* **16**, 3331 (2001)
- [20] J.M. Macak, P. Schmuki, *Electrochim. Acta* **52**, 1258 (2006)
- [21] A.E.R. Mohamed, S. Rohani, *Energy Environ. Sci.* **4**, 1065 (2011)
- [22] M. Paulose, K. Shankar, S. Yoriya, H.E. Prakasham, O.K. Varghese, G.K. Mor, T.A. Latempa, A. Fitzgerald, C.A. Grimes, *J. Phys. Chem. B* **110**, 16179 (2006)
- [23] Q.F. Zhang, T.P. Chou, B. Russo, S.A. Jenekhe, G.Z. Cao, *Angew. Chem. Int. Edit.* **47**, 2402 (2008)
- [24] J.G. Yu, J.J. Fan, B. Cheng, *J. Power Sources* **18**, 7891 (2011)
- [25] J.G. Yu, Q.L. Li, Z. Shu, *Electrochim. Acta* **15**, 6293 (2011)
- [26] Z.S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, *Coord. Chem. Rev.* **248**, 1381 (2004)
- [27] Y.W. Zhang, J. Zhang, P.Q. Wang, G.T. Yang, Q. Sun, J. Zheng, Y.J. Zhu, *Mater. Chem. Phys.* **123**, 595 (2010)
- [28] Y. Shi, L. Zhao, S.M. Wang, J. Li, B.H. Dong, Z.X. Xu, L. Wan, *Mater. Res. Bull.* **59**, 370 (2014)
- [29] W. Shao, F. Gu, L. Gai, C. Li, *Chem. Commun.* **47**, 5046 (2011)
- [30] W.W. Sun, K. Sun, T. Peng, S.J. You, H.M. Liu, L.L. Liang, S.S. Guo, X.Z. Zhao, *J. Power Sources* **262**, 86 (2014)
- [31] P. Zhong, W.X. Que, J. Zhang, Q.Y. Jia, W.J. Wang, Y.L. Liao, X. Hu, *J. Alloys Compd.* **509**, 7808 (2011)
- [32] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese, C.A. Grimes, *Nano Lett.* **2**, 215 (2006)
- [33] S.F. Xie, X.G. Han, Q. Kuang, J. Fu, L. Zhang, Z.X. Xie, L.S. Zheng, *Chem. Commun.* **47**, 6722 (2011)
- [34] K. Asagoe, S. Ngamsinlapasathian, Y. Suzuki, S. Yoshikawa, *Cent. Eur. J. Chem.* **5**, 605 (2007)
- [35] A.M. Bakhshayesh, M.R. Mohammadi, *Ceram. Int.* **39**, 7343 (2013)
- [36] B. Tan, Y.Y. Wu, *J. Phys. Chem. C* **32**, 15932 (2006)
- [37] N.G. Park, J. Lagemaat, A.J. Frank, *J. Phys. Chem. B* **104**, 8989 (2000)
- [38] X.P. Lin, D.M. Song, X.Q. Gu, Y.L. Zhao, Y.H. Qiang, *Appl. Surf. Sci.* **263**, 816 (2012)
- [39] N.R. Neale, N. Kopidakis, J. van de Lagemaat, M. Grätzel, A.J. Frank, *J. Phys. Chem. B* **109**, 23183 (2005)
- [40] W. Xu, X. Jiang, J.M. Chen, R.Q. Tan, W.J. Song, *Acta Metall. Sin. (Engl. Lett.)* **28**, 580 (2015)
- [41] S.M. Park, J.S. Yoo, *Anal. Chem.* **21**, 455 (2003)
- [42] D. Maheswari, P. Venkatachalam, *Acta Metall. Sin. (Engl. Lett.)* **28**, 354 (2015)
- [43] J.H. Hu, J.J. Cheng, S.Q. Tong, L. Zhao, J.X. Duan, Y.P. Yang, *J. Mater. Sci. Mater. Electron.* **27**, 5362 (2016)
- [44] A.M. Bakhshayesh, M.R. Mohammadi, D.J. Fray, *Electrochim. Acta* **78**, 384 (2012)