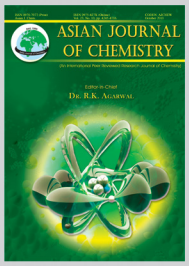
Asian Journal of Chemistry; Vol. 24, No. 1 (2012), 214-216

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Comparison of N and S Doped TiO_2 Electrode for Dye Sensitized Solar Cells

S. WANG[1,*], Z.C. YU[2], L. HAN[3], C.L. DAI[1] and J.Y. SONG[1]

[1]School of Earth Science, Northeast Petroleum University, Daqing, P.R. China
[2]School of Civil Engineering & Architecture, Northeast Petroleum University, Daqing, P.R. China
[3]College of Horticulture Science and Technology, Hebei Normal University of Science and Technology, Qin Huang Dao, P.R. China

*Corresponding author: Fax: +86 459 6504757; Tel: +86 459 6504757; E-mail: yuzi7777@163.com

(*Received*: 8 December 2010; *Accepted*: 15 September 2011) AJC-10402

Doped TiO_2 semiconductor thin films were synthesized using N and S as photovoltaic property-enhancing impurities by micro-plasma oxidation method. The influence of the doping ions on the structural and microstructure of the TiO_2 films were investigated by X-ray diffraction, scanning electron microscopy and electrical impedance spectra. The results show that the dye-sensitized solar cell efficiency fabricated with doped TiO_2 is remarkably better than that of undoped TiO_2. Also, the performance of N-doped TiO_2 electrode is better than that of S-doped TiO_2 electrode in terms of V_{oc}, short circuit current density (J_{sc}) and power conversion efficiency. These phenomena were related to the surface area, crystalline structures and charge transfer kinetics modifications induced by non-metal-ion dopants.

Key Words: Thin film, Doped, Photoelectric performance, Microstructure.

INTRODUCTION

The photoelectric performance of dye-sensitized solar cells (DSSCs) is affected greatly by TiO_2 film electrode[1]. Various prepared method of TiO_2 film have been studied, including sol-gel method, hydro-thermal synthesis and sputtering depositions[2-4]. However, most of these TiO_2 film electrodes were prepared by coating TiO_2 colloid on conductive glass and annealing at high temperature, which is not fast and simple enough to produce the necessary devices with large area[5]. A thin film technology, microplasma oxidation (MPO), can overcome the above-mentioned disadvantages commendably[6]. In this way, producing TiO_2 thin films only needs very short time and the prepared film presents good adherence to the substrates. So, in this paper, TiO_2 film is prepared by microplasma oxidation method.

In order to increase the performance of nanoporous TiO_2 electrodes, composite electrodes based on metal oxides and ions have been used in dye-sensitized solar cell, for example, SnO_2/TiO_2[7,8], TiO_2/ZrO_2[9], TiO_2/Al_2O_3[10], Zn^{2+}-, Fe^{3+}- and Pb^{2+}-doped TiO_2 electrodes[11,12]. Asahi *et al.*[13] firstly proved feasibility of nonmetal doping in TiO_2 by theory calculation. In present research, N- and S-doped TiO_2 films was prepared by microplasma oxidation using $NH_3 \cdot H_2O$ and thiourea as N- and S-doped precursors. Moreover, the photoelectric performance of the N- and S-doped TiO_2 electrodes is compared.

EXPERIMENTAL

Preparation of N- and S-doped TiO_2 film: A titanium sheet (99.9 % in purity) washed in HF-HNO_3 (1:1, v/v) aqueous solution was selected as an anode with a reaction area of 25 mm × 10 mm × 0.5 mm and a copper sheet was introduced as a cathode. TiO_2 film was prepared by using 0.5 mol L^{-1} $(NH_4)_2SO_4$ solutions as electrolyte. The N-doped TiO_2 prepared by adding 6 mL L^{-1} $NH_3 \cdot H_2O$ into above $(NH_4)_2SO_4$ solutions was denoted by N-TiO_2. The S-doped TiO_2 prepared by adding 10 g L^{-1} thiourea into above $(NH_4)_2SO_4$ solutions was denoted by S-TiO_2. The MPO process was conducted for 10 min in 2 stages. A constant current density (14 A dm^{-2}) was first performed until a designated anode-to-cathode voltage (245 V) was reached and then the voltage was maintained until the end of oxidation, with a gradual decrease in the current.

Characterization of thin TiO_2 film: The surface morphology of the films was observed on a MX2600FE scanning electron microscope (SEM) from Cam Scan of England. The X-ray diffraction (XRD) with a CuK_α source (D/max-r B from Ricoh of Japan) was applied to study the crystalline structure of the films.

Solar-cell assembly and photoelectrochemical characteristics: The TiO_2 film was immersed in 0.3 mmol L^{-1} *cis*-di(thiocyanate)-*bis*(2,2-bipyridyl-4,4-dicarboxylate) ruthenium(II) in ethanol solution at room temperature for 24 h.

The dye-coated TiO_2 film was used as working electrode and transparent conducting glass (< 20 Ω/□) was used as counter electrodes. The electrolyte was a solution of 0.5 mol L^{-1} potassium iodide and 0.05 mol L^{-1} iodine in a mixture of *ca.* 80 % acetonitrile and 20 % ethylene glycol. Electrochemical impedance spectroscopy (EIS) was measured with a Z263A impedance analyzer (Princeton Applied 125 Research, USA). The ac amplitude and the applied voltage were 10 mV and set at open-circuit voltage of the cells, respectively. For the I-V curves measurements, the dye-sensitized TiO_2 films were illuminated through the conductive glass using a 500-W high pressure Xe lamp as the simulating sunlight.

RESULTS AND DISCUSSION

Photoelectric performance of TiO_2, N-TiO_2 and S-TiO_2 electrodes: Table-1 shows the averaged data extracted from I-V curve measurements on dye-sensitized nanostructured TiO_2 electrodes. As is shown in the figure, V_{oc}, J_{sc}, fill factor and conversion efficiency of the undoped TiO_2 film is 652 mV, 149 μA/cm^2, 0.39 and 0.094 %, respectively. When the electrolyte is doped the $(NH_4)_2SO_4$ or thiourea, the photoelectric performance is improved. The V_{oc} of the N-TiO_2 and S-TiO_2 electrodes increases to 701 and 697 mV and J_{sc} increases to 165 and 156 μA/cm^2, while photoelectric conversion efficiency increases to 0.121 and 0.109 %, respectively. The highest conversion efficiency has been achieved for the cell, employing the N-TiO_2 film.

TABLE-1
PHOTOELECTRIC PARAMETERS OF TiO_2, N-TiO_2 AND S-TiO_2 ELECTRODES

Sample	V_{oc} (mV)	J_{sc} (μA/cm^2)	FF	η (%)
TiO_2	652	149	0.39	0.095
N-TiO_2	701	165	0.42	0.121
S-TiO_2	697	156	0.40	0.109

Analysis of SEM and XRD results: The surface images are shown in Fig. 1. It can be seen that the surface of microplasma oxidation films are mesoporous. The pore density and size increase when the TiO_2 film is doped in N and S ions. These changes could improve the photo-electricity properties of the films because more mesopores can absorb more OH^- to absorb the *cis*-$RuL_2(SCN)_2 \cdot 2H_2O$, which can increase the utilization ratio of visible light. So, the photoelectric performance of the dye sensitized solar cells assembled by N-TiO_2 and S-TiO_2 is improved.

Table-2 shows the effect of the N- and S-doping on the lattice parameter of the TiO_2. It can be seen (Table-2) that the cell volume increases after N and S ions doped into the TiO_2. Moreover, the cell volume of the N-TiO_2 is larger than that of the S-TiO_2. The above aberrance and expand of the crystal lattice usually produce strain energy. In order to equalize this crystal lattice stress, part of the oxygen atoms on the surface of TiO_2 is easy to escape from the crystal lattice and capture the holes. As a result, the recombination rate of e^-/h^+ is reduced. So, the photoelectric property is enhanced.

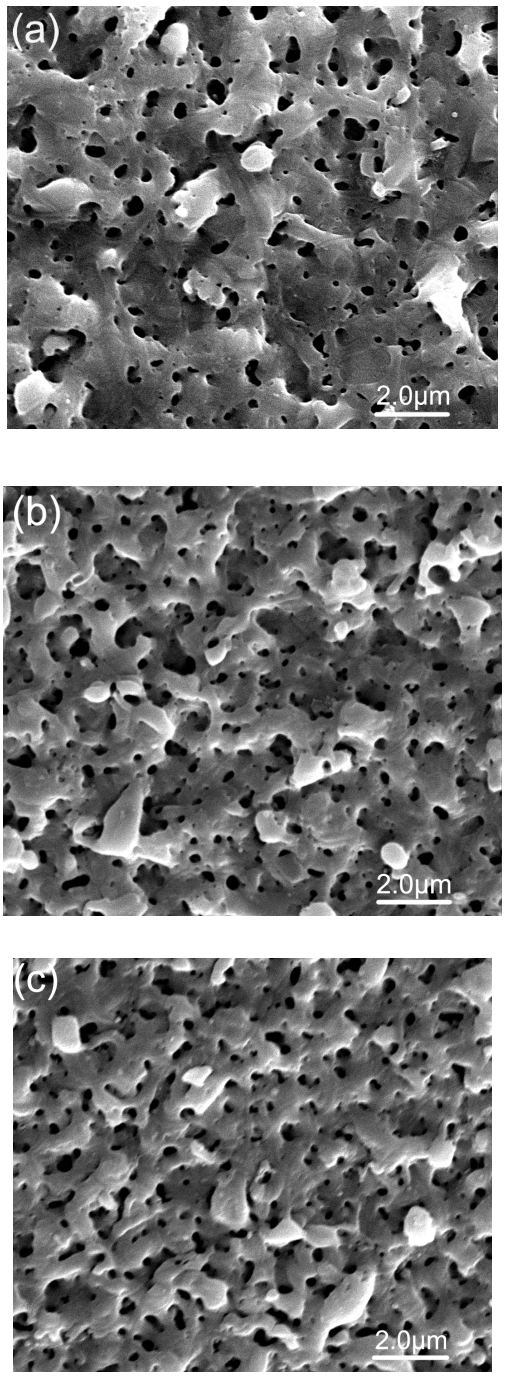


Fig. 1. Effect of dopants on morphology of thin TiO_2 film: (a) TiO_2; (b) N-TiO_2; (c) S-TiO_2

TABLE-2
LATTICE PARAMETER OF N-TiO_2 AND S-TiO_2

Sample	TiO_2	N-TiO_2	S-TiO_2
A = b (nm)	0.4600	0.4607	0.4613
c (nm)	0.2963	0.2963	0.2966
Crystal cell volume (nm^3)	0.0627	0.0629	0.0631

Analysis of EIS results: The photoelectric performance is discussed by EIS (Fig. 2). Every EIS shows only one (slightly flattened) semicircle. But, in general, the EIS spectrum of the dye-sensitized solar cell containing liquid electrolyte shows three semicircles in the measured frequency range of 0.01 Hz to 100 kHz[14]. The reason is that these arcs were so large that

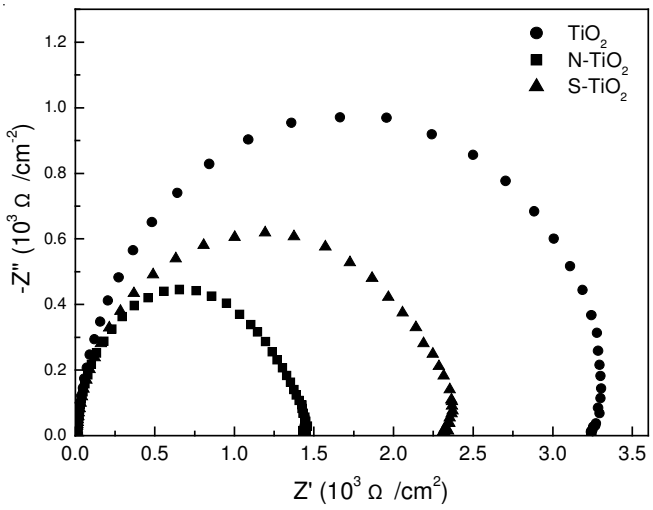


Fig. 2. Impedance spectra of cells assembled N-doped and S-doped TiO_2 electrodes

the other components were not observed. It can also be concluded that the frequency range and the size of the semicircle is associated with kinetic processes at the TiO_2 electrode of the solar cell. Thus, this means that the charge-transfer resistances at the TiO_2 electrodes mainly affect the performance for these samples. The impedance of the N-TiO_2 electrode is the smallest, which results in the superior photocurrent and photovoltage. Also, high interfacial charge-transfer resistance resulting from large semicircle is observed for the dye-sensitized solar cells containing undoped TiO_2 electrode. The above analysis can be supported well by the results of the photoelectric parameter of the TiO_2 electrodes.

Conclusion

N- and S- doping expands the crystal lattice and reduce the surface resistance of TiO_2 which leads to the performance of solar cell based on N-TiO_2 and S-TiO_2 is improved. Furthermore, the photoelectric efficiency of N-TiO_2 is higher than that of the S-TiO_2. In addition, microplasm oxidation shortens the preparation time greatly. These advantages of microplasm oxidation are of great importance to fabricate a large area dye sensitized solar cells in industry.

ACKNOWLEDGEMENTS

This work was financially supported by Educational Commission of Heilongjiang Province of China (No. 11551008).

REFERENCES

1. G.K. Mor, O.K. Varghese, M. Paulose, K. Shankar and C.A. Grimes, *Sol. Energ. Mat. Sol. C*, **90**, 2011 (2006).
2. H. Lindström, A. Holmberg, E. Magnusson, S.-E. Linquist, L. Malmqvist and A. Hagfeldt, *Nano. Lett*., **1**, 97 (2001).
3. M. Guo, P. Diao, X.D. Wang and S.M. Cai, *J. Solid State Chem*., **178**, 3210 (2005).
4. T.N. Murakami, Y. Kijitori, N. Kawashima and T. Miyasaka, *J. Photochem. Photobiol. A*, **164**, 187 (2004).
5. J.G. Doh, J.S. Hong, R. Vittal, M.G. Kang, N.G. Park and K.J. Kim, *Chem. Mater*., **16**, 493 (2004).
6. U. Beck, R. Lange and H.G. Neumann, *Biomol. Eng*., **24**, 47 (2007).
7. Z.Y. Liu, K. Pan, M. Liu, M.J. Wang, Q. Lü, J.H. Li, Y.B. Bai and T.J. Li, *Electrochim. Acta*, **50**, 2583 (2005).
8. K.M.P. Bandaranayake, M.K.I. Senevirathna, P.M.G.M.P. Weligamuwa and K. Tennakone, *Coord. Chem. Rev*., **248**, 1277 (2004).
9. A. Kitiyanan and S. Yoshikawa, *Mater. Lett*., **59**, 4038 (2005).
10. E. Palomares, J.N. Clifford, S.A. Haque, T. Lutz and J.R. Durrant, *J. Am. Chem. Soc*., **125**, 475 (2003).
11. K.H. Ko, Y.C. Lee and Y.J. Jung, *J. Colloid Interf. Sci*., **283**, 482 (2005).
12. Y.Q. Wang, H.M. Cheng, L. Zhang, Y.Z. Hao, J.M. Ma, B. Xu and W.H. Li, *J. Mol. Catal. A*, **151**, 205 (2000).
13. R. Asahi, T. Morikawa and T. Ohwaki, *Science*, **293**, 269 (2001).
14. D. Kuang, P. Walter, F. Nüesch, S. Kim, J. Ko, P. Comte, S.M. Zakeeruddin, M.K. Zazeeruddin and M. Grätzel, *Langmuir*, **23**, 10906 (2007).