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Nd, N-doped TiO_2 anode effect on performance of dye-sensitized solar cells

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Doped TiO_2 semiconductor thin films were synthesized using N and Nd as photovoltaic property-enhancing impurities by micro-plasma oxidation method. The influence of the doping ions on crystal structure and microstructure of the TiO_2 films were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM). Impedance analysis for dye-sensitized solar cells were carried out by electrochemical impedance spectroscopy. The results show that the performance of N-doped TiO_2 electrode is better than that of N-Nd co-doped TiO_2 electrode in terms of open circuit voltage (Voc), short circuit current density (Jsc), and power conversion efficiency. It seems that these phenomena were related to the surface area, crystalline structures and charge transfer kinetics modifications induced by ion dopants.

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1. Introduction

The preparation of dye-sensitized nanocrystalline TiO_2 thin films have attracted considerable attention since Grätzel and coworkers first reported on the highly efficient ruthenium complex sensitized nanocrystalline TiO_2-based dye sensitized solar cells (DSSCs) in the beginning of the 90s [1-3]. Due to the simple production technology and low cost, nanostructured dye-sensitized solar cells have been emerged as a promising alternative to commercially available solar cells based on silicon [4]. Many research groups, institutes and companies are currently looking for different preparation methods [5-7].

The most extensively studied DSSCs are based on TiO_2, which is a wide band gap semiconductor with rutile and anatase phases, and only absorb UV light under 285 nm, which leads to a low utilization of solar energy. There have been some research and application about metal, non-metal doped TiO_2 applied in DSSCs [8-11]. However, there has been no report about non-metal and rare metal co-doped TiO_2 in a DSSC.

So, in this paper, a nano-crystal N–Nd/TiO_2 anode film was prepared by doping N and Nd into TiO_2 using micro plasma oxidation (MPO) method [12]. The objective of this research was to investigate the structural and surface morphologies of the films and to measure their photoelectric performances.

2. Experimental

2.1. Preparation and characterization of TiO_2 films

A titanium sheet (99.9% in purity) as anode was washed in a HF–HNO_3 (1:1, v/v) aqueous solution. The reaction area was $10\times10\times0.5$ mm^3 by the insulation glue and a copper sheet was introduced as cathode. A home-made high-power direct current electrical source with a power of 5 kW was used for MPO of the square samples. The temperature was controlled in the range of 25 ± 0.2℃ by a cold water jacket. The electrolyte solution was consisted of 0.5 M analytical-grade $(NH_4)_2SO_4$. The N, Nd-doped TiO_2 prepared by adding 4g/L $Nd(NO_3)_3$ and different content $NH_3\cdot H_2O$ into the $(NH_4)_2SO_4$ solutions above. The overall MPO process was conducted with a constant current densities 20 A for 10 min. After the end of this reaction, the excess of electrolyte solution on the coated samples was rinsed with distilled water and the produced films were dried in a current of hot air. Then, these dried TiO_2 films were sensitized by *cis*-$RuL_2(SCN)_2\cdot 2H_2O$ in the anhydrous ethanol (3 mmol/L) at 40 ℃ for 12 h. Finally, these thin films were withdrawn from the solution and washed in the anhydrous ethanol for tests.

2.2. Characterization of TiO_2 films

Scanning electronic microscopy (SEM) (D/max-rB) was used to study the surface morphology and the pore distribution of the produced TiO_2 films. The crystalline structure of the films was examined by X-ray diffraction (XRD) with the Cu Kα source. The accelerating voltage and applied current were 40 kV and 30 mA, respectively.

2.3 Photoelectrochemical measurements

The photoelectrochemical experiments were performed in a sandwich-type electrode cells. The dye-coated TiO_2 film was used as working electrode, and transparent conducting glass (F-doped SnO_2, <20 /Ω, Shen Zhen Nanbo Glass Company, China) was used as counter electrodes. A drop of electrolyte was then placed between the electrodes and allowed to wet the surfaces of the electrodes by capillary action. The electrolyte was a solution of 0.5 M potassium iodide and 0.05 M iodine in a mixture of ca. 80% acetonitrile and 20% glycol. The conductive glass is responsible for harvesting simulative sunlight because the titanium substrate is lighttight. The light irradiates the sensitizer through the conductive glass and electrolyte. For the photocurrent–photovoltage measurements, the dye-sensitized TiO_2 films were illuminated through the conductive glass using a 500-W high pressure Xe lamp (Shanghai Aojia) with a IR filter and a 420 nm long pass UV filter served as a light source as the simulating sunlight. The FF (fill factor) of DSSC was obtained according to $FF = (I \times V)_{max}/(I_{sc} \times V_{oc})$ by *I–V* curves. The apparent cell area of TiO_2 electrode was 1 cm^2 (1.0 cm×1.0 cm).

Electrochemical impedance spectroscopy (EIS) was measured with a Z263A impedance analyzer (Princeton Applied Research, American) under air mass (40 mW cm^{-2}) conditions at 25 ℃. The EIS was recorded over a frequency range of 0.01-10^5 Hz. The ac amplitude and the applied voltage were 10 mV and set at open circuit voltage of the cells, respectively.

3. Results and discussion

3.1 Photoelectric performance of TiO_2, TN and TS electrodes

The estimated performance parameters, such as short circuit current density and open circuit voltage, fill factor and photoelectric conversion efficiency (η) of the DSSCs based on the N–Nd co-doped TiO_2 film electrode are summarized in Table 1.

Table 1. Photoelectric parameters of cells assembled by co-doped TiO_2.

$NH_3 \cdot H_2O$ (g/L)	V_{oc} (mV)	J_{sc} (μA/cm^2)	*FF*	η (%)
0	684	157	0.40	0.107
2	662	155	0.38	0.098
4	677	153	0.39	0.101
6	654	148	0.38	0.092
8	649	141	0.37	0.083

From Table 1, it can be seen that the overall efficiency, open voltage and short current of the solar cells first increase and then decrease with $NH_3 \cdot H_2O$ content. When the $NH_3 \cdot H_2O$ content is up to 4 g/L, the short-circuit current and the open-circuit voltage reached maximum and then decreased at the 6 and 8 g/L. The highest conversion efficiency of 0.107% has been achieved for the cell, employing the film prepared with the 4 g/L $Nd(NO_3)_3$. In a word, the photoelectric performance of the Nd doped TiO_2 electrode is higher than that N-Nd co-doped TiO_2 electrode.

3.2. Analysis of SEM and XRD results

Fig. 1 shows crystalline structures of the TiO_2 films prepared by the MPO method.

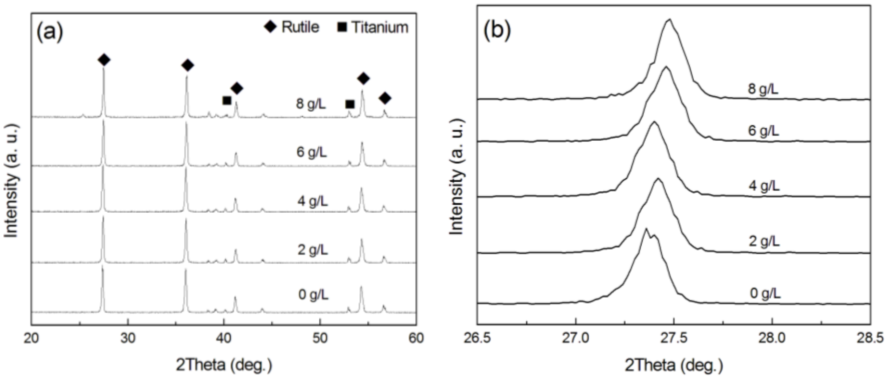


Fig. 1. XRD spectra of films prepared with the N and Nd^{3+} addition electrolyte: (a) full spectrum diffraction peaks in (101) crystal face of rutile phase.

It can be seen from Fig. 1(a) that there are many sharp peaks in the XRD patterns which indicates that the prepared films have been crystallized. According to Joint committee on power diffraction standard data cards, the produced films consist of much rutile phase and the content of rutile TiO_2 reach almost 100%, there are additional peaks of the Ti substrates. Co-doped had an smaller effect on the crystallization phases of Titanium films. From the Fig. 1(b), it can be found that the diffraction peaks of rutile phase shift to higher diffraction angle along with the increase of the concentration of $NH_3 \cdot H_2O$. According to the Scherrer formula, the higher the diffraction peaks is, the larger the particle size of TiO_2 is. Accordingly, the gain size of TiO_2 became big after doping Nd^{3+} into the TiO_2 films. These larger gain size can decrease the surface of TiO_2 film and the photocatalytic reaction sites, which will decrease the photocatalytic activity.

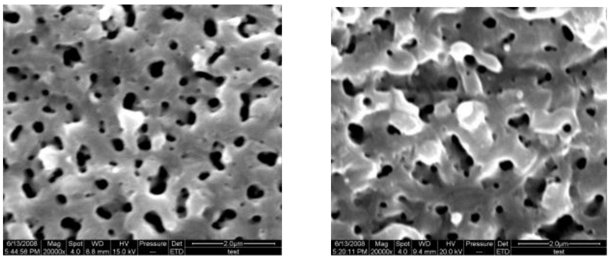
The X-ray diffraction peaks of crystal plane (110) and (101) in rutile are selected to determine the lattice parameter of the produced TiO_2 films. The calculated results of the doped film parameters are shown in Table 2.

Table 2. Crystal lattice parameters of Nd-doped and N, Nd co-doped TiO_2 films.

$NH_3 \cdot H_2O$ Content (mL/L)	0	2	4	6	8
a=b (nm)	0.4609	0.4607	0.4600	0.4605	0.4600
c (nm)	0.2969	0.2965	0.2963	0.2962	0.2964
crystal volumn (nm^3)	0.0631	0.0629	0.0627	0.0632	0.0632
TiO_2 content (%)	89	89	88	86	87

It can be seen from Table 2, the unit cell volume of Nd doped TiO_2 is bigger than that of other films. The larger lattice distortion and inflation usually bring big lattice strain energy. So, in order to compensate this stress, the oxygen atoms on the surface of the TiO_2 crystal lattice is easy to escape from the lattice and traps the hole, which improves separating electron and hole. So, the photoelectric of TiO_2 increases.

The surface images of the obtained films is displayed in Fig. 2.



a) 0 g/L $NH_3 \cdot H_2O$ b) 4 g/L $NH_3 \cdot H_2O$

Fig. 2. SEM of co-doped TiO_2 films.

It is noticed from Fig. 2 that the surface of microplasma oxidation films is mesoporous. The reason is that a large number of bright sparks on the metal surface are visible when the barrier film is broken during the MPO process and the momentary temperature in these small discharge zones can rise to over 2000 °C. The substrate may be temporarily molten and oxidized. Then the oxides are cooled rapidly by the electrolyte and leave many pores. So, the mesoporous TiO_2 thin films can be obtained through MPO method. Also, micropores number of TiO_2 films decrease after doping the N and Nd element, which is not favor of the photoelectric properties of DSSC.

2.2.1 *UV-visible reflection spectrum of the N-Nd co-doped TiO_2 films*

The UV-visible reflection spectrums of the undoped and N-Nd co-doped TiO_2 films are shown in Fig. 3.

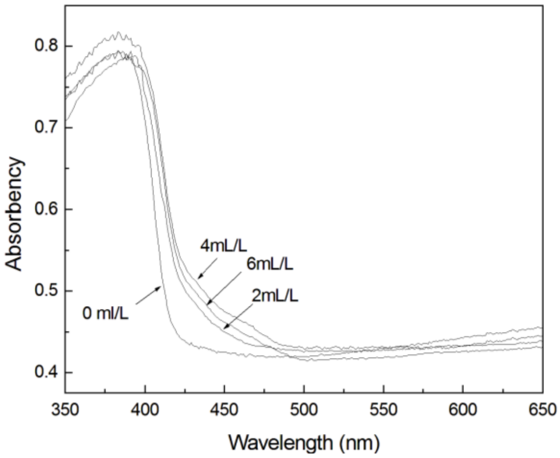


Fig. 3. UV-vis absorption spectrum of films prepared with the co-doped electrolyte.

From Fig. 3, it can be seen that the absorption spectrum of TiO_2 thin film is red-shifted, and the red-shifted degree first increase and then decrease with increase of the doping ion concentration. When the $NH_3 \cdot H_2O$ concentration is 4 g/L, the degree of red-shift reach maximum. The absorption band edges of doped TiO_2 films are 429.5 nm, 431.2 nm and 429.0 nm, respectively. The band widths are 2.887 eV, 2.875 eV and 2.890 eV, respectively. The results show that the band width of the N-Nd doped TiO_2 film is greater than that of Nd-doped thin film.

3.3. Analysis of EIS results

The EIS results are shown id Fig. 4.

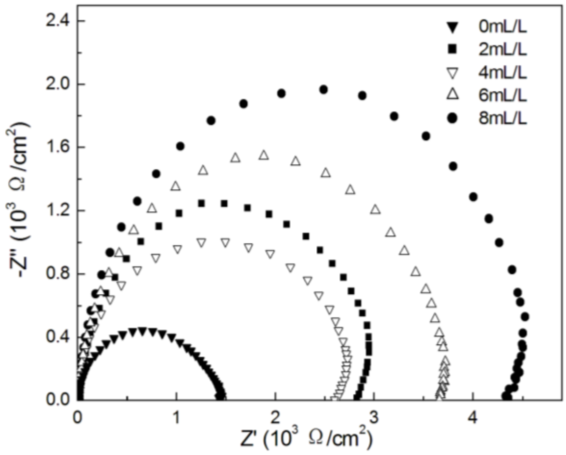


Fig. 4. EIS of cells prepared with the co-doped electrolyte.

In the Fig. 9, every EIS shows only one (slightly flattened) semicircle, and the semicircles are remarkably different from each other. The reason is that these arcs were so large that the other components were unobservable [13]. This means that the charge-transfer resistances at the TiO_2 electrodes mainly affect the performance of DSSCs for these samples.

From the spectra shown in Fig. 4, the impedance is the smallest at 0 g/L $NH_3 \cdot H_2O$, which results in the superior photocurrent and photovoltage (Table 1). Also, high interfacial charge transfer resistance resulting from large semicircle is observed for the DSSC containing TiO_2 electrode prepared at 6 and 8 g/L $NH_3 \cdot H_2O$. So, the performance of the TiO_2 electrodes prepared at 6 and 8 g/L $NH_3 \cdot H_2O$ is lower than that at 0 g/L $NH_3 \cdot H_2O$. On the other hand, it can be noticed that the specific surface area are enlarged by using the TiO_2 electrode prepared with doping 4 g/L $Nd(NO_3)_3$, which results in the inferior performance of DSSCs. Presumably, the performance of DSSCs shows the tendency to decrease when the TiO_2 films are doped by N and Nd elements.

4. Conclusions

The thin TiO_2 films were prepared by the MPO in the $(NH_4)_2SO_4$, NH_3H_2O and $Nd(NO_3)_3$ electrolyte solution and these films were constituted with dye sensitized solar cells. Higher photoelectric performance is obtained using $(NH_4)_2SO_4$ and NH_3H_2O as electrolyte which might be attributed to the lower impedance and larger specific surface area. The dye sensitized solar cell using this TiO_2 electrode exhibits the overall conversion efficiency of 0.107%, which is approximately equal to the conversion efficiency of the flexible solar cells. Also, using MPO to produce TiO_2 electrode is propitious to fabricate a large area dye sensitized solar cells.

References

[1] Yongping Fu, Zhibing Lv, Hongwei Wu, et al., Materials Science, **102**, 212 (2012).
[2] Zion Tachan, Sven Rühle, Arie Zaban. Solar Energy Materials and Solar Cells., **94**(2), 317 (2010).
[3] Hitoshi Kusama, Hironori Arakawa. Solar Energy Materials and Solar Cells., **81**(1) 87 (2004).
[4] Toyohisa Hoshikawa, Tsugio Ikebe, Masashi Yamada, et al. Journal of Photochemistry and Photobiology A: Chemistry. **184**(1–2), 78 (2007).
[5] C. Y. Huanga, Y. C. Hsua, J. G. Chena, et al . Sol. Energ. Mat. Sol. C. **90**, 2391 (2006).
[6] W. Chen, X. D. Sun, Q. Cai, et al . Electrochem. Commun. **9**, 382 (2007).
[7] A. G. Agrios, I. Cesar, P. Comte, et al . Chem. Mater. **18**, 5395 (2006).
[8] Dong Hoe Kim, Sangwook Lee, Jong Hoon Park, et al. Solar Energy Materials and Solar Cells, **96**, 276 (2012).
[9] Jia Liu, Haotian Yang, Weiwei Tan, et al. Electrochimica Acta, **5**(1), 396 (2010).
[10] Bhagwat N. Pawar, Gangeri Cai, Dukho Ham, et al. Solar Energy Materials and Solar Cells., **93**(4), 524 (2009).
[11] Alagesan Subramanian, Jong-Shing Bow, Hong-Wen Wang, et al. Thin Solid Films. **520**(23), 7011 (2012).
[12] Eungsun Byon, Yongsoo Jeong, Akari Takeuchi, et al. Surface and Coatings Technology., **201**(9–11), 5651(2007).
[13] T. Hoshikawa, R. Kikuchi, K. Eguchi. J. Electroanal. Chem. **588**, 59 (2006).

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