Fabrication and I-V Characteristics of Nanocrystalline Titania Electrode Sensitized by Zinc Phthalocyanine

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Abstract. TiO_2 colloids prepared by sol-gel method were autoclaved and then deposited onto a transparent conducting oxide substrate by screen-printing. The TiO_2 films electrode was characterized by XRD, SEM, AFM and Alpha-Step profilometer and then sensitized by zinc phthalocyanine (ZnPc), 2,9,16,23-tetracarboxy zinc phthalocyanine (ZnTCPc) and ZnTCPc/lauric acid respectively. Photocurrent density (I) and photovoltage (V) of the electrode were measured with the solar simulator. The ZnTCPc-sensitized electrode was found the best performance with the short-circuit photocurrent density (I_{sc}) 16.66 $\mu A/cm^2$, the open-circuit photovoltage (V_{oc}) 277.9 mV and the fill factor (FF) 0.39. And the ZnPc-sensitized electrode was found the worst performance with V_{oc} 114.2 mV, I_{sc} 2.26 $\mu A/cm^2$ and FF 0.31. It was also found that lauric acid promoted V_{oc} of the the ZnTCPc sensitized system.

Introduction

Nanocrystalline TiO_2 electrode plays an important role in dye-sensitized solar cells (DSSC). Grätzel and his co-workers reported a high efficient DSSC based on nanocrystalline TiO_2 electrode, which was composed of titania nanocrystalline particles accumulated on a transparent conducting oxide substrate and achieved a high specific surface area for adsorption of a large number of ruthenium complexes [1,2,3]. Ruthenium complexes sensitized a wide band-gap titania semiconductor very efficiently over a broad spectral range in the visible [2]. However, nanocrytalline TiO_2 takes the form of agglomerate, which has a much larger size and lower porosity than the primary particles [4]. Ruthenium complexes have weaker near-infrared response and higher synthesized cost than phthalocyanines [5,6]. As phthalocyanine molecules usually aggregate on the solid surface, the sensitization activity decreases in the solid state [6].

In this paper the TiO_2 electrode was prepared and then soaked in zinc phthalocyanines/DMSO solution. The photovoltaic characteristics of the dye-sensitized nanocrystalline TiO_2 electrode were investigated. The effect of lauric acid on the photovoltaic characteristics of ZnTCPc-sensitized nanocrystalline TiO_2 electrode was also investigated.

Experimental Section

Materials. Titanium isopropoxide, isopropanol, nitric acid, hexachloroplatinic acid, lauric acid, DMSO and carbowax were purchased from Aldrich Co. Ltd. ZnPc, ZnTCPc and deionized water were homemade products. A transparent conductive oxide (TCO, transmission > 85% in visible, sheet resistance 20 ohm/square,) was obtained from Shenzhen South Float Glass Co. Ltd.

Preparation of a nanocrystalline TiO_2 electrode. TiO_2 colloids were prepared by sol-gel method as follows: 12.5 mL titanium isopropoxide in 4 mL isopropanol was dropwisely added into the 0.2 M nitric acid aqueous solution under vigorous stirring at room temperature. Then the suspension was maintained at 80 °C for 8 h under continuously stirring. Afterwards the suspension was concentrated to 60 mL and put into the autoclave for hydrothermal treatment at 230 °C for 16 h. Then the obtained white slurry mixed with 20 wt% carbowax was deposited onto a TCO by screen-printing. The wet films were sintered at 100 °C, 200 °C, 300 °C, 450 °C and 650 °C for 30 min in air respectively.

Sensitization and Pt electrode Preparation. A nanocrystalline TiO_2 electrode was soaked in the 1×10^{-5} M ZnPc/DMSO, ZnTCPc/DMSO and ZnTCPc/lauric acid (ZnTCPc:lauric acid molar ratio 10:1) /DMSO for 36 h respectively. Pt electrode was prepared by spreading a drop of 5 mM hexachloroplatinic acid/isopropanol on a TCO and followed by heating to 450 °C for 30 min.

Characteristics. The thermal characteristics of colloids were measured with DSC-TG (TA Q-600) heating rate 10°C/min in air. The crystallization of the electrode was performed on a Cu Kα source XRD (Shimazu). The films thickness was measured with Alpha-Step profilometer. The surface morphology of the films was observed by SEM (FEI Sirion) and AFM (CSPM-3400, Being Nano-Instruments Co. Ltd.). I-V measurements were made in a two-electrode sandwich cell, which was an effective area of ca. 0.2 cm^2. The electrolyte contained 0.5 M KI and 0.05 M I_2 in propylene carbonate. An Oriel 91192 solar simulator served as the light source and the I-V characteristics were carried out on a Keithley 2400 SourceMeter.

Results and Discussion

Structures of the nanocrystalline TiO_2 electrode. Fig. 1 shows the DSC-TG curves of TiO_2 colloids with 20 wt% carbowax. A broad endothermic peak exists at around 150 °C due to the desorption of water and isopropanol [6], which is analogous to the narrow peak of carbowax at 132 °C due to the desorption of water. The relatively small exothermic peak at 324 °C comes from the decomposition of carbowax contained in the colloids [7], which is identified by the strong exothermic peak of carbowax at 277 °C. At that high temperature carbowax decomposed into water and carbon dioxide. At about 425 °C, a small exothermic peak is observed due to crystallization. Similarly, anatase crystalline formation at 450 °C is observed in Fig. 2. TG curve of colloids shows weight loss 8.1 % at temperatures between 50 °C and 400 °C, which was caused by dehydration and decomposition of carbowax contained in the TiO_2 colloids. The weight loss 0.24 % exists at temperature between 400 °C and 700 °C. This is attributed to the oxidation of carbon residue and evaporation of chemisorbed water [8].
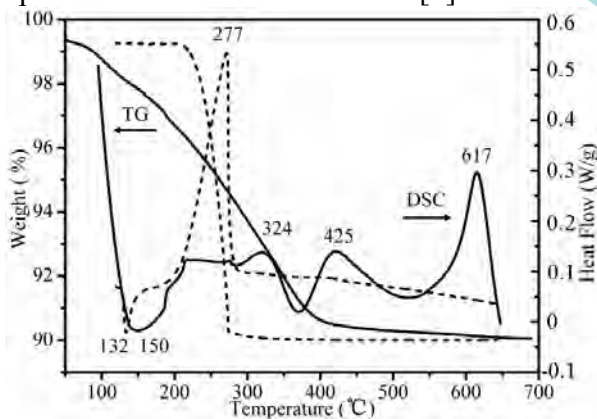

Fig. 1 DSC-TG: TiO_2 colloids mixed with 20 wt% carbowax (solid), carbowax (short dash)
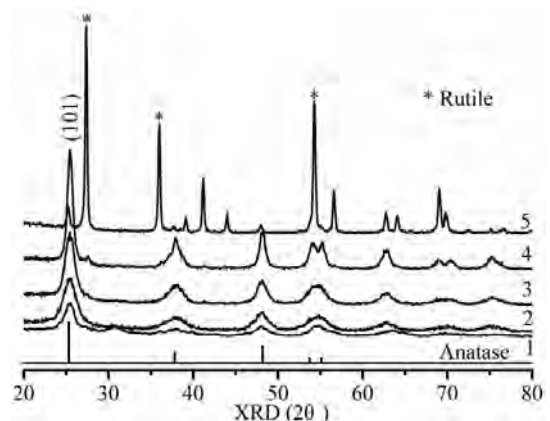
Fig. 2 XRD: nanocrystalline TiO_2 electrode 1-100°C,2-200°C,3-300°C,4-450°C,5-650°C

Fig. 2 shows that the anatase component increases between 100 °C and 450 °C. However, over 650 °C the rutile (three strong peaks marked by asterisk) begins to appear. The size of anatase crystalline was determined from β, which is the full width at half-maximum (fwhm) of the strongest X-ray diffraction peak (101), using the Scherrer equation [9]:

$$D = \frac{0.89\lambda}{\beta\cos\theta} \qquad (1)$$

where λ is the X-ray wavelength 0.1542 nm and θ the Bragg angle. The calculated size of anatase crystalline was 20.2 nm.

Fig. 3 (a) shows the SEM images of the TiO_2 particles which indicate that the average diameter about 20 nm in agreement with calculated value as above. The films thickness was 10 μm as measured with the Alpha-Step profilometer. Fig. 3 (b) shows the AFM images of the morphology of

the TiO_2 electrode. It is observed that the surface of the electrode is rough and porous. The mean grain sizes are measured with a computer to be 20 nm and the mean roughness (RMS) 0.8. As it shows in Fig. 1, carbon dioxide appearing at 324°C can promote the porosity of the electrode when the gas escapes from the films. In contrast to the suspension without carbowax, RMS was 0.5. TiO_2 suspension untreated by autoclave can also be deposited onto a TCO. However, Fig. 3 (c) AFM images show TiO_2 particles form agglomeration and the results are harmful to roughness and porosity of the electrode. Under the condition, RMS was 0.1.
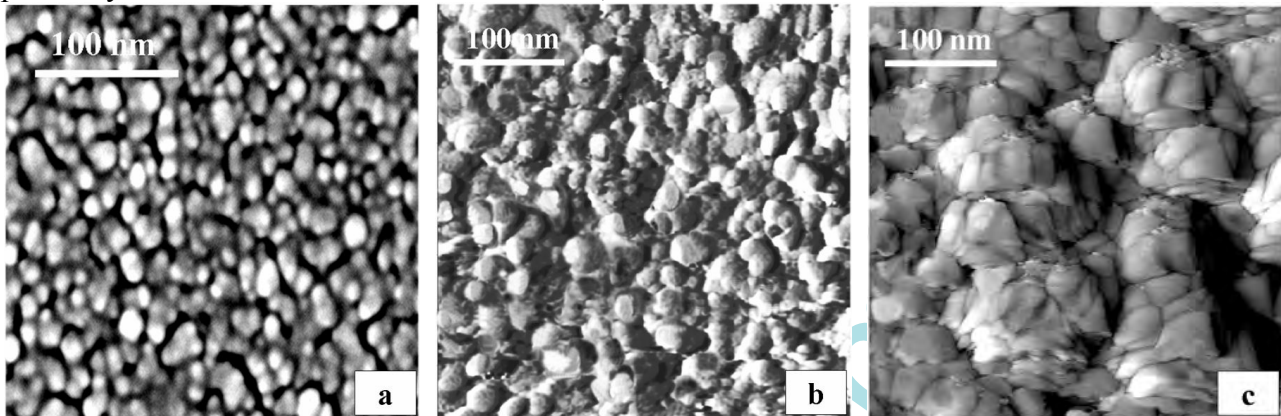
| (a) SEM: average diameter 20 nm | (b) AFM: treated by autoclave | (c) AFM: untreated by autoclave |

Fig. 3 SEM micrographs and AFM morphology of the TiO_2 films electrode surface

I-V characteristics of a nanocrystalline TiO_2 electrode. Fig. 4 shows ZnPc sensitization has the lowest V_{oc} and J_{sc} of the three systems. The reason is that ZnTCPc has another more four carboxyl groups on the structure than ZnPc. The carboxyl groups can react with the hydroxyl groups of anatase surface to form esters. That chemical bond connection anchors on TiO_2 surface more tightly and offers electron channels from ZnTCPc to TiO_2 electrode surface [10]. So the results cause V_{oc}, I_{sc} and FF to improve. Fill factor is defined as the ratio:

$$FF = \frac{V_{opt} I_{opt}}{V_{oc} I_{sc}} \qquad (2)$$

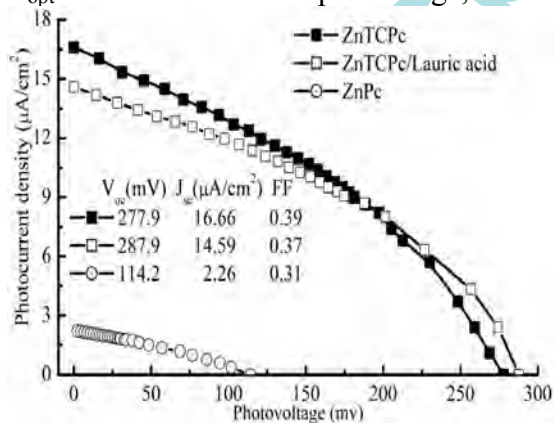Where V_{opt} is the maximum output voltage, the maximum output current I_{opt}.
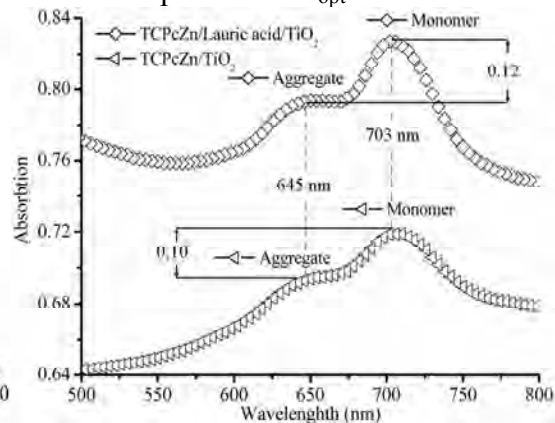
| Fig. 4 I-V characteristics | Fig. 5 Absorption spectra |

Comparing with ZnTCPc, ZnTCPc/lauric acid co-sensitization has higher V_{oc}, lower I_{sc} and FF. In Fig. 5 UV-vis shows ZnTCPc aggregates on the TiO_2 electrode surface at 645 nm, which passivates the sensitization activity to decrease V_{oc} [11]. To suppress the aggregation, lauric acid was adsorbed onto the electrode. The results show that absorbance coefficient difference increased from 0.10 to 0.12 and the V_{oc} increases from 277.9 mV to 287.9 mV in Fig. 5 and Fig.4 respectively. However, the I_{sc} and FF decreased appreciably. Lauric acid is easy to form a layer of membrane, which increases the resistance between ZnTCPc and TiO_2 electrode surface [12].

Furthermore, different films thickness holds different sensitizer absorption and photocurrent loss [3,13]. Maximum output power (P_{opt}) was also calculated by formular (2) and the result is that FF, V_{oc} and J_{sc} multiply. As shown in Table 1, the 10 μm thicknesses films hold the P_{opt}. With thickness

increasing the resistance of the films increases and the probability of recombination also increases. On the contrary, with thickness decreasing the sensitizer absorption reduces sharply and the light harvest efficiency also declines [2,14].

Table 1 Effect of films thickness on the photovoltaic characteristics of nanocrystalline TiO_2 films electrode sensitized by ZnTCPc

Thickness (μm)	V_{oc} (mV)	J_{sc} ($\mu A/cm^2$)	FF	P_{opt} (mW/cm^2)
6	247.2	5.49	0.30	0.407
8	269.7	8.54	0.32	0.737
10	277.9	16.66	0.39	1.81
12	277.6	13.45	0.36	1.34
14	275.6	12.14	0.33	1.10

Conclusions

Nanocrystalline TiO_2 films electrode has been prepared by sol-gel method. Hydrothermal treatment holds back nanocrystalline agglomeration on the TiO_2 electrode surface. During sintering, the decomposition of carbowax promotes the roughness of the electrode. Zinc phthalocyanines with carboxyl groups improve the photovoltaic characteristics of the nanocrystalline electrode. Lauric acid suppresses the ZnTCPc molecule aggregates and promotes V_{oc}. In ZnTCPc sensitization system 10 μm thicknesses films hold the optimal photovoltaic characteristics.

Acknowledgements

Reference

[1] B.O. Regan, M. Grätzel: Nature Vol. 353 (1991), p.737

[2] M. Grätzel: Inorg. Chem. Vol. 44 (2005), p.6841

[3] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humpbry-Baker, E. Miiller, P. Liska, N. Vlachopoulos and M. Grätzel: J. Am. Chem. Soc. Vol. 115 (1993) p.6382

[4] D. Skarmoutsos, F. Tietz, P. Nikolopoulos: Fuel Cells Vol. 1 (2001) p.243

[5] H.M. Liu, W.S. Yang, Y. Ma, Y.A. Cao and T.D. Hu: Langmuir Vol. 19 (2003) p.3001

[6] M. Grätzel: Journal of Photochemistry and Photobiology A: Chemistry Vol. 164 (2004) p.3

[7] J.G. Yu, X.J. Zhao, Q.N. Zhao: Thin Solid Films Vol. 7 (2000) p.379

[8] J.C. Yu, J. YU, Wingkei Ho, Z.T. Jiang and L.Z. Zhang: Chem. Mater. Vol. 14 (2002) p.3808

[9] N. Sakai, Y. Ebina, K.Takada and T. Sasaki: J. Am. Chem. Soc. Vol. 126 (2004) p.5851

[10] J.J. He, A. Hagfeldt, and S.E. Lindquist: Langmuir Vol. 17 (2001) p. 2743

[11] Y. Amao and T. Komori: Langmuir Vol. 19 (2003) p.8872

[12] Y. Amao and T. Komori: J. Porphyrins Phthalocyanines Vol. 7 (2003) p.131

[13] Yasuhiro Tachibana, Kohjiro Hara, Shingo Takano, Kazuhiro Sayama and Hironori Arakawa: Chemical Physics Letters Vol. 364 (2002) p.297

[14] M. Grätzel: Journal of Photochemistry and Photobiology A: Chemistry Vol.164 (2004) p.3