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Research Article

A Convenient Method for Manufacturing TiO_2 Electrodes on Titanium Substrates

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Thin titanium dioxide films were successfully prepared on titanium plates in ammonium sulfate solution with the micro-plasma oxidation method. The thin TiO_2 films were sensitized with a *cis*-$RuL_2(SCN)_2 \cdot 2H_2O$ (L = *cis*-2, 2′-bipyridine-4, 4′-dicarboxlic acid) ruthenium complex, and implemented into a dye sensitized solar cell configuration. The influence of current density on the surface structure and photoelectric performance of the TiO_2 films was investigated. The results show that the thin TiO_2 films are porous, and the dye-sensitized solar cell based on the film prepared at 14 A/dm^2 has exhibited higher overall light-to-electricity conversion efficiencies of 0.095% under the illumination at 40 mW/cm^2.

1. Introduction

The dye-sensitized solar cell (DSSC) has attracted much attention as the next generation solar cell during the last decade [1, 2]. Remarkably, high enough efficiency and low cost of manufacturing are important characteristics to make the DSSC as a substitute of the conventional silicon and thin film photovoltaic devices. Various methods of preparing dye-sensitized solar cells have therefore been developed [3–5]. At present, the TiO_2 photoelectrode of DSSC is usually prepared by depositing a suspension or paste-containing TiO_2 nanoparticles with organic additives onto conductive glass substrates or polymer substrate [6, 7]. The deposited film is then subject to a posttreatment with the purpose of forming a continuous nanoparticle network with sufficient adherence and electrical contact to the substrate and between the nanoparticles. Although the conventional preparation method of using conductive glass substrate can achieve good interconnection between particles, a batch process must include heat treatments, which is not fast enough to produce the necessary devices. In addition, the use of glass substrates with frangibility limits the manufacture process and the practical application of DSSCs. The use of plastic substrates is another choice of the TiO_2 suspension [8, 9]. However, these methods present a weak adherence of the films to the substrates, and obtain very thin films.

In this paper we, therefore, looked into the possibility of developing microplasma oxidation (MPO) method to prepare TiO_2 thin films on the thin light titanium substrates. This method is based on the anodic oxidation, which occurs at potentials above the breakdown voltage of the oxide film growing on the anode surface, such as Al, Mg, Ti, Nb, and Zr. As the process combines electrochemical oxidation with a high voltage spark treatment in an electrolyte bath, metal oxides are synthesized inside high voltage breakthrough channels across the former oxide layer. So the prepared thin oxide films have good adherence with substrate metal and can endure strong impact [10, 11]. In addition, the process of preparing thin films by MPO need very short time. In this paper, MPO in the ammonium sulfate solution with different current densities was used to prepare TiO_2 films on the surface of Ti substrate. The objective of this research was to investigate the structure and surface morphology of the films and measure their photoelectricity performance as photo anode of the DSSC.

2. Experimental

2.1. Preparation of Films. Plate samples of a titanium sheet (99.9% in purity) with a reaction dimension of 2 mm^2 were washed in 40% HF and 65% HNO_3 (1 : 1 in volume) aqueous solution. A home made-electrical source with the power at

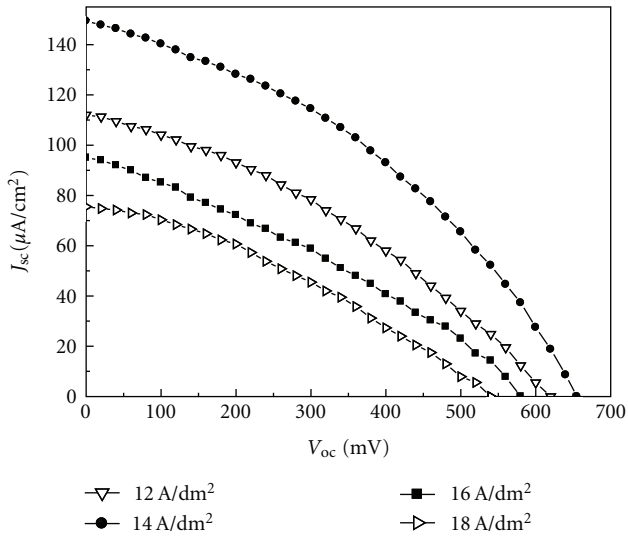


Figure 1: Results from *I–V* characteristics of TiO_2 electrodes prepared at different current density.

5 kW was used for microplasma oxidation of the samples in a water-cooled electrolyte, and a copper sheet serves as the counterelectrode. The reaction temperature was controlled to below 30°C by adjusting the cooling water flow. The electrolyte used in the experiment is ammonium sulfate solution (0.5 mol/L). The set-up scheme is shown in the past report [12]. The whole MPO process was carried out under different current densities (12, 14, 16, and 18 A/dm^2) for 10 min. After the treatment, the coated samples were flushed with water and dried in 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°C for 12 h.

2.2. Characterization of Films. The photoelectrochemical experiments were performed in two sandwich-type electrode cells. The dye-coated TiO_2 film was used as working electrode, and transparent conducting glass (<20/Ω) 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. 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 with a water IR filter, and a 420 nm long pass UV filter served as a light source as the simulating sunlight.

The surface morphology of the films was observed on an S-570 scanning electron microscope (SEM) from Hitachi. The X-ray diffraction (XRD) with a Cu K_source (D/max-r B from Ricoh) was applied to study the crystalline structure of the films with an accelerating voltage and an applied current of 40 kV and 30 mA, respectively. Surface roughness of the TiO_2 films were examined with a digital Instruments Nanoscope III atomic force microscope. The thickness of the films are measured by CTG-10.

Table 1: Results from *I–V* characteristics of TiO_2 electrodes prepared at different current density.

Type (A/dm^2)	V_{oc} (mV)	J_{sc} (μA/cm^2)	*FF*	η (%)
12	619	112	0.35	0.061
14	652	149	0.39	0.095
16	581	95	0.32	0.044
18	542	76	0.33	0.034

3. Results and Discussion

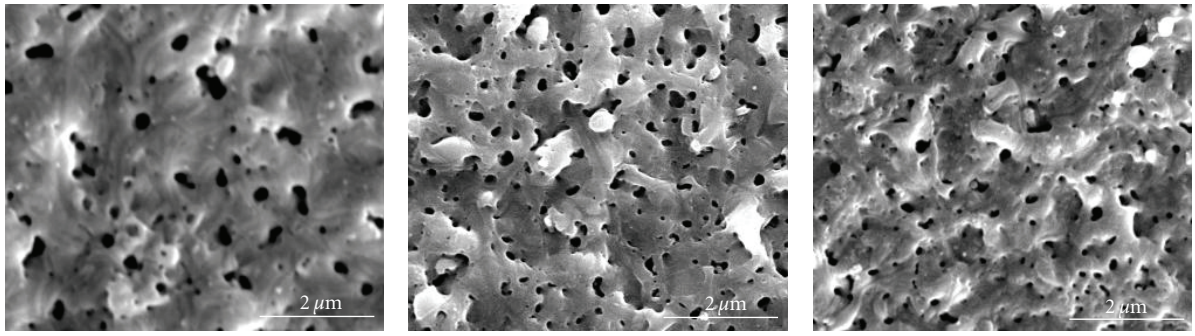
3.1. Photoelectricity Properties of the Films. The distinct structure of TiO_2 films lead to dissimilar photoelectricity properties. A *I–V* curves between the TiO_2 films prepared with different current density are given in Figure 1. Table 1 shows the averaged data extracted from *I–V* curve measurement on dye-sensitized nanostructured TiO_2 electrode.

As is shown in Figure 1 and Table 1, the overall efficiency (η), open circuit voltage (V_{oc}), and short circuit current (J_{sc}) of the dye-sensitized solar cells firstly increase and then decrease with current density of MPO. The V_{oc} increases from 619 to 652 mV, while the J_{sc} increases from 112 to 149 μA/cm^2 when the current density increase from 12 A/dm^2 to 14 A/dm^2. The J_{sc} and the V_{oc} reach maximum at 14 A/dm^2 and then decrease at the 16 and 18 A/dm^2. The highest conversion efficiency of 0.095% has been achieved for the cell, employing the film prepared at 14 A/dm^2.

3.2. Morphology of the Films. The TiO_2 films prepared at different current densities have different surface images (see Figure 2). It can be seen that the surface of prepared films are mesoporous and the microporous size increase with the current density. The mean roughness values of the TiO_2 films prepared at 12, 14, 16, and 18 A/dm^2 are 110.25, 138.65, 131.36, and 128.49 nm, respectively. When the current density is 14 A/dm^2, the TiO_2 film obtains the largest roughness and then decreases with the increasing of the current density. The rough surface is propitious to absorb the sensitizer. The thickness of the films prepared at 12, 14, 16, and 18 A/dm^2 are 3.7 μm, 5.6 μm, 7.9 μm, 12.5 μm, respectively.

3.3. Structural Analysis of the Films. Figure 3 shows crystalline structures of the TiO_2 films. It can be noticed that the films consist of much rutile phase and less Ti substrates when current density is below 14 A/dm^2. The content of rutile TiO_2 reaches almost 100% at the current density of 16 and 18 A/dm^2. And the disappearance of Ti substrate peak could result from the increase of film thickness.

From *I–V* curve and SEM photographs, it can be seen that TiO_2 crystallite and pores are formed on the surface of the Ti substrate, and this kind of films have photoelectricity properties. From SEM photographs, the surface grain size and the density of the pores reach the maximum at 14 A/dm^2. These changes could improve the photoelectricity 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 overall efficiency, short circuit current and open circuit voltage of the TiO_2 film



(a) (b) (c)

Figure 2: SEM images under different current densities: (a) 12 A/dm^2, (b) 14 A/dm^2, and (c) 16 A/dm^2.

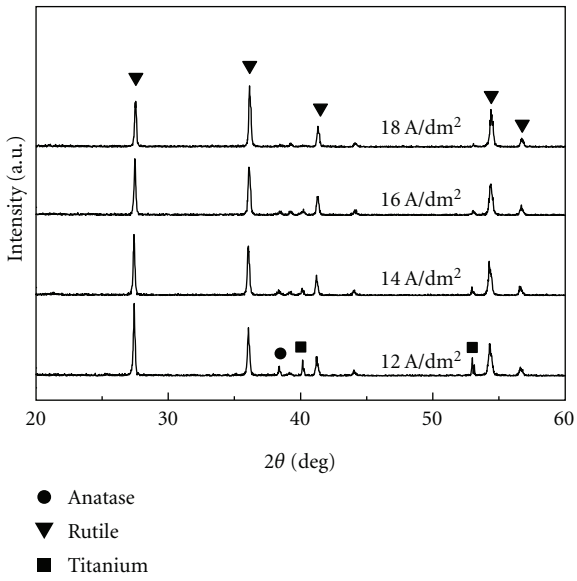


Figure 3: XRD of films prepared under different current densities.

prepared at 14 A/dm^2 are higher than that of the films prepared at 12 A/dm^2. When the current density of MPO is up to 16 A/dm^2, the efficiency of the fabricated cell decline. The reason is that the reaction temperature increases simultaneity with the increasing of the current density, and many bigger blocks TiO_2 are formed around the pores (see Figure 2). The sample showed inferior performance owing to the decreased surface area, the reduction in the pore size, which is related to the amount of dye adsorption.

4. Conclusion

In conclusion, uniform and porous thin TiO_2 films have been successfully prepared with the microplasma oxidation method in the $(NH_4)_2SO_4$ electrolyte solution. This method can prepare TiO_2 electrode conveniently. A higher photoelectric performance of TiO_2 electrode is obtained when the electrode is prepared by MPO under the current density of 14 A/dm^2. The dye-sensitized solar cell using this TiO_2 photoanode exhibited the overall conversion efficiency of 0.095% (AM-1.5, 40 mW/cm^2).

Acknowledgments

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