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Research Article

$TiCl_4$ Pretreatment and Electrodeposition Time Investigations of ZnO Photoelectrodes Preparation for Dye Sensitized Solar Cells

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$TiCl_4$ pretreatment is used in the fabrication of high performance photoanodes for dyes-sensitized solar cells (DSSCs). In this paper, $TiCl_4$ pretreatment was used on fluorine doped tin oxide (FTO) before fabricating ZnO films by electrochemical method. The effects of $TiCl_4$ pretreatment on some important parameters of solar cells, such as short-circuit current (Jsc) and filling factor, were investigated. The morphology of ZnO films was changed after $TiCl_4$ pretreatment, which can offer large surface area to absorb much more dyes. When the time of electrodeposition was 3 min, the dyes-sensitized solar cells (DSSCs) based on $TiCl_4$ pretreatment ZnO films showed more superior photoelectrochemical performance. The parameters of DSSCs are greatly improved. The DSSC based on ZnO films after $TiCl_4$ pretreatment has a very promising value for fabricating high performance solar cells.

1. Introduction

As a promising solar-to-electric energy converter, DSSCs have attracted much of attention due to their high efficiency and low cost [1]. With regard to photovoltaic devices, the conventional silicon-based solar cells are usually too bulky and heavy for flexible applications. Fortunately, new generation photovoltaic devices, such as dye-sensitized solar cells (DSSCs) and organic solar cells, make it possible to utilize solar energy more efficiently. As a result, invented new methods have recently attracted much attention to mesoporous film in the photoelectrodes of dye-sensitized solar cells (DSSCs) and quantum dots-sensitized solar cells (QDSCs) [2–6]. However, insufficient internal surface area limits conversion efficiency at a relatively low level owing to deficient dyes loading and light harvesting.

ZnO is one of the most important semiconductor materials as the photoelectrodes of DSSCs and QDSCs due to its suitable energy-band structure and excellent physical properties. Up to now, to get high performance, many methods have been explored to prepare ZnO porous films to offer large specific surface area for high device performance, such as doctor-blade (DB) method, chemical bath deposition, and electrodeposition (ED) [7–11]. In this paper, we expected to fabricate high performance photoanodes for dyes-sensitized solar cells (DSSCs). $TiCl_4$ pretreatment was used on FTO before fabricating ZnO films by electrochemical method. The morphology of ZnO films was changed after $TiCl_4$ pretreatment, which can offer large surface area to absorb much more dyes. We tried different electrodeposition times. When the time of electrodeposition was 3 min, the quantum dyes-sensitized solar cells (DSSCs) based on $TiCl_4$ pretreatment ZnO films showed more superior photoelectrochemical performance.

2. Experimental

2.1. Preparation of ZnO Electrode. The base electrolyte used for the electrodeposition of ZnO films contained 0.1 M $Zn(NO_3)_2$ and 0.1 M KCl. Bath temperature was controlled at 65°C and the electrolyte was stirred vigorously before electrodeposition using a magnetic stirrer (Figure 1). The cathode substrate and graphite anode were dipped into the electrolyte solution about 1 cm deep below solution level controllably. Adjustment distance between electrode and

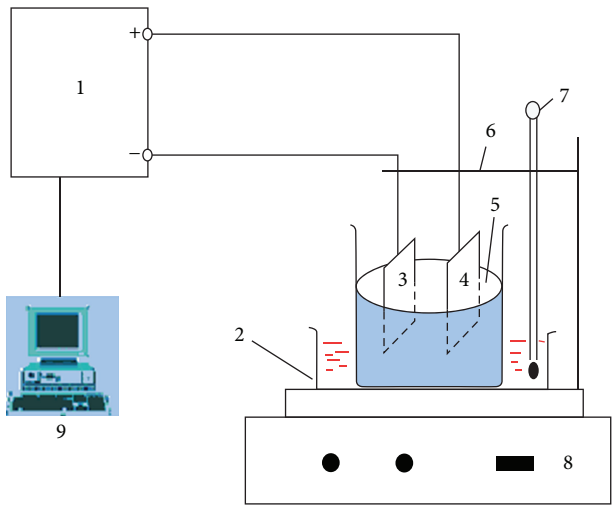

Figure 1: Schematic diagram of DC electrochemical deposition device. (1) Electrochemical workstation, (2) constant temperature water bath, (3) the cathode substrate, (4) graphite anode, (5) electrolyte solution, (6) bracket, (7) node thermometer, (8) thermostat magnetic stirrer, and (9) computer.

counter electrode is 2 cm. The electrodeposition was carried out under the potentiostatic condition. After the reaction, the reaction products ZnO/FTO was dipped into deionized water, soaking and cleaning. Then, after annealing for 30 min, ZnO/FTO was taken out from furnace when temperature decreased to 80°C through natural cooling and dipped into the dye (N719, 0.03) for 12 h. Finally they were washed with de-ionized water.

In order to make a performance comparison between $TiCl_4$ pretreatment and no $TiCl_4$ pretreatment on ZnO films and photoelectric performance influence, we fabricated another ZnO electrode. To be different, FTO was treated with $TiCl_4$ solution before making ZnO electrode and annealing 30 min at temperature 450°C.

2.2. $TiCl_4$ Pretreatment of FTO. The FTO was treated with $TiCl_4$ solution before fabricating TiO_2 films by method which can be found in the literatures elsewhere. With the pretreatment process, not only adsorption was stronger between TiO_2 films and FTO but also impede carriers recombination between I^{3-} and FTO. The conversion efficiency increased as Jsc increased. In this paper, $TiCl_4$ pretreatment was used on FTO before fabricating ZnO films by electrochemical method and at work current (30 mA) growth 4 min, then annealing 30 min at temperature 450°C.

3. Results and Discussion

Figure 2 shows the comparison after fabricating ZnO films, whether if there has been $TiCl_4$ pretreatment used on FTO or not, before fabricating ZnO films. It can be readily seen that the fabricated ZnO films are porous flakes, no matter they have $TiCl_4$ pretreatment or not. Compared with no $TiCl_4$ pretreatment, fabricated ZnO flake is smaller with $TiCl_4$ pretreatment. In addition, a large number of ZnO nanorods were produced which can offer large surface area to absorb much more dyes.

Table 1: The performance parameters of DSSCs with $TiCl_4$ pretreatment and without $TiCl_4$ pretreatment.

Samples	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Without $TiCl_4$	0.3977	1.07	0.2820	0.12
$TiCl_4$	0.4759	2.86	0.3967	0.54

Figure 3(a) shows that the UV-Vis absorption spectra of ZnO films used $TiCl_4$ pretreatment or not after dye sensitized (N719) for 12 h. It can easily be seen that under the same conditions, relative to without $TiCl_4$ pretreatment, the absorbance of ZnO films increased after $TiCl_4$ pretreatment and light absorption cutoff wavelength presented a remarkable red shift, effectively broadening the range of ZnO on the absorption of sunlight.

The prepared ZnO films were immersed into dyes (N719) for 12 h; then with Pt electrodes they assembled into dye-sensitized solar cells (DSSCs) and performance was tested. *J-V* curves obtained from DSSCs are presented in Figure 3(b). Table 1 presents the parameters of DSSCs. It can be seen by the *J-V* curve that the performance of DSSCs with $TiCl_4$ pretreatment is much better than the DSSCs without $TiCl_4$ pretreatment. This experimental result is consistent with the test results of U-V absorption spectrum. As shown in Table 1, the short-circuit current (Jsc), open-circuit voltage, conversion efficiency, and filling factor of DSSCs with $TiCl_4$ pretreatment are greatly improved. The main reason for the results is that ZnO absorbed more dyes with the surface area increasing from ZnO films. Meanwhile, after $TiCl_4$ pretreatment, a layer of dense TiO_2 on FTO is formed and impede carriers recombination between I^{3-} and FTO effectively, thus, the short-circuit photocurrent density is improved, so the conversion efficiency was increased; this is consistent with literature reported.

Keeping the same experimental conditions, the electrodeposition times of the preparation of ZnO samples were 2 min, 3 min, 4 min, and 5 min, respectively, at the constant current of electrodeposition of 30 mA. Figure 4 shows the SEM of ZnO films under different electrodeposition times. From the SEM photos it can be seen that when the electrodeposition time is 2 min, we can get the ZnO sheet structure, which is composed of small particles with size of about 300 nm. Along with the growth of the electrodeposited time, flakes began to accumulate, at the same time, composed of a small piece of particle size that also increases (electrodeposition time of 4 min, the small particle size increased to 500 nm), resulting in decreased ZnO films surface area. With the electrodeposition time of 5 min, from amplifier SEM photos, it can be seen that the dense ZnO films are significantly higher than 4 min. But too dense film is not conducive to the dyes adsorption.

The XRD pattern in Figure 5(a) reveals the ZnO films under different electrodeposition times. We can get from the XRD that 2θ angle of 31.8°, 36.6°, and 56.64° corresponded to the ZnO thin films (100) (101) (110) diffraction crystal

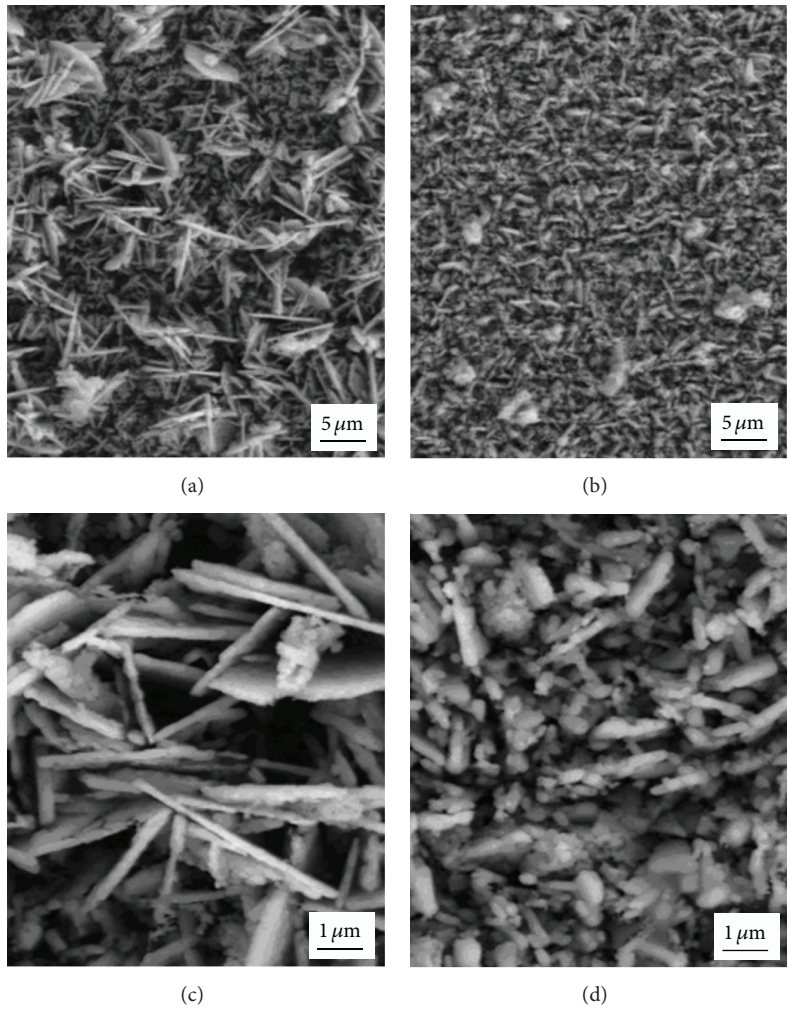

Figure 2: SEM images of $TiCl_4$ pretreatment used on FTO or not. (a) $TiCl_4$ pretreatment. (b) Without $TiCl_4$ pretreatment. (c) and (d) The amplification figure of (a) and (b), respectively.

face, respectively, consistent with the standard peak of XRD patterns (JCPDS no. 74-534). In addition, some weak peaks also appeared, (002), (102), (103), (112), and (201). As can be seen by the XRD patterns, ZnO films prepared under different electrodeposition time XRD peak are almost the same with a difference in the peak intensity.

ZnO films prepared under the different deposition times immersed in the N719 dye-sensitized for 12 h, and then, with Pt electrodes, they assembled into DSSC performance testing, *J*-*V* characteristic curve shown in Figure 5(b). The performance parameters of DSSCs are listed in Table 2.

As can be seen from Figures 5(a) and 5(b), when other experimental conditions are unchanged, with the growth of the electrodeposition time, the DSSC short-circuit current, filling factor, and the photoelectric conversion efficiency first increase and then decrease. When electrodeposition time is 3 min, the DSSC performance is the best. The main reason is: when the electrodeposition time is short, flake particle size is small and specific surface area is large, but the relatively dense and thin deposition layer is not conducive to the adsorption of the dyes, so, short circuit current density of the DSSC is low, the filling factor and conversion efficiency are low too. The small particle size also increases with the growth time. At this point, the thickness of the sediments layer gradually increased and occupied the leading position; combined effect is conducive to dyes adsorption, making the short-circuit current density, filling factor, and efficiency also increase. However, along with the growth time, small flake particle size gradually get big, resulting in specific surface area of ZnO

Table 2: The parameters of DSSCs under different electrodeposition time.

Electrodeposition time (min)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
2	0.6897	2.91	0.3787	0.76
3	0.6922	3.34	0.4758	1.10
4	0.6774	3.38	0.3974	0.91
5	0.6835	3.17	0.3692	0.80

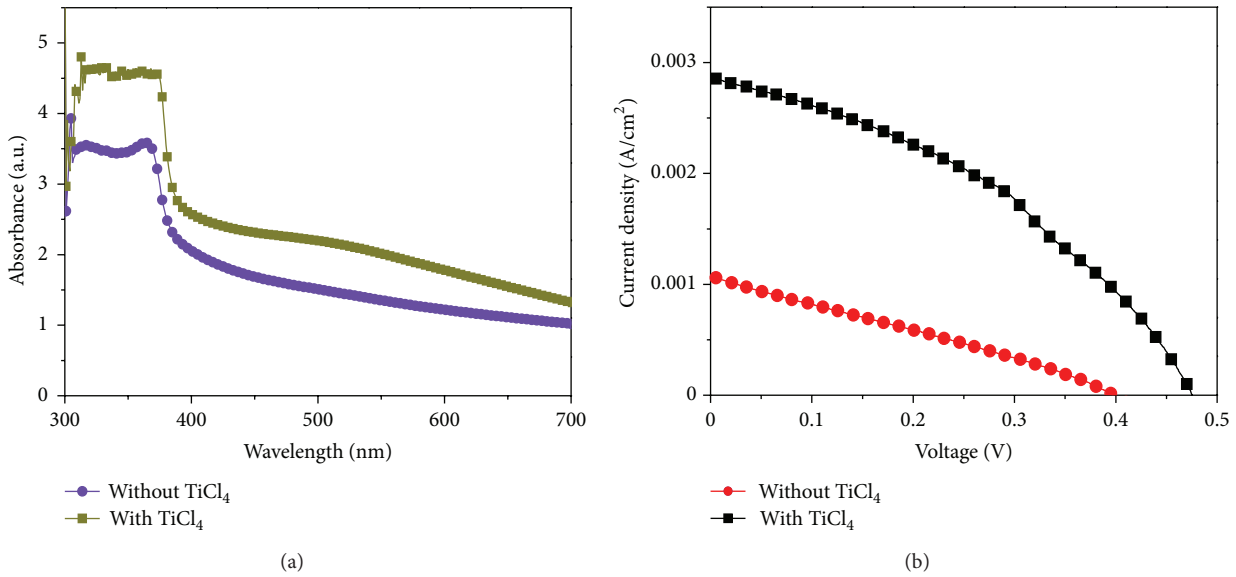

Figure 3: (a) UV-Vis absorption spectra of ZnO films. $TiCl_4$ pretreatment (dark yellow). Without $TiCl_4$ pretreatment (blue). (b) *J-V* curves obtained from DSSCs with $TiCl_4$ pretreatment (black) and DSSCs without $TiCl_4$ pretreatment (red).

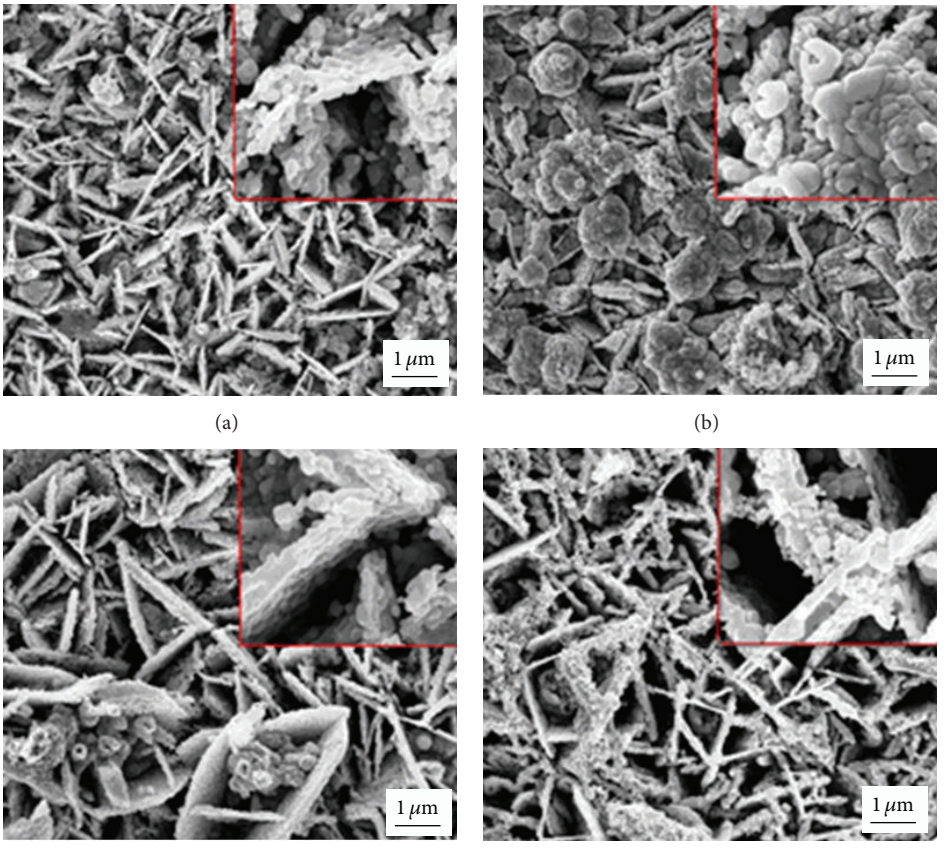

Figure 4: SEM images of preparation ZnO under different electrodeposition times: (a) 2 min, (b) 3 min, (c) 4 min, and (d) 5 min. Part of the insert of the red box for enlargement.

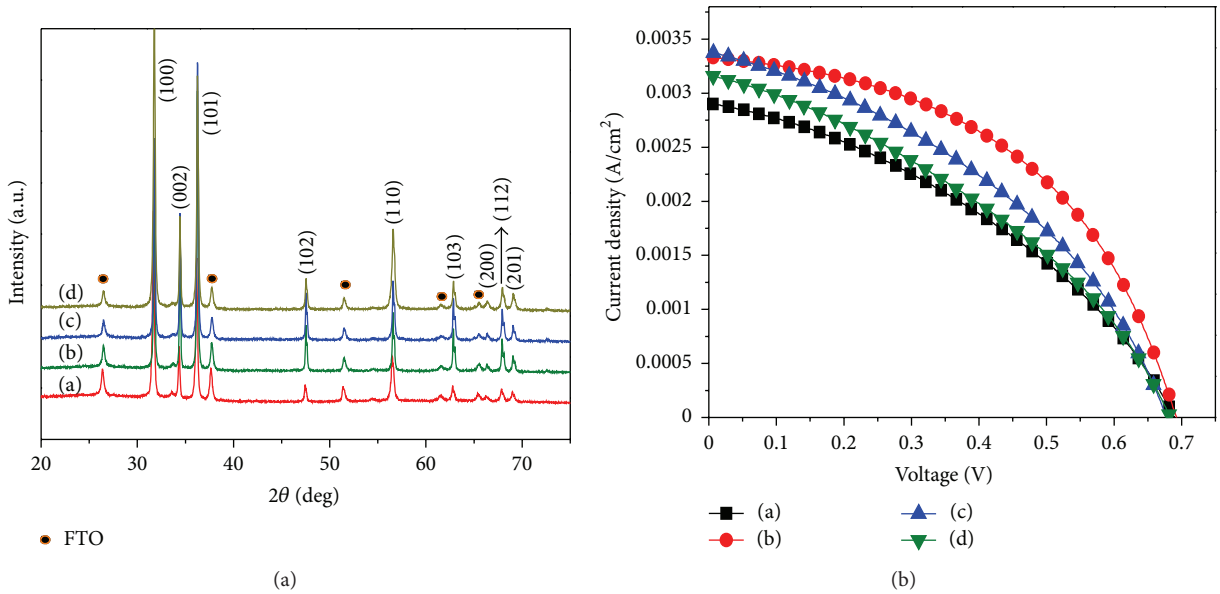

FIGURE 5: (a) XRD pattern of the ZnO films under different electrodeposition times. (b) J-V curves obtained from DSSCs under different electrodeposition times: (a) 2 min, (b) 3 min, (c) 4 min, and (d) 5 min.

films decrease, therefore the performance of the DSSCs get degradation.

4. Conclusions

We have demonstrated an efficient method to prepare high performance ZnO electrode. The ZnO electrode has many porous flakes after $TiCl_4$ pretreatment. In addition, a large number of ZnO nanorods were produced which can offer large surface area to absorb much more dyes. The absorbance of ZnO electrode is increased after $TiCl_4$ pretreatment and light absorption cutoff wavelength presents a remarkable red shift, effectively broadening the range of ZnO on the absorption of sunlight. The solar energy-conversion efficiency which is shown by DSSC fabricated following $TiCl_4$ pretreatment is relatively higher than without $TiCl_4$ pretreatment, when the time of electrodeposition was 3 min, the DSSC based on $TiCl_4$ pretreatment ZnO films showed more superior photoelectrochemical performance under the illumination of one sun (AM 1.5, under 100 mW/cm^2). Since the ZnO films fabricated following $TiCl_4$ pretreatment and deposition of a suitable time, it shows much prospect to be applied in the photoelectrodes of flexible QDSCs or DSSCs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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