Preparation and Properties of Nano ZnO Dye Sensitized Solar Cells on (Titanium) Substrates

Ping Cao
School of Science, Changchun Institute of Technology, Changchun, Jilin Province, 130012, China
caoping@ccit.edu.cn

Abstract. Nowadays, the development of science and technology has been increasing demand for energy. Energy problem has become a bottleneck to restrict the development of international social economy. People pay more and more attention to the development and research of renewable resources. Solar energy is a kind of renewable resource with great potential and no pollution. The commercialized solar cells are mainly silicon solar cells, among which the conversion efficiency of single silicon solar cells is the highest, but the cost of silicon solar cells is high. Therefore, people have been exploring new materials, among which titanium based nano ZnO dye sensitized solar cells have been paid more and more attention by scientists at home and abroad. Based on this, the preparation and performance of nano ZnO dye sensitized solar cells based on titanium are studied. In this paper, the optical anode materials of DSSC are used as the research objects. Three-dimensional ZnO nanoband, one-dimensional graded ZnO nanotube array and one-dimensional sub grade ZnO nanowire array are prepared by anodizing and hydrothermal synthesis. The photovoltaic properties of the three materials are studied. One dimensional graded ZnO, nanotube array films were prepared by two-step hydrothermal synthesis. One dimensional hierarchical ZnO nanowire array is obtained by two-step hydrothermal synthesis. The results show that DSSC is assembled by one-dimensional graded ZnO nanotube array film, and the photoelectric conversion efficiency is 5.1%. Compared with one-dimensional ZnO nanowire array, the efficiency is improved by nearly 90%. The ZnO nanowire of the sub grade is used instead of DSSC The efficiency of photoelectric conversion is only 4% in the photoanode, which is higher than that of the smooth ZnO nanowire photocell.

Keywords: Titanium Substrate, Nano ZnO, Dye Sensitized Dssc, Performance Study.

1. Introduction
The problems of ecological damage, environmental pollution and global warming caused by the arbitrary exploitation of fossil energy and large consumption threaten human survival security increasingly [1-2]. Compared with fossil energy, solar energy and tidal energy have the advantages of abundant resources, wide distribution, safe and pollution-free and other benefits for green development [3-4]. Because the utilization efficiency of new energy is generally low, it can not be widely used. We should strengthen the development of new energy and promote its efficient utilization, so as to effectively alleviate the social problems caused by the depletion of traditional energy and prevent environmental pollution from the source, and finally realize the healthy and sustainable development of human society [5-6]. Compared with other new solar energy sources, the advantages are obvious: safe
and reliable compared with nuclear energy; and not subject to geographical conditions compared with tidal energy and wind energy [7-8].

In the preparation and performance of nano ZnO dye sensitized solar cells on titanium substrate, many experts and scholars have done in-depth research on it, and have achieved good practical results. For example, the DSSC assembled by the low FW composite pair electrode with porous WO$_3$/P obtained 8.9% conversion efficiency, which was 10% higher than that of Pt on DSSC assembled by electrode [9]. The DSSC assembled by the quasi solid electrolyte of low molecular weight large organic gel factor studied by Priyono B obtained the highest photoelectric conversion efficiency of 9.61% [10].

In order to carry out the research, the research status of the photoanode materials of titanium based nano ZnO dye sensitized solar cells is briefly summarized. The photoelectric performance index of nano ZnO dye sensitized solar cells based on titanium is further analyzed. Secondly, based on the photoanode materials of DSSC, one-dimensional graded ZnO, nanotube array films were prepared by two-step hydrothermal synthesis. One dimensional hierarchical ZnO nanowire array is obtained by two-step hydrothermal synthesis. Therefore, in order to verify the effectiveness of this experiment, we have carried on the in-depth analysis to the experimental data.

2. Preparation and Performance of Nano ZnO Dye Sensitized Solar Cells Based on Titanium

2.1 Photoelectric Performance Index of Nano ZnO Dye Sensitized Solar Cells Based on Titanium

In the experiment of DSSC photoelectric conversion, light source is very important. Argon lamp is usually used as the light source in laboratory, because the spectrum of dense lamp is close to that of solar light. The filter is used to remove the strong infrared and ultraviolet rays emitted by argon lamp to obtain white light in visible area, which is used to simulate the solar light for photoelectric test. The radiation condition for defining sunlight is air mass (AM). The radiation flux of light used in photoelectric test in laboratory is AM 1.5. The photoelectric test index of DSSC mainly includes the following points:

1) Short circuit current density: refers to the current of the battery when the resistance of the external circuit of DSSC is 0 (output voltage is zero), which is the maximum photocurrent of the battery. Its value is equal to the absolute number of electron hole pairs converted into photons.

2) Open circuit voltage: refers to the output voltage of the battery when the circuit is disconnected (the output photocurrent is zero), which is the maximum optical voltage of the battery. Theoretically, its value is equal to the difference between the Fermi energy level of ZnO and the energy of the oxidation-reduction pair in the electrolyte when the sun is irradiated on the optical anode.

3) Photoelectric conversion efficiency: refers to the ratio of the maximum output power per unit area to the energy of incident light, and is the most important index to measure the photoelectric performance of DSSC. The properties of dyes, the properties of photoanode, the ability of electronic recombination and the internal resistance of the battery will greatly affect the photoelectric conversion efficiency of DSSC. Therefore, the properties of the optical anode of DSSC have a great influence on the photoelectric conversion efficiency.

2.2 Research Status of Nano ZnO Dye Sensitized Solar Cell Photocatalyst Based on Titanium

The working electrode of solar cell mainly consists of three main parts: the sensitivity of conductive electrode base, porous semiconductor nano film and other dyes. Porous nano semiconductor battery film mainly refers to a dye adsorption carrier and optical electronic signal transmission carrier, which are the most important core of solar battery structure. It is a new type of photoanode material. The porous semiconductor film used by it needs to have a large specific surface area in the air. Therefore, it can directly absorb more dyes and produce more photogenerated electrons. A certain amount of energy is needed between semiconductor, dye molecule and electrolyte called oxidation or reduction, only by the way can the dynamic performance of electrons be met.

Objective at present, in the application of DSSC photoanode materials, semiconductor ZnO nanofilms have the advantages of low production cost, simple preparation process, good stability and
high photoelectric conversion efficiency, but they are still an important hotspot in the research and development of science and technology in recent years. It is found that the preparation technology, crystal types and other microstructure of porous nano semiconductor films have an effect on the photoelectric conversion efficiency of DSSC.

2.3 Calculation Formula
Open circuit voltage is a kind of light voltage when the whole circuit is in or in the open state of the switch. The calculation formula is shown in the following formula (1):

$$ V_{OC} = \frac{1}{q(E_{femi} - E_{OX} / \text{Rad})} $$

(1)

The formula for filling factor is shown in formula (2):

$$ \text{FF} = \frac{P_{opt}}{I_{SC} \times V_{OC}} = \frac{I_{opt} \times V_{opt}}{I_{SC} \times V_{OC}} $$

(2)

Photoelectric conversion efficiency: the total photoelectric conversion efficiency of the battery can be calculated by the following formula (3):

$$ \eta = \frac{\text{FF} \times I_{SC} \times V_{oc}}{I_s} $$

(3)

3. Preparation and Performance of Nano ZnO Dye Sensitized Solar Cells on Titanium Substrate

3.1 Experimental Design of DSSC Performance of One-Dimensional Graded ZnO Nanotube Array Film
Nano ZnO is a n-type semiconductor with a bandwidth of 3.37eV, and has many advantages such as good stability, safety, non-toxic and high refractive index. In the research of DSSC, in order to improve the efficiency of DSSC, the ZnO nanofilm, which is one-dimensional porous structure of photoanode material, has been favored by many researchers at home and abroad. Compared with the traditional ZnO nanocrystal particles, one dimensional ZnO nanorods and nanotubes have better photovoltaic properties: stronger scattering ability to incident light, faster transmission speed of photogenerated electrons in their internal structure, lower probability of recombination of photogenerated electrons and dye molecules in electrolyte solution than before, and the longer use time of photoelectrons has an effect of prolonging. In the research of one-dimensional ZnO nano films, the preparation of photoanode of ZnO nanotube film and its application in DSSC are the hot spots. Compared with the ti_o nanoarray film obtained by the first hydrothermal reaction, the graded ZnO nanotube array film can effectively increase the specific surface area of the film on its tubular structure and the surface covered with various nano cell particles, and improve the adsorption capacity of dye. The DSSC can be assembled by the nano tube array thin film material, which can be divided into ZnO and can be divided into three grades. The conversion efficiency of photoelectric signal is 5.0%.

3.2 Experimental Research and Design of DSSC Performance for One Dimensional Graded ZnO Nanowire Array Film
ZnO is a wide band gap semiconductor, and its structure and physical properties are in some way connected with TiO₂. However, ZnO has higher electron mobility and faster electron transmission is conducive to reduce the charge recombination in the battery. ZnO has been widely used in DSSC. Although the efficiency of ZnO battery is lower than that of using ZnO as material cell, ZnO is still regarded as the only material that can replace the dye-sensitized solar cell photoanode of ZnO.
Dye sensitized solar cell is a new type of solar energy which is developed by imitating the principle of photosynthesis. The nano crystalline semiconductor film has a high specific surface area, so it can form many monolayer and absorb a lot of dyes. At the same time, the porous structure enables the light irradiated on the battery to pass through the semiconductor film repeatedly, which greatly improves the utilization of solar light.

4. Preparation and Performance of Nano ZnO Dye Sensitized Solar Cells Based on Titanium

4.1 Performance Analysis of DSSC of One-Dimensional Graded ZnO Nanotube Array Film

The effect of the scattering ability of semiconductor nano film on the light current is studied. Table 1 shows the diffuse reflectance spectra of the ZnO nanowire array and the graded ZnO nanotube array.

Table 1. Diffuse reflectance spectra of ZnO nanowire arrays and graded ZnO nanotube arrays

| Wavelength(nm) | rod | tube |
|----------------|-----|------|
| 300            | 9   | 8    |
| 350            | 13  | 12   |
| 400            | 43  | 85   |
| 500            | 44  | 84   |
| 600            | 43  | 83   |
| 700            | 59  | 82   |
| 800            | 56  | 81   |

Figure 1. Diffuse reflectance spectra of ZnO nanowire arrays and graded ZnO nanotube arrays

It can be seen from Figure 1 that the graded ZnO nanotubes have better scattering ability of incident light in the visible spectrum range. The graded ZnO nanotubes have hollow tubular structure and more rough surface structure covered with nanoparticles. Compared with the graded ZnO nanowires, the multiple reflection of incident light in the film effectively increases the transmission distance in the film, increases the optical current and improves the photoelectric conversion efficiency of DSSC.

4.2 DSSC Performance of 4.2-Dimensional Graded ZnO Nanowire Array Film
The scattering ability, light capture efficiency and short circuit current of semiconductor thin films are studied in this paper. Classification grade of ZnO nanowire film and other components the diffuse reflectance spectrum visible in UV is shown in Table 2:

### Table 2. UV Vis diffuse reflectance spectra of ZnO Nanowire Films and graded ZnO Nanowire Films

| Wavelength(nm) | 300 | 350 | 375 | 400 | 650 | 750 | 800 |
|----------------|-----|-----|-----|-----|-----|-----|-----|
| W              | 12  | 32  | 58  | 55  | 48  | 54  | 53  |
| HW             | 5   | 6   | 50  | 80  | 79  | 78  | 77  |

![Figure 2. UV Vis diffuse reflectance spectra of ZnO Nanowire Films and graded ZnO Nanowire Films](image)

According to the test results in Figure 2, the radiation ability of graded ZnO nanowire film for the incoming light is significantly higher than that of ZnO nanowire film. The main reason is that after the second step solvent heating reaction, we need to get a large number of nanorods, which are connected between the incident light and the surface. In addition, they also cover the gap between the two nanowires in the light, which effectively enhances the ability of nanowires to deviate from the light.

### 5. Conclusions

High efficiency has been achieved in dye-sensitized ZnO solar cells, but the further improvement of DSSC efficiency is limited. This is because in the process of electron transfer, the electrons recombine with the dye molecules in the oxidation state or the electron acceptors in the electrolyte. With the increase of the thickness of the photoanode, the phenomenon of electron recombination will be more obvious. Based on the titanium substrate, the method of optimizing the experimental conditions can be used to reduce the diameter of the tube, so as to achieve the purpose of adsorbing more dyes and improve the photoelectric conversion performance of DSSC.

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