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Research on solar cell preparation technology for cutting-edge technology

Zhuoran Ji

UCL (University College London), London, United Kingdom

zccajix@ucl.ac.uk

Abstract. Flexible dye-sensitized solar cells are highly valued as a practical technology with low production costs. In this paper, we study flexible dye-sensitized solar cells consisting of nanocrystalline TiO2 thin-film electrodes based on titanium metal and counter electrodes based on conductive coated polymers. In order to improve the photoelectric conversion efficiency, nanocrystalline TiO2 film electrodes and TiO2 nanotube film electrodes based on titanium metal and TiO2 nanotube film electrodes are prepared by DC low-field electrophoretic deposition, electrochemical anodizing and screen printing under DC and pulse voltages combined with high-temperature sintering methods; and platinum-carrying counter electrodes and carbon counter electrodes based on conductive coated polymers are prepared by low-temperature techniques, such as constant-current electrochemical deposition and chemical reduction. The mechanisms and characteristics of different preparation methods and optimization techniques are analyzed and discussed, and the performances of nanocrystalline TiO2 thin film electrodes and counter electrodes prepared by different methods are compared. On this basis, the all-flexible solar cell is developed, and the maximum photoelectric conversion efficiency reaches 6.74%.

Keywords: frontier technology; solar cell; preparation technology.

1. Introduction

Dye-sensitized solar cells based on semiconductor nanocrystalline thin films have received widespread attention due to their high efficiency and low cost. In particular, the ease of fabrication process technology makes it show great potential in reducing the cost of mass production. In order to achieve the goal of practicalization and make its products competitive in the market, research efforts over the years have focused on improving the photoelectric conversion efficiency, increasing the service life and reducing the production cost. Currently reported photoelectric conversion efficiencies reach ~11%, close to the level of amorphous silicon cells. By replacing the liquid electrolyte with a conductive polymer electrolyte and realizing the solid state of the electrolyte, the stability of the cell is improved and the service life is increased. At the same time, in order to more effectively reduce production costs and simplify the fabrication process, to facilitate large-scale industrial production, as well as to expand its application range, the development of flexible solar cells as a competitive and practical technology has been highly valued and has made great progress.

2. Frontier Technology Trends and Research

With the increasing global demand for renewable energy, the research and development of solar cell preparation technology is of great significance as a clean and sustainable energy conversion device. In this paper, we will discuss the research on solar cell preparation technology for frontier technology.

Chalcogenide solar cells: Chalcogenide-type materials have great potential in the field of solar cells due to their excellent photovoltaic properties. At present, the research and development of chalcogenide solar cells are mainly focused on improving photoelectric conversion efficiency, stability and cost reduction.

Heterojunction solar cells: Heterojunction solar cells are a cell structure that combines two different materials to utilize their respective advantages. This cell structure can effectively improve light absorption and carrier separation efficiency, thus improving photoelectric conversion efficiency.

Transparent Conductive Oxide (TCO) Solar Cells: TCO solar cells are a type of solar cell that can utilize visible light, and the key technology is to find efficient, stable and cost-appropriate TCO materials.

Chalcogenide solar cell preparation: The key lies in finding suitable chalcogenide materials and optimizing the film preparation process to achieve efficient, stable and low-cost chalcogenide solar cells. Specifically, the photoelectric conversion efficiency can be improved by adjusting the components of the chalcogenide material, controlling the film thickness, and optimizing the film crystallization process.

Heterojunction solar cell preparation: It is necessary to optimize the growth conditions of the two materials separately and achieve a perfect combination between them. For example, the thickness and interfacial structure of the materials can be precisely controlled by processes such as molecular beam epitaxy (MBE) or chemical vapor deposition (CVD) to achieve efficient carrier transport and light absorption.

TCO solar cell preparation: The key lies in finding suitable TCO materials and optimizing the thin film preparation process. For example, sputtering, evaporation, spraying and other processes can be used to prepare TCO films, while optimizing the conductivity and optical properties of the film by adjusting the process parameters.

3. Preparation and performance of flexible nanocrystalline TiO2 thin film electrode

Flexible nanocrystalline TiO2 thin film electrodes were prepared by high temperature sintering using titanium metal foil as the substrate and the following different methods were used to analyze and compare their properties.

3.1 DC low-field electrophoretic deposition

Electrophoretic deposition refers to the directional movement of charged particles in the suspended liquid under the action of a DC electric field, deposited on the electrically opposite substrate, forming particle aggregation and distribution.

The formation of a porous structure with uniform particle aggregation and distribution. The suspension liquid used for electrophoretic deposition of nanocrystalline TiO2 thin film electrodes was dispersed by ultrasonication in a solvent mixture of n-butanol, isopropanol, and anhydrous ethanol (8:4:2), with the addition of an appropriate amount of TiO2 nanocrystalline particles (P25). Two titanium foils were placed symmetrically and parallel to each other in the suspension as cathode and anode, respectively.

3.1.1 Chemical treatment to optimize nanocrystalline TiO2 thin film electrodes

Chemical treatment is to change and optimize the physical and chemical properties of the electrode surface by surface modification and adsorption of organic or inorganic molecules. The specific treatment process is to dip the nanocrystalline TiO2 thin-film electrode with titanium foil as the substrate into 0.2M tetrabutyl titanate (TBT) in butanol solution, and then dried at 100 ℃ for 1 h. X-ray diffraction (XRD) analysis revealed that the nanocrystalline TiO2 thin-film electrode showed typical anatase-type and rutile-type XRD peaks before the chemical treatment of TBT, and the XRD peaks did not change after the chemical treatment of TBT. did not change. It indicates that the TBT chemical treatment has no effect on the crystalline type of the nanocrystalline TiO2 thin film electrode. The effect of chemical treatment is that the hydrolysis of TBT generates TiO2 with amorphous structure during the treatment process, which is transformed into anatase structure when the nanocrystalline film is subsequently heated and sintered at 450 ℃. TiO2 generated by hydrolysis of

TBT wraps around electrophoretically deposited nanocrystalline grains, which effectively strengthens the adhesion of the nanocrystalline grains with each other and with the titanium foil substrate.

3.1.2 Light scattering effect increases light energy absorption

Theoretical and experimental studies have proved that the use of TiO2 grains of light scattering effect can increase the dye-sensitized nano-crystalline TiO2 film electrode light energy absorption, which is an effective way to improve the photocurrent and photoelectric conversion efficiency of photovoltaic cells.TiO2 grains have the characteristics of strong light scattering, through the scattering of the grains, you can increase the absorption of photons in the dye-sensitized nano-crystalline TiO2 film electrode, thus increasing the absorption distance. The absorption of light energy. For this reason, we designed a double-layer structure nanocrystalline TiO2 thin film electrode consisting of a light scattering layer and a transparent layer. The preparation method is to add an appropriate amount of TiO2 large grains (100 nm) to the organic suspension of TiO2 nanocrystalline grains (P25) as described above, and electrophoretic deposition of the titanium foil first in the organic suspension containing a mixture of TiO2 large and small grains to form a light-scattering layer doped and interconnected by the grains with a particle size of 100 nm25 nmTiO2 grains. Then on the light scattering layer was further electrophoretically deposited in an organic suspension of TiO2 nanocrystalline grains (P25) in a transparent layer interconnected by TiO2 grains with a particle size of 25 nm, and the light scattering layer and the transparent layer were subjected to TBT chemical treatment and sintering, respectively. The bilayer structure of the nanocrystalline TiO2 thin film electrode with a film thickness of 11 μm, of which the thickness of the light scattering layer was about 6 μm, was electrophoretically deposited under DC low field, followed by high-temperature sintering, which is a simple and feasible method to prepare flexible TiO2 nanocrystalline thin film electrodes based on titanium foil. Adjusting the current, time and suspension composition of electrophoretic deposition can effectively control the thickness of the thin-film electrode and optimize the porous microstructure parameters. The chemical treatment further improves the mutual adhesion between the nanocrystalline grains and enhances the adhesion between the grains and the titanium foil substrate, which increases the electron transport rate. Meanwhile, the surface defects of the nanocrystals were passivated, which reduced the photogenerated electron compounding chance and greatly increased the electron collection efficiency. On this basis, the light scattering effect of TiO2 grains was utilized to significantly increase the absorption of light energy and improve the photocurrent output efficiency, so that the photoelectric conversion efficiency of the photovoltaic cell reached 6.33% (Table 1）

Table 1 Photoelectric conversion performance of the flexible working electrodes

flexible working electrode TiO2 /Ti	JSC mA/cm2	VOC mV	η%	ff	thickness μm	Loading amount mol/cm2
Electrophoretic deposition	14.15	697	6.33	0.65	11	0.90×10－7
anodization	8.33	722	4.28	0.71	40	1.06×10－7
anodization+electrophoretic deposition	14.37	635	6.28	0.69	40	1.68×10－7
Pulse anodization	19.25	619	7.36	0.62	40	1.96×10－7
Screen printing	14.91	675	6.99	0.75	18	2.20×10－7

3.2 Electrochemical anodizing

Electrochemical anodic oxidation of titanium foil in fluoride-containing electrolyte resulted in the formation of highly ordered, vertically aligned array structure of TiO2 nanotubes on its surface. Due

to the hollow structural characteristics of the nanotubes, the formed ordered arrayed TiO2 nanotube structure has a large inner surface, which provides more locations for adsorption of monolayer dyes than the usual nanocrystalline TiO2 film, thus greatly increasing the amount of dye monolayer adsorption. Electron transport in the one-dimensional structure of TiO2 nanotubes is mainly along the axial direction of the nanotubes and does not pass through the grain interfaces, thus accelerating the electron transport and reducing the electron complexation chance. In addition, the TiO2 nanotube structure has strong light scattering properties, which is conducive to improving the absorption of light energy.TiO2 nanotube films have these unique properties, so that the dye-sensitized solar cells with TiO2 nanotube films as photoanodes show obvious advantages in improving the photoelectric conversion efficiency. The electrochemical anodic oxidation of titanium foil was carried out in a two-electrode electrolytic cell with titanium foil as the anode and platinum sheet as the cathode, with an applied DC voltage of 60 V. The anodic oxidation process was carried out for 40 h. From the scanning electron microscope morphology (Fig. 1), vertically oriented and ordered TiO2 nanotubes were formed in a cylindrical morphology on the titanium foil substrate. The inner diameter of the nanotube pores is 90 nm, and the thickness of the tube wall is 20 nm, with a relatively smooth outer surface.

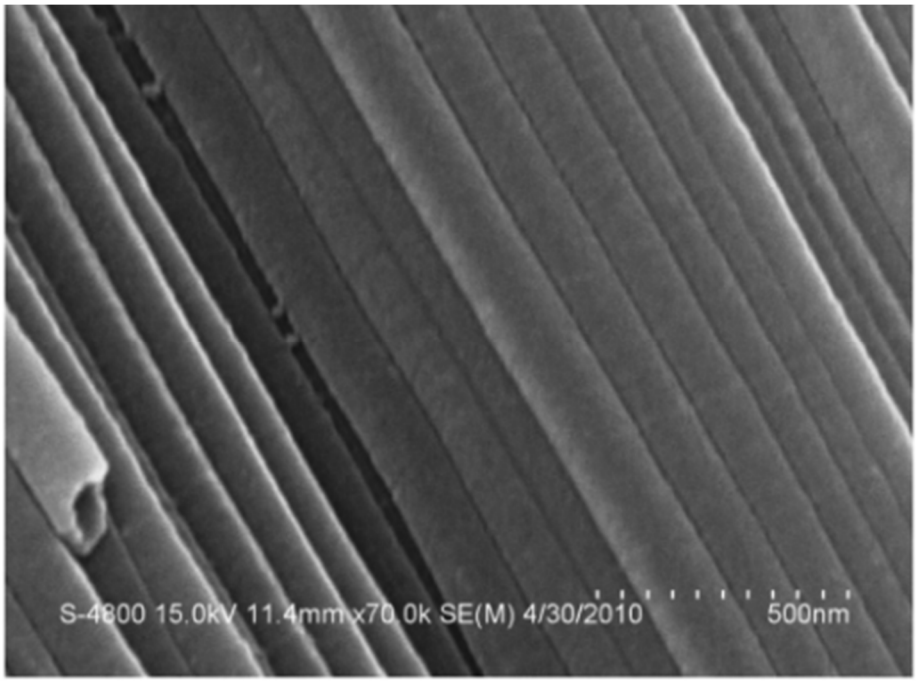

Fig. 1 SEM image of TiO2 nanotube film electrode prepared by electrochemical anodization under DC voltage

In order to further increase the specific surface and dye adsorption, the TiO2 nanotube film electrode prepared above was further electrophoretically deposited in an ethanol suspension containing 20% TiO2 pellets (particle size 10 nm) (DC voltage 20 V, deposition time 30 s). XRD analysis indicated that the TiO2 nanotube film electrode and further electrophoretically deposited TiO2 pellets were amorphous before high-temperature sintering. amorphous crystalline form before high temperature sintering and transformed to anatase crystalline form after high temperature sintering. From the data listed in Table 1, it can be seen that the TiO2 nanotube film electrode, through further electrophoretic deposition of TiO2 colloidal particles, effectively increases the specific surface, which is manifested as an increase in the adsorption of dyes, which greatly improves the absorption of light energy, leading to a significant increase in the photocurrent of the photocell, and improves the photoelectric conversion efficiency from 4.28% to 6.28%.

2.2.1 Anodizing under pulse voltage

The anodic oxidation of titanium foil was carried out under pulsed voltage (i.e., 45 V for 100 ms and 60 V for 25 ms alternately) for 40 h. The morphology of TiO2 nanotubes formed is shown in Fig. 2. The inner diameter of the nanotube pores and the thickness of the wall of the nanotubes are similar

to that of the nanotubes generated by the anodic oxidation under DC voltage, which are 90 nm and 20 nm, respectively, and the outer surface of the tubes appears regular knobbed ripples, and the spacing of the ripples is about 70 nm. Due to the existence of nodular ripples on the outer surface, the surface roughness was effectively increased, which led to a significant increase in dye adsorption, which was conducive to the enhancement of the light energy absorption of the TiO2 nanotube thin-film electrodes, resulting in an increase in the photocurrent of the photovoltaic cell, and the photovoltaic conversion efficiency reached 7.36%. The electrochemical anodic oxidation method can realize the self-assembled directional growth of ordered arrangement of TiO2 nanotubes on the titanium foil substrate, forming TiO2 nanotube thin film electrodes with titanium foil as the substrate. As the photoanode of the flexible solar cell, the inner diameter, outer diameter, length and the morphology of the outer surface (wall) of the TiO2 nanotubes have a crucial influence on the photoelectric conversion performance of the photovoltaic cell. The biggest advantage of the electrochemical anodizing method is that the structural parameters affecting the photoelectric conversion performance can be easily regulated in a wide range by changing various conditions of the anodizing process. Further surface modification and modification techniques such as chemical treatment can also be used to optimize the structural parameters of the nanotube morphology. Therefore, due to the geometric structure of TiO2 nanotube thin film electrode itself, as well as in the electrochemical anodic oxidation process is easy to achieve the regulation and optimization of its structural morphology parameters, so that TiO2 nanotube thin film electrode produces many characteristics superior to the nano-crystalline TiO2 thin film electrode, to improve its photoelectric performance and photovoltaic efficiency of photovoltaic batteries to show a lot of potential.

4. Preparation and performance of flexible pair electrode

To assemble the counter electrode of flexible solar cell with nanocrystalline TiO2 thin film electrode based on titanium foil, it is required to use polymer material with good light transmittance as the substrate.

It requires the use of a polymer material with good light transmission as the substrate to ensure that the loss of light energy incident from one side of the counter electrode is minimized. Polymer thin ITO-PEN (Indium Tin Oxide Conductive Layer/Polyethylene Naphthalene Dicarboxylate) with conductive coating has good light transmittance, airtightness and flexibility, high electrical conductivity, resistance to organic solvents, and light weight, easy to transport, easy to process, and it is a flexible substrate material that meets the requirements for the preparation of counter electrodes.

4.1 Low temperature preparation of platinum-carrying counter electrode

In dye-sensitized solar cells, the I3-reduction reaction on the counter electrode is electrochemically irreversible, especially in the organic electrolyte.The catalytic activity of FTO conductive glass for the I3-reduction reaction is very low, so in order to improve the kinetic behavior of the I3-reduction reaction process and reduce the energy loss of the counter electrode, it is required to use a platinum-loaded substrate in the FTO conductive glass. Therefore, in order to improve the kinetic behavior of the I3-reduction reaction process and reduce the energy loss to the electrode, it is required to load the precious metal platinum with catalytic properties on the FTO conducting glass to form a platinum-carrying counter electrode, Pt/FTO, in order to improve the electrocatalytic performance of the counter electrode. In order to obtain ITO-PEN-based Pt-carrying counter electrodes for flexible solar cells, we have investigated the low-temperature preparation technique of Pt/ITO-PEN and the performance of low-temperature prepared Pt/ITO-PEN. The electrochemical AC impedance spectroscopy study was applied to analyze the electrocatalytic performance of the prepared Pt/ITO-PEN counter electrode for the I3- reduction reaction (I3-+3e→3I). The frequency range of the AC impedance spectrum, 10 Hz-100 kHz, reflects the resistive-capacitive (RC) process at the electrode/electrolyte interface, which can be expressed in terms of the interfacial charge transfer resistance, Rct, and the interfacial bilayer capacitance (the frequency ranges of >100 kHz and <10 Hz reflect the series resistance and Nernst diffusion impedance of the system, respectively). Therefore,

estimation of Rct from the measured AC impedance spectra allows the analysis of the electrocatalytic performance of the deprotonated electrodes. The Rct of the electrodeposited Pt/ITO-PEN was 2.18 Ohm-cm2, indicating that the Pt/ITO-PEN has good electrocatalytic performance.

4.2 Low temperature preparation of carbon counter electrode

Carbon materials are characterized by high electrical conductivity, high chemical and thermal stability, especially resistance to iodine corrosion, and good electrocatalytic activity for I3-reduction reaction. Moreover, the material price of carbon is considerably lower than that of metallic platinum, making it the most attractive alternative material to metallic platinum in the study of counter electrodes for dye-sensitized solar cells. In order to reduce the cost of cell production, the study of counter electrodes based on various carbon materials such as graphite, activated carbon, carbon black, carbon nanotubes, etc. has received wide attention in recent years. Mesoporous carbon (MC) has a large specific surface favorable for improving electrocatalytic performance. For this reason, we chose mesoporous carbon as an alternative material to platinum and prepared MC/ITOPEN counter electrodes by a low-temperature method.

Mesoporous carbon powder (specific surface area 400m2g-1, pore size 6.8nm), crushed by ball milling, mixed with a small amount of TiO2 pellets (2wt%), dispersed in tetrabutyl titanate (TBP) n-butanol solution, this mixture was uniformly coated with the surface of the ITO-PEN substrate, rinsed with distilled water after drying, and finally put in the air atmosphere at 140°C. The purpose of mixing a small amount of TiO2 particles and TBP in the mesoporous carbon coating solution is to increase the adhesion between the mesoporous carbon particles and the adhesion with the substrate. The small amount of TiO2 particles mixed in the mesoporous carbon coating solution was transformed into TiO2 nanocrystals (particle size of about 20 nm, anatase crystal type) after heat treatment at 140°C. The TBP in the coating solution was hydrolyzed during distilled water rinsing and heat treatment, and TiO2 nanocrystals were grown in-situ, which greatly enhanced the electrical and mechanical properties of the electrodes by MC/ITO-PEN, with the combined effect of the externally applied and in-situ grown TiO2 nanocrystals. electrical and mechanical properties were greatly enhanced.

In fact, the contents of TiO2 nanocrystals and TBP in the coating solution have a great influence on the performance of MC/ITO-PEN. When too much was added, it not only caused serious agglomeration of mesoporous carbon particles, but also reduced the electrical conductivity and effective area, leading to a decrease in the electrocatalytic performance, which adversely affected the improvement of the photoelectric conversion efficiency of the photovoltaic cells. The photovoltaic conversion efficiency of photovoltaic cells assembled with Pt/ITO-PEN counter electrodes prepared by electrochemical deposition is higher than that of Pt/ITO-PEN counter electrodes prepared by chemical reduction, while the photovoltaic conversion efficiency of photovoltaic cells assembled with MC/ITO-PEN counter electrodes is lower. This reflects the difference in electrocatalytic performance of the counter electrodes prepared by different methods.

5. Conclusion

The research of solar cell preparation technology oriented to frontier technology is an important research direction in the current energy field. Although there are still some challenges, such as material stability, manufacturing cost, large-scale production and other issues, with the continuous deepening of scientific research and the development of new materials and processes, we have reason to believe that these challenges will be gradually overcome. In the future, with the advancement of technology and the expansion of application fields, solar cells will play a more important role in the transformation of global energy structure.

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