Study on photoelectric performance of dye-sensitized solar cells based on ZnO composite photoanodes

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Abstract: Photoanodes are an indispensable part of dye-sensitized solar cells (DSSCs). The preparation process and method of photoanodes are important factors affecting the photoelectric performance of DSSCs. In this study, ZnO photoanodes were prepared on FTO conductive glass coated with ZnO seed layer by hydrothermal method, and a light scattering layer was introduced, and DSSCs were assembled. SEM and XRD were used to study the microstructure and phase structure of the generated crystals, and the photoelectric performance of the assembled dye-sensitized solar cells was tested by an electrochemical workstation. The results show that the photoelectric performance is better when ZnO nanosheets are placed in 0.07M zinc nitrate/urea growth solution at 90℃ for 4h reaction light scattering layer. The Short-circuit current density (Jsc), Open-circuit voltage (Voc), Fill factor (Fill factor) of the obtained cell were obtained. FF) and photoelectric conversion efficiency (PCE) are 17.05mA/ cm-2, 0.61V, 0.59 and 6.05%, respectively.

Key words: Dye-sensitized solar cell; ZnO composite photoanode; Hydrothermal method; Photoelectric performance

Introduction

In 1991, Professor Michael Gratzel of the Federal Ecole Polytechnique in Lausanne, Switzerland, prepared dye-sensitized solar cells (DSSCs) for the first time, and obtained a photoelectric conversion efficiency of 7.1%. DSSCs are composed of a conductive glass substrate, a photoanode, a dye photosensitizer, a REDOX electrolyte and a counterelectrode. Due to the wide spectral response range, low cost, stable performance and environmental friendliness of DSSCs, TiO2 and Zno-based DSSCs have attracted extensive attention from researchers in recent years, and their photoelectric conversion efficiency is up to 14.3%. However, the photovoltaic conversion efficiency of DSSCs with TiO2 as photoanode still lags behind that of silicon-based solar cells. This is because: the disordered structure on the surface of TiO2 nanoporous films makes the electron transport path tortuous and the electron diffusion coefficient small; The photogenerated carrier is constantly missing in the process of transport; The efficiency decreases with the increase of the area, and the morphology is relatively simple, which leads to a certain limit on the breakthrough of its subsequent photoelectric performance. As a semiconductor material, ZnO has a molecular weight of 81.39, a density of 5.605g/cm3, a melting point of 1975℃, a band-gap width of 3.37eV, high electron mobility advantages, ZnO crystallinity is good, and the morphology is more rich than TiO2. Excellent ZnO photoanode structure should have: strong dye-adsorption performance; Fast, direct electron transport channel; Large specific surface area; It is widely used in light emitting diode, nano generator, DSSCs and so on

It was found that three-dimensional nanoflowers, nanoaggregates (NAs), nanosheets (NSs) and other multi-level structures have a large enough specific surface area to be used as a light scattering layer to improve the light trapping ability of the photoanode film. In 2020, K. Rajan Aneesiya et al. prepared Cu2+ doped ZnO photoanode by one-step coprecipitation method, which significantly increased the Voc of this battery and increased the photoelectric efficiency. This is because Cu ions are incorporated into the ZnO structure and Fermi level guide band edge shift results. Y T Shi et al. used ultrasound to prepare ZnO NSs with composite structure. The nano-sheets of this composite structure are stacked on each other to form a three-dimensional nanoflower structure. The photoanode of this structure has a large specific surface area and light scattering ability, and its DSSCs have obtained a photoelectric efficiency of 6.42%. And ZnO nanoaggregates have better light scattering ability, so that the transmission path within the film is increased, the production of DSSCs photoanode materials often use it. Especially in 2010, the PCE reached 6.1% by preparing Li-doped ZnO NAs structured photoanodes. The nanocrystalline size increased from 10nm to 12nm, resulting in the formation of ZnO nanocrystalline agglomeration of good monodisperse ZnO nanospheres, broaden the light absorption spectrum, in which Li+ played a role in inducing the growth of ZnO crystals. However, there are a large number of gaps and surface defects in the NAs structure, and the transport path of photogenerated electrons in the photoanode film is reduced, which reduces the electron collection rate. In this paper, ZnO composite photoanode was prepared by hydrothermal method with zinc nitrate hexahydrate/urea as raw material. The effects of growth liquid concentration and reaction time on photoelectric properties of composite ZnO were studied.

1 Experiment

1.1 Experimental Ingredients

Zinc (Zn(NO3)2•6H2O) hexahydrate, diethylene glycol (HOCH2CH2OCH2CH2OH), Huainan Chemical Reagent Factory, Anhui Province; Zinc acetate dihydrate (C4H10O6Zn), lithium acetate dihydrate (C2H7LiO4) Isopropyl alcohol (C3H8O), Sinopod Chemical Reagent Co., LTD.; Chloroplatinic acid (H2PtCl6), Sodium hydroxide (NaOH), Urea China Sinoppharma Group Shanghai Chemical Reagent Co., LTD.; Fluorinated SnO2 conductive glass, Pilkington Group Co., LTD.; N719 dye, Taiwan Yongguang Chemical Industry Co., LTD.

1.2 FTO conductive glass cleaning

After the FTO conductive glass was soaked in acetone and anhydrous ethanol, ultrasonic washing was carried out to remove surface dirt, followed by ultrasonic cleaning with deionized water for 20 min, repeated 3 times, and finally dried in a 90℃ oven and put into a clean container for use.

1.3 Preparation of ZnO nanosheet film

Firstly, a certain amount of Zn(NO3)2•6H2O and urea were added to 300 mL of deionized water, and then fully stirred to obtain 0.15mol. L-1 growth solution. Preheat the growth solution until the solution becomes turbid, and then tilt the FTO glass into the growth solution at 90℃ for 4h. After the reaction, the sample is repeatedly rinsed in deionized water to remove surface impurities and dry. The sample was placed in Muffle furnace and annealed for 30min in oxygen atmosphere at 350°C.

1.4 Preparation of ZnO agglomerate-nanosheet composite film

The synthesis method of ZnO agglomerate-nanosheet composite film is described in the literature. ZnO composite film was prepared by hydrothermal method, and different concentrations of hexahydrate zinc nitrate/urea growth liquid were prepared into the reactor, and then the prepared ZnO aggregate film was tilted in the growth liquid with the film face down, and then reacted in the oven at 90℃ for 4h. After the reaction, the sample was repeatedly rinsed and dried. Finally in 350℃ oxidizing atmosphere for 30min annealing heat treatment, that is to get ZnO aggregate - nanosheet composite film.

The ZnO aggregate film was placed in a reactor containing 0.07 mol.L-1 growth liquid and reacted at 90℃. The influence of reaction time on the photoelectric properties of composite ZnO was investigated. After the reaction, the samples were taken out and rinsed with deionized water repeatedly until clean, dried and calcined to obtain ZnO composite film.

1.5 Preparation of electrolyte and dye

The electrolyte solution was purchased from Wuhan Semak Biotechnology Co., LTD. It contains a mixture of acetonitrile, LiI and I2.

The 0.5 M N719 dye solution was prepared by dissolving a certain amount of N719 dye in ethanol and tert-butanol solution with a volume ratio of 1:1.

1.6 Assembly and test of ZnO dye-sensitized solar cells

The ZnO NAs/NSs composite structural photoanode was impregnated for 2h in N719 ethanol solution at 60℃ under the condition of avoiding light in order to fully absorb the dye. After sensitization, the ZnO photoanode and platinum electrode were packaged into a battery, and the liquid electrolyte was injected into the battery to test the photoelectric performance parameters under the sunlight simulated light source.

2 Results and discussion

2.1 Study on ZnO composite photoanode with growth solution concentration

Because ZnO aggregates have good light scattering ability, and ZnO nanosheets have high specific surface area and excellent dye adsorption capacity. In this experiment, ZnO composite photoanodes were prepared by combining ZnO aggregates with ZnO nanosheets, and the effect of growth solution concentration on ZnO composite photoanodes was studied. The specific methods are as follows: in the concentration of 0.05M, 0.07M, 0.15M, 0.20M, 0.25M growth liquid hydrothermal reaction to obtain ZnO composite photoanode film. They are numbered as 0.05-ZnO, 0.07-ZnO, 0.10-ZnO, 0.15-ZnO, 0.20-ZnO, 0.25-ZnO, where 0-ZnO is ZnO NAs photoanode film, as a comparison reference.

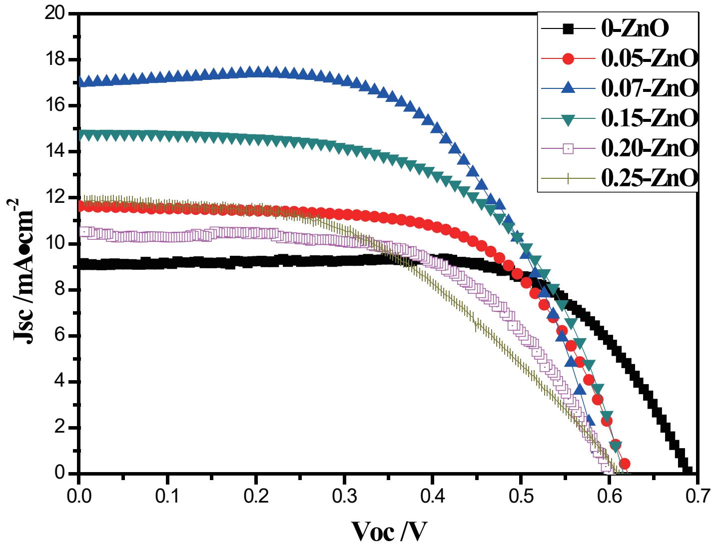

Fig.1 Current density-voltage characteristic for DSSCs with different growth solution concentrations

Tab.1 Photovoltic parameters of DSSCs with different growth solution concentrations

Samples	Jsc /mA•cm-2	Voc /V	FF	PCE/%
0-ZnO	9.21	0.64	0.60	3.61
0.05 - ZnO	11.43	0.64	0.62	4.55
0.07 - ZnO	17.05	0.61	0.59	6.05
0.15 - ZnO	14.77	0.61	0.60	5.41
0.20 - ZnO	10.55	0.61	0.59	3.76
0.25 - ZnO	11.89	0.61	0.46	3.40

FIG. 1 shows the voltammetry characteristic curves of DSSCs with different growth solution concentrations, and Table 1 shows their photoelectric performance parameters. As can be seen from the figure, the photoelectric conversion efficiency also showed an increasing trend with the increase of growth liquid concentration. The composite photoanode grown in 0.07M growth solution has the best photoelectric performance, and the Jsc, Voc, FF and PCE of DssCs are 17.05 mA•cm-2, 0.61V, 0.59 and 6.05%, respectively. Compared with single ZnO NAs photoanode, both PCE and Jsc are significantly increased, which is caused by the recombination of more electron hole pairs when electrons are transferred to the electron transport layer, so the photoelectric efficiency is further improved.

2.2 Explore the study of reaction time on ZnO composite photoanode

Through the experiment of 2.1, it is found that the photoelectric efficiency of composite ZnO photoanode is better than that of single ZnO NAs photoanode. In order to further obtain better photoelectric efficiency, the experiment improved the Voc or FF by regulating the reaction time, thereby increasing the PCE. The reaction time of the reactor was set to 2h, 3h, 4h and 5h, and the numbers were F2, F3, F4 and F5 respectively.

3 Conclusion

ZnO NAs films were prepared by hydrothermal method and ZnO NSs composite films were prepared by introducing ZnO NSS light scattering layer grown with Zn(NO3)2•6H2O and urea as raw materials. The effects of the concentration of growth solution and reaction time on the photoelectric properties of Zno-based DSSCs were studied. The results show that the photoelectric conversion efficiency of ZnO composite photoanodes is significantly higher than that of single ZnO NAs photoanodes. When reacting in 0.07M growth solution for 4h, the obtained ZnO composite photoanode has the best photoelectric performance, and its performance parameters are as follows: Voc=0.61V, Jsc=17.05 mA•cm-2, FF=0.59, PCE=6.05%. With the increase of reaction time, the internal defects of the photoanode film will increase, the internal resistance of the battery will increase, the electron hole pair will decrease, and the photoelectric conversion efficiency of the battery will be reduced.

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