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Preparation and characterization of TiO_2 anode film with spinodal phase separation structure in dye-sensitized solar cells

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ABSTRACT

Low electronic transmission efficiency and high charge recombination are the existing problems of photoanode film in traditional dye sensitized solar cells (DSSCs). This paper put forward the photoanode TiO_2 films with spinodal phase separation structure (SPSS) and continuous TiO_2 skeleton which were triggered by the photopolymerization of organic monomers in a photomonomer-inorganic precursor system. The photoanode TiO_2 films fabricated by different precursor solution compositions and different coating layers were characterized mainly by scanning electron microscopy (SEM), photocatalysis and photoelectric performance test. The results indicated that, the as-prepared TiO_2 anode film with seven coating layers and heat treated at 500 °C showed higher photoelectric conversion efficiency at about 2% than that of other samples with less coating layers and lower heat treatment temperature. The film also showed excellent photocatalytic activity by using methylene blue (MB) dye as a model organic substrate under fluorescent lamp irradiation. It is suggested that the film with SPSS structure has the potential to improve the electronic transmission efficiency and reduce the carrier recombination due to its particular structure, higher surface area, and lack of bottleneck in electronic transmission. It is worth noting that the SPSS structure provides new ideas to develop new photoanode films and further improve the photoelectric conversion performance of the DSSC in future.

1. Introduction

TiO_2 photoanode, a key component of DSSC, have much effect on the energy conversion efficiency of DSSC. The specific surface areas of the photoanode film, carrier transport in the semiconductor electrode and electron recombination are the key factors for the photoelectric conversion efficiency of DSSC. For most photoanode TiO_2 films, the nanoparticles provide large specific surface area for the films, however the surface states in nanoparticles slow down the electron transport speed [1]. Similarly, there are surface states for porous nanocrystalline TiO_2 anode as well. Therefore, the electron is very easy to be captured by the trap when moving in the TiO_2 conduction band, and it will greatly increase the recombination chance of electrons and oxidation electrolyte. Moreover, due to only a few nanometers scale for the nanoparticles, the electron migration is easy to be influenced by the grain boundary obstacles in nanoparticles [2,3].

Therefore, the TiO_2 anode film with high specific surface area, a direct transport path for electron migration and rapid collection of photogenerated electrons was proposed to increase the cell efficiency of energy conversion [4–6]. However, among current challenges is how to design such kind of photoanode and improve the conversion efficiency of the DSSC. Much effort has been devoted by structural design, material fabrication, morphology and crystallinity controlling, and much performance has been studied by photovoltaic characterization and mechanism analysis. Yoko proposed a kind of TiO_2 film as the photoanode of DSSC [3,7] which has a continuous skeleton structure and micron macropores using polyoxyethylene(20) nonylphenyl ether (NPE-20) as surfactant. The as-prepared DSSC showed very high photoelectric conversion efficiency and photocatalytic activity because of the large specific surface area and no grain boundaries in the film [3,7,8]. The continuous skeleton structure is beneficial to decrease the boundary obstacles, and micron macroporous structure can help to reduce the defects of the film and improve the specific surface area of the film [3,7,8]. But the shortage is that the film phase separation happened accompanying by the rapid gelation process of the film, therefore it is difficult to control the emerging structure in the films. In addition, the surface morphology of the film affected by the environmental (such as air humidity), coating operation process (such as coating speed), etc. and the repeatability of the structure in the film is quite low.

In view of the above questions, we took example by the polymerization induced phase separation method of liquid crystal/polymer grating [9] to synthesize TiO_2 anode film with spinodal

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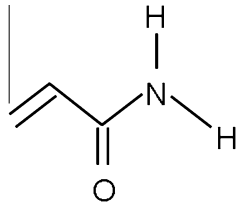
phase separation structure and micron macroporous continuous skeleton [10,11]. First, acrylamide (AM) monomer which has the performance of photopolymerization [10] was added into the precursor sol. After dip-coating, the AM film was UV irradiated to cause the polymerization of AM (PAM). Here, AM was chosen as the photomonomer because of the amide groups of AM which could hydrogen bond to ethanol and water. Then, the new generated polymer PAM was separated from the residual monomer and TiO_2 oligomer. Finally, TiO_2 anode film with special SPSS structure obtained after removing the organics by heat treatment. Although there were grains in the film, the continuous skeleton of SPSS structure could greatly decrease the obstacles of the grain boundaries [7,8], ensure the effective transmission of electrons and prevent the recombination of the carriers, then the grain boundaries would not influence the performance of the film [7,8]. In addition, the micron-scale of the structure was beneficial to reduce the defects in the film, and increase the specific surface area of the film [3,7]. Therefore, the SPSS structure with continuous macroporous skeleton could solve the problems we mentioned above for photoanode film of DSSC.

In this work, TiO_2 photoanode film with SPSS structure was prepared by the photopolymerization induced phase separation method. The SPSS structure was triggered by the UV illumination of the organic monomer polymerization which means that the phase separation process was induced by the strong interactions between the inorganic oligomers and the organic polymers. The structures and the performances of the TiO_2 films with different coating layers and different precursor solution compositions were investigated by SEM, photocatalysis and *I–V* measurements under AM 1.5 illumination. The objective in this study is to searching an appropriate anode film to improve the electron transport speed and reduce the charge recombination for DSSC.

2. Experimental

2.1. Materials

Tetrabutyl titanate ($Ti(OC_4H_9)_4$, TBOT) was used as the titanium source. Acrylamide (C_3H_5ON, AM) was used as the photomonomer, whose structure is shown in Scheme 1. 2,2′-Azobisisobatyronitrile ($C_{18}H_{12}N_4$, AIBN) was used as the radical initiator. The reagents were purchased from enterprise group chemical reagent Co., LTD including poly(vinyl pyrrolidone) (PVP K30, ~30,000), N,N-Dimethylformamide (C_3H_7NO, DMF), C_2H_5OH (EtOH), and HNO_3 (66 wt%). Sensitizing organometallic dye *cis* -dithiocyanate-*N*,*N*′-bis-(4-carboxylate-4-tetrabutylammonium carboxylate-2,2′-bipyridine) ruthenium(II) (N719, $C_{58}H_{86}O_8N_8S_2Ru$, Solarnix), electrolyte solution (0.05 mol/L I_2, 0.5 mol/L LiI, 0.05 mol/L 4-tert-butylpyridine 0.3 mol/L DMPII ionic liquid, solvent is acetonitrile), and Pt counter electrode (Thermal decomposition preparation) were purchased from Wuhan Ge Ao Science and education instrument Co., LTD in China. Conductive glass substrates (fluorine-doped tin oxide overlayer, i.e., FTO glass) with a sheet resistance of 14 Ω/square were purchased from Beijing Ai Gesen technology Co., LTD in China. All solvents and chemicals were reagent grade and were used as received without further purification.



Scheme 1. Structure of AM.

2.2. Pretreatment of quartz plate

First, the quartz plates were washed with cleanser essence, and then soaked in the potassium dichromate/strong sulfuric acid washing liquor for 15 min to remove the organics on the surface. After that, the quartz plates were ultrasonic cleaned with deionized water and ethanol about 15 min, respectively. Finally, the quartz plates were flushed with deionized water and dried spare.

2.3. Preparation of TiO_2 precursor sol

AM was dissolved in the quantitative EtOH and stirred about 15 min, then PVP was added in and the mixture solution was stirred until PVP dissolved, denoted as solution I. In ice-water bath, quantitative DMF and TBOT were added into another EtOH and vigorously stirred for about 15 min, then HNO_3 and deionized water were added dropwisely into it under stirring, after the whole solution was stirred for about 10 min, AIBN was added and stirred for another 15 min, denoted as solution II. Finally, solution I was added into the solution II and the mixture solution was stirred for about 15 min, then the TiO_2 precursor sol was obtained. The molar ratio for the sol was TBOT:EtOH:H_2O:HNO_3:DMF:AM = 1:18. 3:3:0. 5:5:6, TBOT was 0.025 mol. In addition, the amount of AIBN was about 1 wt% of AM monomer, and the amount of PVP was about 5.3% of the total quality of sol.

2.4. Fabrication of the TiO_2 film

The precursor sol was placed in a dip-coating chamber. The quartz plates cleansed before were used as the substrates and the withdrawal speed was down 2 cm/min and up 9 cm/min. After dip-coating by different times, the resultant gel films were irradiated by ultraviolet low pressure mercury lamp (LP, 18 W, λ = 254 nm, light intensity is 900 μW/cm^2) for 30 min. Then the films were heat-treated at 200 °C for 10 min, 500 °C for 10 min.

2.5. Fabrication of DSSC

Firstly, the heat treated TiO_2 anode film was soaking in N719 dye solution at 40 °C for 24 h. Then, the film was flushed with EtOH and dried in the oven. After that the as-prepared photoanode film was clipped with pt electrode together. At last, electrolyte was injected between the electrodes for seconds and then DSSC was obtained.

2.6. Characterization

The morphology of products was characterized by a Quanta 200 F field emission scanning electron microscope (FESEM), FEI Singshine Hongkong (30 kV, 30 mA). XRD patterns were recorded on a D8 ADVANCE diffractometer using Cu Kα radiation at 40 kV and 40 mA. The photodegradation of MB as a function of time under the irradiation of fluorescent ultraviolet lamp (18 W, λ = 365 nm) of 2 mW/cm^2 was monitored by UV–visible spectrophotometer (Shimazu UV-2450). A synthetic quartz cell of 3 cm^3 was used as the reaction container, and it was filled with 3 mL of methylene blue (MB) solution (6×10^{-5} M), where the film sample of 7 mm × 13 mm in size was immersed. The MB concentration was determined by measuring the maximum absorbance around 664 nm in UV–vis absorption spectra. The *I–V* performance was recorded by using a 150 W solar simulator as light source and standard silicon cell calibrating the light intensity (SRC-1000-TC-QZ from VLSI Standards Incorporated). Under the white light irradiation of 100 mW/cm^2, recording the data from KEITHLEY 2400 SourceMeter and getting the *I–V* curve.