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Influence of process parameters on synthesis of hierarchical porous titania photoanode prepared by controlled phase separation for dye sensitized solar cell

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Abstract

Utilization of hierarchical porous structure in photoanode of dye sensitized solar cell (DSSC) not only allows the diffusion of electrolyte species through micro-channels, but also provides the high surface area in mesoporosity. The hierarchical porous titania photoanodes are synthesized through the sol–gel assisted controlled phase separation method and then the DSSCs based on these photoanodes are fabricated. The effects of different parameters of water, stabilizer, and polyethylene glycol (PEG) contents, as well as deposition speed on macropore formation are considered. X-ray diffraction results show that the photoanodes are mainly comprised of anatase phase. Field emission scanning electron micrographs reveal that the macropore sizes decrease with decreasing water or PEG contents. However, increasing stabilizer content or deposition speed has an inverse effect on macropore sizes. The efficiencies of the cells show direct relationship to surface area of the photoanodes, measured by the dye adsorption test. These hierarchical porous photoanodes exhibit scattering effect with incident photons in the visible region and display high recombination resistance at the TiO_2/dye/electrolyte interface.

Keywords: A. Sol–gel processes; D. TiO_2; Hierarchical porosity; Phase separation; Dye sensitized solar cell

1. Introduction

The growing energy demand and the fast consumption of conventional energy sources along with global warming threat have motivated researchers to utilize a low cost more efficient renewable energy [1–3]. Dye sensitized solar cells (DSSCs) have attracted tremendous attention in recent years due to the advantages of low fabrication cost, relatively high performance, promising stability under normal condition, functioning at both normal and diffuse light, and possibilities to design solar cells with a large flexibility in shape, color, and transparency [4–6].

DSSC devices are photoelectrochemical cells based on mesoporous wide band gap oxide semiconductor films (usually TiO_2) coated on transparent conductive oxide such as fluorine doped tin oxide (FTO). The mesoporous film is sensitized with molecular dye (commonly ruthenium based complexes). The dye is excited upon illumination and the excited electrons are injected to the conduction band of mesoporous film. The dye is regenerated by redox species in electrolyte (usually an organic solvent containing iodine/iodide redox species) and the injected electrons in the mesoporous film are transported to FTO. In other side, the oxidized species in electrolyte diffuse to cathode and are reduced by platinum catalyst. These processes cause the charge current in external circuit [7,8].

Although the efficiency of DSSC devices has reached so far to 12% [9], further improvements in efficiency and stability of these cells are still needed. The major bottlenecks in these devices are low stability, nearly narrow absorption range in solar spectrum, and relatively low electron lifetime [10–12]. The hierarchical porous structures are proposed as one of the

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Table 1
Different hierarchical photoanodes used in DSSCs.

Morphology	Synthesis method	Highest reported efficiency (%)	Refs.
TiO_2/ZnO aggregates	Sol–gel or hydrothermal	8.44	[18]
TiO_2/ZnO hollow spheres	Sacrificial polymeric molds	5.8	[19]
TiO_2 beads	Solvothermal	7.2	[20]
TiO_2 spheres	Modified solvothermal	7.43	[18]
Nano-urchin	DC arc plasma reaction	3.2	[21]
TiO_2/ZnO forests	Pulsed laser deposition	4.9	[22]
Wrinkled TiO_2 nanotubes	Modified anodization	3.6	[23]
Hyper-branched nanorods	Chemical bath deposition	3.96	[24]
Nano-pillars	Micro-patterning	3.37	[25]
Electrospun nanowires	Electrospinning	9.52	[26]
Photonic crystals	Sacrificial polymeric beads	3.7	[27]
Nano-flowers	Hydrothermal method	1.9	[28]
ZnO nanowalls	Chemical bath deposition	4.27	[29]

promising material for improving the cell performance for solving these problems. In the hierarchical porous structures, which are the porous films that contain at least bimodal pore size distribution, mesopores provide the large surface area necessary for the interface reactions and macropores act as micro-channels which permit rapid transports of reactants or redox couples to the interface [13]. Furthermore, the large macropores allow the penetration of solid state electrolyte to inner parts. These solid state DSSCs are promising candidates for future DSSCs with high stability [14,15]. Moreover, the molecular dye can be substituted by semiconductor quantum dots (QDs) with higher absorption coefficient and tunable band gaps, which can presumably improve the light harvesting efficiency and absorption region in the device. Since QDs and electrolyte species can possibly block the mesoporosities, larger porosity is needed in case of quantum dot sensitized solar cells. Thus, hierarchical porous photoanode is a promising choice in this case.

The hierarchical structures with the advantages of large area available for dye adsorption, light scattering effect caused by large macropores, enhanced charge transport by minimizing the interfaces between particles, and improved electrolyte diffusion by introducing large micro-channels [16,17], have been used in DSSCs in different forms as shown in Table 1. Sol–gel induced phase separation for the preparation of hierarchical porous photoanode of DSSCs offers the advantages of low organic residues, simplicity, cost effectiveness, and tunable morphology with vast majority of parameters for controlling the microstructure. In this method, the sol composition is chosen near the gel point. The solvent evaporates and the sol concentrates during film deposition. Suddenly, spinodal decomposition takes place, causes segregation of hydrophilic phase from the hydrophobic phase. Simultaneously the gelation occurs, which results in formation of macroporosities. Mesopores are formed after calcination process [30–32].

In this article, the hierarchical meso/macroporous titania photoanodes were synthesized through the sol–gel based phase separation method. Effects of process parameters including water, stabilizer, and structure directing agent (SDA) contents, as well as deposition speed on morphology of the films and efficiency of the device were investigated.

2. Materials and method

2.1. Materials

Ethanol (EtOH), 1-propanol (1PrOH), tert-butanol (tBuOH), nitric acid (HNO_3), hydrochloric acid (HCl), tetrapropyl ortotitanate (TTiP), tetrabutyl ortotitanate (TBT), titanium tetrachloride ($TiCl_4$), diethanol amine (DEA), acetonitrile (AN), polyethylene glycol (PEG, average molecular weight 1000), and hexa chloroplatinic acid (H_2PtCl_6) were all in reagent grade and purchased from Merck. Deionized water (DIW, 18.2 MΩ) was used in all the experiments. The fluorine doped tin oxide conductive glass substrates (FTO, 15 Ω/square), cis-di(thiocyanato)-N-N′-bis(2,2′-bipyridyl-4-carboxylic acid-4′-tetrabutyl ammonium carboxylate) ruthenium II dye (N719), Surlyn ionomer, and iodine/iodide electrolyte were all purchased from Dyesol. All chemicals were used as received without further purification.

2.2. Blocking layer preparation

The sol preparation method for depositing blocking layer was discussed elsewhere [33]. Typically, the TTiP was dissolved in 1PrOH. The hydrolyzing solution containing DIW, HCl, and 1PrOH was added drop-wisely to TTiP solution and stirred for 30 min. The sol composition was TTiP:DIW:HCl = 1:4:0.5 with 0.17 M concentration. FTO substrates were cleaned ultrasonically with detergent solution, ethanol, acetone, and deionized water. The transparent sol was spin coated on cleaned FTO substrates with spin rate of 3000 rpm for 30 s and then dried at 100 °C. The coated substrates were calcined at 450 °C.

2.3. Hierarchical porous photoanode preparation

Synthesis of hierarchical porous photoanode was previously reported [34]. Briefly, the TBT solution in EtOH was prepared and stirred for 30 min. The stabilizer of DEA was added to this solution and stirred for 2 h. In another beaker, the hydrolyzing solution containing DIW and EtOH was added drop-wisely to the former solution and stirred for 1 h. Finally, the PEG was added to the resultant sol and stirred for another 1 h. The final composition of the sol was TBT:DEA:DIW = 1:1:1 with 0.75 mol/L concentration and 1 g/L PEG. The sol was dip coated on FTO/TiO_2 substrates with dipping speed of 60 mm/min and dried at 300 °C. The process of dip coating