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Electrodeposition of hierarchical ZnO nanorod arrays on flexible stainless steel mesh for dye-sensitized solar cell

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ABSTRACT

Hierarchical ZnO nanorod arrays (ZNRAs) were synthesized on flexible stainless steel mesh (SSM) in large scale by a two-step facile electrodeposition method. The structure and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The growth mechanism of the ZnO hierarchical nanostructures was also discussed. Moreover, the effect of ZnO morphology on the photovoltaic performance of the flexible DSSCs based on SSM supported ZnO nanostructures was investigated in detail. It is shown that the flexible DSSCs exhibited a relatively higher power conversion efficiency of 1.11% compared with that based on primary ZNRAs.

1. Introduction

Within the past decades, the transparent conductive oxide (TCO) coated glass (FTO/ITO) has been commonly used as electrode material of dye-sensitized solar cells (DSSCs) [1,2], however, lots of drawbacks such as expensive, rigid and heavy-weight are distinctly revealed from the commercial production. Recently, flexible DSSCs have attracted considerable attention due to the increasing requirement for the portable and convenient applications [3–5]. Various flexible substrates including indium tin oxide (ITO) coated polyethylene terephthalate (PET) and polyethylene naphtalate (PEN) substrate [6,7], as well as metal sheet have been used for fabrication of flexible DSSCs [8,9], unfortunately, the corresponding performance still remains low value which may be ascribed to the poor thermo-stability for plastic substrates and the opaque property for metal sheet. Therefore, how to select the suitable substrate for flexible DSSC devices is still a challenge issue. Stainless steel mesh (SSM) which has many advantageous properties such as good flexibility, low cost and good electric conductivity, becomes one of the most promising candidates of flexible substrates for DSSCs [10]. To date, some researchers have devoted lots of efforts to the preparation of nanocrystalline semiconductors (TiO_2, ZnO) on SSM substrate mainly by hydrothermal and dip coating methods [11–13]. In 2011, Birnie III et al. [11] found a lower series resistance for SSM electrodes compared to FTO substrates and the SSM was first used to fabricate TiO_2 photoanodes by dip coating method for flexible DSSCs with a power conversion efficiency of 1.68%. Marbán [12] synthesized the ZnO nanorod arrays (ZNRAs) on SSM by hydrothermal process, and no property was investigated. In 2013, Kim et al. [13] fabricated solid flexible DSSC based on SSM supported ZNRAs (about 9.7 μm) by hydrothermal method and a power conversion efficiency of 2.57% was achieved. Considering that ZnO has higher electron mobility, lower combination rate and easier controllable preparation, various nanostructured ZnO, especially ZNRAs and hierarchical ZNRAs are more suitable for photoanodes in DSSCs compared with TiO_2. In recent years, many methods such as chemical vapor deposition (CVD) [14], thermal evaporation [15], spray pyrolysis [16], hydrothermal synthesis [17–19] and electrodeposition process [20,21] are used for synthesis of the hierarchical ZnO nanostructures. Among these approaches, electrodeposition has been recognized as one of the most effective methods to prepare nanomaterial because of its lower temperature process, higher growth rate and convenient operation. Wang et al. [22] presented a two-step electrochemical deposition process to synthesize hierarchical ZnO nanowire arrays on FTO substrate and obtained a power conversion efficiency of 0.88%. In the same year, hierarchical nanorod–nanosheet structures were synthesized on ITO substrate via the same electrochemical deposition process and the DSSCs based on this structure exhibited an improved conversion efficiency of 3.12% [23]. However, no effort has been taken on electrodeposition of hierarchical ZNRAs on the flexible SSM for DSSCs, and it is still a challenge to improve the power conversion efficiency of ZnO-based flexible DSSCs.

In this paper, hierarchical ZNRAs, namely, ZnO nanorod–nanorod arrays and ZnO nanorod–nanorod–nanoparticle arrays were

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electrodeposited on SSM substrates. The effects of ZnO morphology on the photovoltaic performance of the flexible DSSCs based on SSM were studied in detail. Moreover, the power conversion efficiency of DSSCs based on different ZnO hierarchical nanostructures was also investigated. The results indicated that the DSSCs constructed by hierarchical ZNRAs exhibited a relatively higher conversion efficiency compared with that based on primary ZNRAs, and coating ZnO nanoparticles (ZNPs) on the surface of the different ZnO nanostructures is an effective way to improve the power conversion efficiency.

2. Experimental

2.1. Materials

Flexible conductive SSM (300-count and 99.5% purity) used in the experiments was obtained from Beijing DOTRUST Co., Ltd. and cut into strips with dimensions of 1×2.5 cm^2. SSM used was firstly immersed in diluted hydrochloric acid for a short time and then washed in thermal soap and absolute ethyl alcohol with ultrasonic for 10 min respectively, fully rinsed with deionized water. All chemicals, which were of analytical grade, were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. The zinc acetate colloid was prepared by dissolution of zinc acetate dehydrate and equivalent molar ethanolamine in 2-methoxyethanol with magnetic stirring at 60 °C for 30 min. The concentration of zinc acetate was controlled by tuning the molar ratio of zinc acetate dehydrate and equivalent molar ethanolamine to 2-methoxyethanol.

2.2. Preparation of hierarchical ZNRAs on SSM

All the electrochemical depositions were carried out using a CHI 760C electrochemical working station with saturated calomel electrode (SCE) as the reference electrode, a Pt wire as the counter electrode and the flexible SSM as the working electrode, respectively. The hierarchical ZNRAs were synthesized by a two-step electrodeposition process. Firstly, the primary ZNRAs were electrodeposited on SSM substrate under a potential of −1.0 V vs. SCE for 1800 s. Secondly, prior to the second-step deposition process, the as-synthesized ZnO nanorods were immersed in 0.75 mol dm^{-3} zinc acetate colloid for a certain time and then annealed in the air at 350 °C for 10 min to produce uniform ZnO nanoseed layer [24]. Hierarchical ZNRAs were finally obtained by using the treated ZnO nanorods as working electrode and the second electrodeposition process was done under a potential of −1.0 V vs. SCE for 1800 s. For both the first and second step deposition process, the electrolytes used were $ZnCl_2$ (0.0005 mol dm^{-3}) aqueous solutions bubbling with saturated O_2 during the reaction process, and the growth temperatures were well controlled at 80 °C in a thermostat-controlling water tank. Meanwhile, the 0.1 mol dm^{-3} KCl was introduced into the solution as supporting electrolyte.

2.3. Characterization

The morphology of the products was examined by field emission scanning electron microscope (Zeiss Supra-55, operated at 10 kV), transmission electron microscope and high-resolution transmission electron microscope (Tecnai F20 operated at 200 kV). The crystal structure was characterized by X-ray diffraction (XRD) using Cu Kα radiation (Rigaku Dmax-2500). The photocurrent–voltage curves of the DSSCs were measured by a simulated sunlight system (Newport Corporation, 100 mW cm^2) with electrochemical instrument (CHI 760C) under an AM 1.5 simulated light radiation. Moreover, in order to measure the dye adsorption capacity, the sensitized photoelectrodes (cut into strips with dimensions of 1 cm^2) were separately immersed into a 10 mL NaOH water–ethanol solution (volume ratio of 1:1) with a concentration of 0.1 mol dm^{-3} to desorb the dye molecule (N719) from photoelectrodes. Then the absorbance of the resulting solution was analyzed by UV–Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., TU-1901). The adsorbed amount of dye can be calculated by the following equation,

$$A = \varepsilon * C * l \tag{1}$$

where A is the absorption, ε (L mol^{-1} cm^{-1}) is the molar extinction coefficient, C (mol dm^{-3}) is the adsorbed amount of dye and l (cm) is the length of cuvette. Usually, the adsorbed amount of dye (N719) was determined by the molar extinction coefficient of 1.41×10^4 L mol^{-1} cm^{-1} at 515 nm as reported previously [25].

2.4. Photoelectrochemical measurement

The SSM substrate supported ZnO nanostructures were annealed in the air for 30 min at 300 °C to obtain better crystallization and then sensitized by immersing them into an ethanolic solution of 0.0003 mol dm^{-3} cis–bis (isothiocyanato) bis (2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium (N719, Solaronix) for 6 h at room temperature, followed by rinsing with ethanol to remove excess dye adsorbed. For the fabrication of DSSCs, the flexible SSM substrates supported ZnO nanostructures were pasted on the conductive side of ITO glass and used as photoanode, it should be noted that the glass had a small hole on the corner of the surface for the injection of electrolyte. Subsequently, the photoanode and the Pt counter electrode were assembled to a sandwich-type cell and sealed with a polymer sealant of 25 μm thickness, which also served as a spacer between the electrodes. The area of active electrode was 0.25 cm^2 and the internal space of the two electrodes was filled with an electrolyte, which was composed of 0.1 mol dm^{-3} LiI, 0.5 mol dm^{-3} 1,2-dimethyl-3-propylimidazoliumiodide, 0.03 mol dm^{-3} I_2 and 0.5 mol dm^{-3} *tert*-butylpyridine in acetonitrile. The current–voltage curves were tested by a scan rate of 10 mV s^{-1} and the potential interval from 0 V to 1.0 V. The fill factor (*FF*) and photo-to-electric conversion efficiency (η) were calculated according to the following equations [26],

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}} \tag{2}$$

$$\eta(\%) = \frac{P_{max}}{P_{in}} \times 100 = \frac{FF \times V_{oc} \times I_{sc}}{P_{in}} \times 100 \tag{3}$$

where η (%) is the solar-to-electric conversion efficiency, V_{oc} (V), J_{sc} (mA cm^{-2}), and *FF* are open-circuit voltage, short-circuit current density and fill factor, respectively. P_{in} (100 mW cm^{-2}) is the incident light energy and P_{max} (mW cm^{-2}) is maximal power output.

3. Results and discussion

3.1. Structural and morphological characterization of hierarchical ZNRAs on SSM

Electrodeposition of ZnO nanostructures is a combination of electrochemical and chemical processes, and the reduction of oxygen precursor at the interface of electrode is the most important aspect in the zinc chloride aqueous solution. The cathodic electrodeposition mechanism of ZnO nanostructures on SSM substrate is basically clear and proposed as follows [27],

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{4}$$

$$Zn^{2+} + xOH^- \leftrightarrow Zn(OH)_x{}^{2-x} \tag{5}$$

$$Zn(OH)_x{}^{2-x} \leftrightarrow ZnO + H_2O + (x-2)OH^-. \tag{6}$$