Research Article

Low-Temperature Preparation of Amorphous-Shell/Nanocrystalline-Core Nanostructured TiO₂ Electrodes for Flexible Dye-Sensitized Solar Cells

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An amorphous shell/nanocrystalline core nanostructured TiO₂ electrode was prepared at low temperature, in which the mixture of TiO₂ powder and TiCl₄ aqueous solution was used as the paste for coating a film and in this film amorphous TiO₂ resulted from direct hydrolysis of TiCl₄ at 100°C sintering was produced to connect the particles forming a thick crack-free uniform nanostructured TiO₂ film (12 μm), and on which a photoelectrochemical solar cell-based was fabricated, generating a short-circuit photocurrent density of 13.58 mA/cm², an open-circuit voltage of 0.647 V, and an overall 4.48% light-to-electricity conversion efficiency under 1 sun illumination.

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1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) [1–3] have been extensively studied more than a decade because they presented high-efficient, cost-effective, and environmentally friendly advantages. In the cell dye-sensitized semiconductor, photoelectrode plays an essential role, and conventionally nanocrystalline porous TiO₂ electrode is prepared by coating a paste containing organic additives on a rigid conductive glass substrate, following a procedure of high-temperature sintering to remove the organic additives [1, 2], which are necessary to form a thick crack-free uniform film and optimize the microstructure of the electrode for photosensitization [1–4].

Flexible DSSCs [5–14], based on the substrates of indium tin oxide (ITO) coated polyethylene terephthalate (PET), or polyethylene naphthalate (PEN) substituting for rigid glass substrates, are regarded as one possible breakthrough in the field of DSSC regarding their commercialization, because flexible DSSCs have presented great advantages of low cost of production and wide application. Conductive plastic sub-

strates, such as ITO/PET or ITO/PEN, can be processed by a continuous process like roll-to-roll production for porous nanocrystalline film coating, therefore, greatly decreasing the production cost of the solar cells. Meanwhile, flexible DSSCs can become part of a variety of every-day products and turn them into energy sources. The possibility to produce the flexible DSSCs in any shapes would open almost endless opportunities to the designers of such products. In addition, it is light weight, having portable character.

Underlying the flexible DSSCs, the necessary low-temperature preparation of porous nanocrystalline metal oxides semiconductor films has been a well-highlighted and ongoing challenge up to today, because the conventional method of high-temperature preparation cannot be applied to prepare films on flexible plastic substrates, which only endure temperature of up to around 150°C. So far, there have been a number of efforts concerned with the preparation of nanoporous films at low temperature. The methods reported were low-temperature heating [5, 6], compression [7, 8], microwave irradiation [9, 10], electron-beam annealing [11] and chemical-vapor deposition with UV irradiation [12],

FIGURE 1: SEM photographs of the TiO_2 electrodes (a) before and (b) after sintering.

and hydrothermal crystallization [13, 14]. However, the conversion efficiencies of the flexible DSSCs achieved so far are lower than those obtained by high-temperature sintering. One main reason is that low-temperature films have low level of crystallization of interconnection between particles comparing with high-temperature film [5–14]. It is showed that low-temperature film has poor interconnection between nanocrystalline particles, because the above-mentioned methods that have been developed so far cannot result in as perfect interconnection as high-temperature sintering did [5–14]. In fact, the part of low level of crystallization worked as the interconnection of nanocrystalline particles in the low-temperature film existed in all flexible DSSCs. So the part of low level of crystallization in the low-temperature film played an important role in the chemical reaction at interface of the cell. To well understand how it works and further improve the performance of low-temperature film, therefore, in this study, we developed a simple method and prepared an amorphous shell/nanocrystalline core nanostructured film under 100°C sintering. The amorphous shell not only is responsible for the interconnection between nanocrystalline particles, but also plays an important role in the interface chemical reaction. The as-prepared films were mechanically stable. It is showed that amorphous TiO_2 can work effectively in DSSCs. Its performance was compared with that of nanocrystalline porous film prepared at both high and low temperature.

2. EXPERIMENTAL

Nanostructured TiO_2 electrode with the structure of amorphous shell/nanocrystalline core was prepared by the following method. 0.8 g P25 (Degussa, Germany, 30% rutile and 70% anatase, BET surface area $55\text{ m}^2/\text{g}$, particle size 25 nm) and 0.5 M TiCl_4 water solution were ground in an agate mortar for about 2 hours to get viscous paste, then coated on the fluorine doped SnO_2 -coated conductive glass (sheet resistance ca. $10\ \Omega/\square$) by doctor-blade technique. Subsequently, the film was sintered at 100°C for 12 hours. The resulting film thickness was $12\ \mu\text{m}$ but can be varied by changing the paste concentration or the adhesive tape thickness. The electrode was directly immersed in an ethanol solution of *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(thiocyanato)ruthenium(II), N3 dye (0.05 mM) overnight at room temperature. This dye-sensitized electrode was employed as a working electrode and platinized conductive

FIGURE 2: XRD patterns of the TiO_2 electrodes (a) before and (b) after sintering as well as (c) the TiO_2 resulted from 0.5 M TiCl_4 water solution sintered at 100°C for 12 hours (small peaks resulted from SnO_2 conductive glass).

glass as a counter electrode for assembling a sandwich-type dye cell. The electrolyte was 0.5 M KI and 0.03 M I_2 in ethylene carbonate-acetonitrile (4:1 by volume). No special efforts were made to optimize the composition of the electrolyte. Photoelectrochemical measurements were performed on the TiO_2 film electrodes under white light illumination by a 500 W Xe lamp equipped with IR and $<420\text{ nm}$ cutoff filters from the side of the conductive glass back contact. Surface morphology of the electrode was observed by a Topcon ABT-150FS scanning electron microscope (SEM). X-ray diffraction patterns (XRD) of the electrodes were measured by a Rigaku RAD-2R using Cu $K\alpha$ radiation at 40 kV and 20 mA by scanning at $2^\circ\ 2\theta\ \text{min}^{-1}$.

3. RESULTS AND DISCUSSION

The SEM photographs of the TiO_2 electrodes before and after sintering at low temperature of 100°C are presented in Figure 1. It revealed morphological homogeneity of both electrodes with micropores and interconnected particles, but before sintering at low temperature of 100°C the average particle size was approximately like the one of P25, while after sintering it was increased obviously and the connection between particles was also improved. The XRD patterns of the TiO_2 electrodes before and after sintering at low temperature of 100°C are shown in Figure 2. No new peak was observed after sintering at low temperature of 100°C and, even both the relative intensity and line width of crystal peak were not changed before and after sintering, showing neither new compound nor crystal TiO_2 was formed in the film during the sintering. According to the Scherrer equation [$L = 0.9\lambda/B(2\theta)\cos\theta$, where L is the crystallite size and $B(2\theta)$ is the line width] together with the results of XRD measurement, the crystal size should not

be changed before and after sintering at low temperature of 100°C. Therefore, it conflicted with the results of SEM measurement. Figure 2 also shows XRD pattern of TiO₂ resulted from 0.5 M TiCl₄ water solution sintered at 100°C for 12 hours. From Figure 2, one can see no any crystal TiO₂ peaks were observed, showing that amorphous TiO₂ was formed during the sintering. So we can think that in the film TiCl₄ was condensed at the surface of the crystal TiO₂ of P25 before sintering and, during the sintering at low temperature of 100°C amorphous TiO₂ resulted from TiCl₄ grew on the surface of crystal TiO₂ of P25 forming amorphous shell/nanocrystalline core particles, resulting in increments of the sizes of particles as well as improvement of the connection between particles in the film. So the formed electrode was crack free, robust, and uniform.

The amount of adsorbed N3 dye on the nanostructured TiO₂ electrode was 1.1×10^{-7} mol/cm²,² and from this data the calculated surface roughness factor was about 1000,¹⁵ showing that the electrode had large surface area and the dye of N3 can also strongly adsorb on the amorphous TiO₂ surface. The photocurrent-voltage characteristic of the cell based on this nanostructured TiO₂ electrode after sintering at low temperature of 100°C is presented in Figure 3. Under 1 sun illumination, a short-circuit photocurrent density (I_{sc}) of 13.58 mA/cm², an open-circuit voltage (V_{oc}) of 0.647 V, and a fill factor of 51% were obtained, yielding an overall 4.48% light-to-electricity conversion efficiency. Figure 4 shows the dependence of V_{oc} on illumination intensity. Within the range of the measurement the open-circuit voltage versus incident light intensity was a liner relationship and its slope was 130 mV per decade, yielding a rectification coefficient of 2.5. This value was higher than that of 1 to 2 [15–17] of dye-sensitized solar cell based on the nanocrystalline TiO₂ electrode sintered at 450°C for 30 minutes, meaning the density of surface state in this amorphous electrode was higher which may result in larger recombination [15]. However, this value was lower than that of 3.2 [5] of the cell based on TiO₂ electrode sintered at 100°C for 24 hours, showing that amorphous TiO₂ improved the connection between particles in the film and decreased some recombination therefore, larger I_{sc} and conversion efficiency was observed. All these experiments showed that the dye of N3 can inject electrons into amorphous TiO₂ effectively and the recombination rate was lower and amorphous TiO₂ can also collect and transport electrons effectively. Therefore, the cell based on the amorphous shell/nanocrystalline core nanostructured TiO₂ electrode prepared at low temperature had high-conversion efficiency up to 4.48%. However, when this amorphous electrode was further sintered at 450°C the amorphous became into well crystal, which was confirmed by XRD measurement of TiO₂ from the decomposition of TiCl₄ with 450°C sintering. A DSSC based on it presented a short-circuit photocurrent density of 20.2 mA/cm², an open-circuit voltage of 0.69 V, and a fill factor of 51% were obtained, yielding an overall 7.1% light-to-electricity conversion efficiency under 1 sun illumination. Obviously, both photocurrent and photovoltage were improved with the improvement of the level of nanocrystalline interconnection, suggesting that amorphous interconnection has lower collec-

FIGURE 3: Photocurrent-voltage characteristic of a cell based on the amorphous shell/nanocrystalline core nanostructured TiO₂ electrode after sintering. Light intensity was 100 mW/cm². Electrode area was 0.28 cm².

FIGURE 4: Open circuit voltage as a function of incident light intensity for N3-sensitized amorphous shell-nanocrystalline core nanostructured TiO₂ electrode.

tion efficiency of electrons and higher recombination rates of electrons. The unchanged fill factor implies that amorphous interconnection has close resistance in the real cell when it works. The lower photocurrent and photovoltage should come from the higher surface states in the amorphous shell which worked as interconnection.

In summary, amorphous TiO₂ can effectively work as interconnection to form robust nanostructured films, however, it is not effective for electron collection. It presented large recombination rate of electrons comparing with nanocrystalline porous films with nanocrystalline interconnection. It is suggested that low-temperature preparation methods should improve the crystal lever of the interconnection, which plays essential roles in the forming of film and chemical reaction in the interface, while it is not easy to achieve at low temperature. The flexible DSSCs would present as high conversion efficiency as that of sintered DSSCs when it would be achieved.

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