An amorphous shell/nanocrystalline core nanostructured TiO$_2$ electrode was prepared at low temperature, in which the mixture of TiO$_2$ powder and TiCl$_4$ aqueous solution was used as the paste for coating a film and in this film amorphous TiO$_2$ resulted from direct hydrolysis of TiCl$_4$ at 100°C sintering was produced to connect the particles forming a thick crack-free uniform nanostructured TiO$_2$ film (12 μm), and on which a photoelectrochemical solar cell-based was fabricated, generating a short-circuit photocurrent density of 13.58 mA/cm$^2$, 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 TiO$_2$ 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 substrates, 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],
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 TiO2 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 TiO2 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 m2/g, particle size 25 nm) and 0.5 M TiCl4 water solution were ground in an agate mortar for about 2 hours to get viscous paste, then coated on the fluorine doped SnO2-coated conductive glass (sheet resistance ca. 10 Ω/□) by doctor-blade technique. Subsequently, the film was sintered at 100°C for 12 hours. The resulting film thickness was 12 μm 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 glass as a counter electrode for assembling a sandwich-type dye cell. The electrolyte was 0.5 M KI and 0.03 M I2 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 TiO2 film electrodes under white light illumination by a 500 W Xe lamp equipped with IR and <420 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 Ka radiation at 40 kV and 20 mA by scanning at 2° 2θ min⁻1.

3. RESULTS AND DISCUSSION

The SEM photographs of the TiO2 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 TiO2 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 TiO2 was formed in the film during the sintering. According to the Scherrer equation [L = 0.9 λ/B(2θ) cos θ, where L is the crystallite size and B(2θ) 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 TiO$_2$ resulted from 0.5 M TiCl$_4$ water solution sintered at 100°C for 12 hours. From Figure 2, one can see no any crystal TiO$_2$ peaks were observed, showing that amorphous TiO$_2$ was formed during the sintering. So we can think that in the film TiCl$_4$ was condensed at the surface of the crystal TiO$_2$ of P25 before sintering and, during the sintering at low temperature of 100°C amorphous TiO$_2$ resulted from TiCl$_4$ grew on the surface of crystal TiO$_2$ 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 TiO$_2$ electrode was $1.1 \times 10^{-7}$ mol/cm$^2$, and from this data the calculated surface roughness factor was about 1000, showing that the electrode had large surface area and the dye of N3 can also strongly adsorb on the amorphous TiO$_2$ surface. The photocurrent-voltage characteristic of the cell based on this nanostructured TiO$_2$ electrode after sintering at low temperature of 100°C is presented in Figure 3. Under 1 sun illumination, a short-circuit photocurrent density (Isc) of 13.58 mA/cm$^2$, an open-circuit voltage (Voc) 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 Voc 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 TiO$_2$ 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 TiO$_2$ electrode sintered at 100°C for 24 hours, showing that amorphous TiO$_2$ improved the connection between particles in the film and decreased some recombination therefore, larger Isc and conversion efficiency was observed. All these experiments showed that the dye of N3 can inject electrons into amorphous TiO$_2$ effectively and the recombination rate was lower and amorphous TiO$_2$ can also collect and transport electrons effectively. Therefore, the cell based on the amorphous shell/nanocrystalline core nanostructured TiO$_2$ 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 TiO$_2$ from the decomposition of TiCl$_4$ with 450°C sintering. A DSSC based on it presented a short-circuit photocurrent density of 20.2 mA/cm$^2$, 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. 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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