DNA-like dye-sensitized solar cells based on TiO₂ nanowire-covered nanotube bilayer film electrodes

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted increasing attention for their relatively low manufacturing cost and high energy conversion efficiency [1]. Typically, the photoanode of a traditional DSSC is built up as a flat-type structure which consists of a transparent conductive oxide (TCO) glass covered with a mesoporous TiO₂ nanoparticle (NP) film. However, due to the multiple trapping/detrapping events occurring within the grain boundaries between the 3D networks of interconnected nanoparticles [2,3], the electron transportation rate in the NP film is slow, which will lead to the high interface recombination reactions and will finally lower the efficiency.

In recent years, many 1D TiO₂ materials, such as nanowires (NWs) [4], nanotubes (NTs) [5], and nanorods (NRs) [6] have been successively synthesized and applied on the DSSCs since they could provide direct pathways for electrons from the injection points to the TCO substrate and have the potential to increase the charge collection efficiency. However, most of these studies only applied one kind of 1D TiO₂ materials on the DSSCs, few research were reported for the composite 1D TiO₂ bilayer film to complement each other [7].

In this manuscript, we will report a two step formation of a TiO₂ NW-covered NT bilayer film technique. It is expected that not only the NTs can be used as the blocking layer [7] but also the NWs play a role as the light trapping layer to increase the light harvesting efficiency. Besides, our previous work [8] has investigated a DNA-like DSSC which showed superiority of sunlight utilization from all directions. In order to go on optimizing this kind of bionic DSSC, we will apply such technology on this device.

2. Experimental

2.1. Preparation of TiO₂ NW-covered NT bilayer film

All the chemicals have been purchased from Sigma Aldrich (USA). First a Ti sheet was exposed to an etching fluid comprising of a hydrofluoric acid and a nitric acid to get a textured surface and then it was washed with acetone and ethanol in an ultrasonic bath for 3 min. The anodization was performed in a two-electrode configuration with the Ti sheet as the working electrode and a platinum foil as the counter electrode under constant potential (30 V) at room temperature (23 °C) for about 20 h. The Ti sheet was anodized in the electrolyte containing a mixture of ethylene glycol (50.86 wt%), polyethylene glycol 600 (47.38 wt.%), H₂O (1.31 wt.%) and NH₄F (0.43 wt.%) to grow the NT layer. After anodization, the anodized sample was rinsed with deionized water and dried in a nitrogen stream. Thermal annealing was carried out at 450 °C (heating/cooling rate of 10 °C/min) in air.

The TiO₂ NWs were directly grown onto the TiO₂ NT layer by putting the anodized Ti sheet into a Teflon reactor (50 mL), containing 27 mL of 1.0 mol/L NaOH solution. Then the reactor was sealed and hydrothermally heated at 230 °C for 4 h to grow the TiO₂ NWs. When the reaction period ended, the sample was immersed into a 0.1 M HCl aqueous solution for 10 h and then washed with deionized water. Finally, the sample was sintered at 450 °C for 30 min.

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This paper reports a two-step formation of a TiO₂ nanowire-covered nanotube bilayer film technique and its application in DNA-like dye-sensitized solar cells. The bilayer film was prepared by the electrochemical anodization first and then the hydrothermal method. From the reflectivity spectrum and scanning electron microscopy it is observed that the nanowire layer on the top cannot only decrease the reflectivity of the film, but also play a role to modify the film cracks. Compared with the dye-sensitized solar cells based on a single layer electrode, the cell with the bilayer film showed higher photovoltaic parameters and a lower dark current, which is due to its higher light harvesting efficiency and lower charge recombination between the electrolyte and the substrates.

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2.2. Assembly of the DNA-like DSSCs

Detailed process for the fabrication of DNA-like DSSCs is specified in our previous work [8]. In the present study, we just applied the TiO$_2$ NW-covered NT bilayer film as the photoanode material to fabricate the DNA-like DSSCs. For comparison, TiO$_2$ NT-based electrodes and TiO$_2$ NW-based electrodes were also made to fabricate the reference devices, as shown in Fig. 1.

Fig. 1. Schematic diagram of the DNA-like DSSCs based on the NT film, NW film and NW-covered NT bilayer film electrodes.

Fig. 2. SEM images of the NW-covered NT bilayer film: (a) top view; (b) cross-section view; (c) and (d) cracks.
2.3. Measurement

The morphology of the samples was characterized by scanning electron microscopy (SEM, JEOL 6490). Reflectivity spectrum of the films was analyzed by a UV–Visible–NIR spectrophotometer (HITACHI, U-4100). The DSSC photovoltaic characteristics were measured by a Keithley meter under Oriel solar simulator illumination. (AM 1.5, 100 mW/cm²).

3. Results and discussion

Fig. 2 shows the representative SEM images of the as-prepared TiO2 NW-covered NT bilayer film. As shown in Fig. 2a, highly well-oriented TiO2 NWs entangled each other to form a macroporous structure. From the cross-section view (Fig. 2b) we could see the TiO2 NWs rooted firmly from the top of the TiO2 NT layer. The TiO2 NWs are 0.15–0.3 μm in width and 1–3 μm in length. Here we also find something interesting. It is common that there would be some cracks in the film due to the difference of the expansion coefficients between the substrate and the NWs. It is observed that the TiO2 NWs could also be directly synthesized from the sides of the crack and connected together. To observe the crack more clearly, the NW layer on the top was removed by the ultrasonic treatment. As shown in Fig. 2d, a high density of NWs filled the crack. This phenomenon indicates that the NWs may play a role to modify the surface cracks of the lower layer (NT layer), which is beneficial to lower the dark current of the DSSCs (to be shown later).

The reflectance spectra of the TiO2 NW-covered NT bilayer film, the TiO2 NW film and the TiO2 NT film are shown in Fig. 3, which were respectively measured by the UV–Vis–NIR spectrometer. It can be observed that in the spectral range from 430 to 1100 nm, the NW film exhibits the highest diffuse reflectance, followed by the NT film and finally the TiO2 NW-covered NT bilayer film. This result explains two important issues. First, only the NW film cannot effectively reduce the reflectance of the substrate since the coverage of the NWs on the substrate is not enough. Second, the NWs could go on decreasing the reflectance of the NT film because they could reflect the incident light several more times, which would further increase the light harvesting efficiency. Consequently, compared with the TiO2 NW film and the TiO2 NT film, the TiO2 NW-covered NT bilayer film is more suitable as a light trapping layer.

The photovoltaic characteristics of the DNA-like DSSCs based on TiO2 NW film, TiO2 NT film and TiO2 NW-covered NT bilayer film are shown in Fig. 4. It could be seen that the cell based on the TiO2 NW-covered NT bilayer film generates an open-circuit voltage (Voc) of 0.62 V, a short-circuit current (Isc) of 1.6 mA, a fill factor (FF) of 52% and a maximum power (Pmax) of 0.51 mW, which is a remarkably improved result compared with those resulting from the NT cell (Voc = 0.58 V, Isc = 1.35 mA, FF = 51%, Pmax = 0.4 mW) and the NW cell (Voc = 0.6 V, Isc = 0.64 mA, FF = 36.5%, Pmax = 0.14 mW). It is partially due to the relatively high light harvesting efficiency of the bilayer film. Besides, from the dark current measurement of the cells in the upper right corner of Fig. 4, we could see the dark current of the DSSC based on a bilayer film is the lowest, which could be attributed to the modification of the film cracks by the NWs. With the decrease of the dark current, the charge recombination between the electrolyte and the substrate could be reduced and the photovoltaic performance is improved.

4. Conclusions

A simple and facile method is described to synthesize the TiO2 nanowire-covered nanotube bilayer film and its application in DNA-like DSSCs. Compared with the NW electrode and NT electrode, the bilayer film electrode showed higher light harvesting efficiency and lower charge recombination between the electrolyte and the substrate, which led to higher photovoltaic performance.

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References


Fig. 3. Reflectance spectra of the NT film, NW film and NW-covered NT bilayer film.

Fig. 4. I–V performance of the DSSCs based on NT film, NW film and NW-covered NT bilayer film under AM 1.5 illuminations (100 mW/cm²) and in the dark (insert).