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Highly crystalline Titania nanotube arrays realized by hydrothermal vapor route and used as front-illuminated photoanode in dye sensitized solar cells

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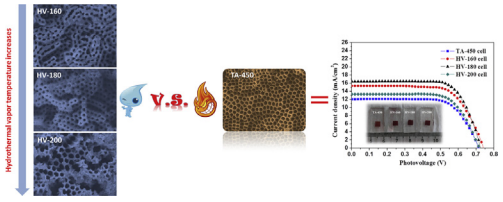
HIGHLIGHTS

- Highly crystalline TNTAs can be realized under low temperature by a new way.
- The TNTAs possessed excellent properties for light scattering and dye adsorption.
- The TNTAs exhibited better photovoltaic response than thermal annealing TNTAs.
- An optimum PCE of DSSCs based on the TNTAs can reach ~8.11 ± 0.11%.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly crystalline TiO_2 nanotube arrays (TNTAs) film is easily realized by treating its amorphous film under the hydrothermal vapor (HV) environment. The freestanding TNTAs film can be lift-off from the Ti foil, which serves as photoanode based on FTO substrate after the transplanting procedure. Compared to the thermal annealing (TA) treated TNTAs photoanode, the HV treated photoanode possesses some excellent properties, such as long optical path, fast charge transporting and easy adsorption of the sensitizer molecules, which can result in high short current density. Notably, the N719 dye sensitized HV treated photoanode prepared under 180 °C shows relatively high photovoltaic response in the visible range due to its hierarchical structure, which gives an impressive performance conversion efficiency of 8.11% without any surface modification. And the present work sheds light on the application of the mild crystalline strategy for performance improvement of the DSSCs based on TiO_2 nanotube arrays photoanode.

1. Introduction

Over the past few decades, dye sensitized solar cells (DSSCs) have attracted much more interest because of their low-cost and impressive performance conversion efficiency (PCE) compared to conventional p–n junction solar cells [1–3]. For the classical configuration of DSSCs, a mesoporous TiO_2 film on TCO substrate utilized as photoanode is, firstly, modified by a monolayer of dye molecules (Ru-complexes), subsequently assembled with redox electrolyte (I^-/I_3^-) and counter electrode (Pt/TCO). Up to now, the highest PCE (exceeding ~13%) of DSSCs reported in literature still lags behind those of their competitors [4]. There are several factors which affect outperformance of DSSCs: properties of dye, surface area for loading dye, transport kinetics of the electrons, regenerative ability of electrolyte, losses of recombination and back

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reactions [5,6]. Mesoporous TiO_2 film is found to play a crucial role in DSSCs, because not only it provides platform for loading dye sensitizers but also serves as electron acceptors for transporting electrons to the TCO substrate. However, the random network and tremendous grain boundaries in the mesoporous TiO_2 film severely limit electrons diffusion length, which increase the recombination probability of the electrons with redox species in electrolyte and oxidized dye [7]. Therefore, one of the most effective ways to boost PCE of DSSCs is to suppress the recombination losses in the mesoporous TiO_2 film.

For this purpose, one dimensional (1D) TiO_2-based nanoarrays such as nanotubes, nanowires, and nanorods which are promising to improve electron transportation and minimize charge recombination have been exploited as photoanode in DSSCs [8–10]. Among them, anodic TNTAs have been widely investigated owing to their uniquely ordered tubular structure, which can facilitate adsorption of dye sensitizers and filling of electrolyte for improving PCE [11]. However, three major problems still remain with TNTAs: opaque Ti substrate, low surface, polycrystalline structure [12–14]. There were some efforts devoted to tackle the first two issues. For the former, various routes have been proposed to obtain the free-standing TNTAs film detached from the Ti foil, such as mechanical deamination (ultrasonication), physical parameter regulation (general for voltage control), chemical separation (CH_3OH/Br_2, H_2O_2, HCl, $HgCl_2$) [15], with subsequent transplantation onto the TCO substrate as the front-side illuminated photoanode, which can overcome high fabrication cost of anodizing the high quality Ti film sputtered on the TCO substrate reported early [16]. For example, $TiCl_4$ treated TNTAs photoanode based on TCO substrate has pushed the PCE of DSSCs to 9.02% not long ago [17]; For the latter, setting the typical $TiCl_4$ solution treatment aside, bamboo-type TNTAs with high surface area for loading enough dye sensitizers were designed to optimize the outperformance of DSSCs and PCE of ~6.8% was achieved [18]. Unlike other TiO_2 based nanoarrays, as-anodic TNTAs with dominated amorphous-phase needs to be further crystallized to improve their electron mobility, and the normal way is to expose them to thermal annealing environment ($\geq$450 °C), which results in polycrystalline anatase-phase structure (crystal size: 20–30 nm) [19]. It was reported that the large crystal size could lead to the more occurrence of trap-free diffusion zone in the TNTAs film, which facilitate electron collection [20]. In order to improve crystallization of TNTAs, Yu et al., for the first time, reported the fabrication of highly crystalline TNTAs consisted of large-sized crystals by vapor and hydrothermal treatment, and proved that vapor treatment performed better in inducing crystallization of TNTAs film [21]. Based on the study, Kuo et al. demonstrated that compared to the TNTAs crystallized by thermal annealing route, the hydrothermally treated TNTAs used as photoanode in DSSCs can promote PCE from 6.40% to 7.13%. However, it's worth noting that TNTAs couldn't preserve their original morphology under the hydrothermally basic condition which might be beneficial for further improving crystallization of TNTAs, even if pre-sintering technique was carried out [22]. Hence, it is still a big challenge to seek for some reliable routes to improve crystallization of TNTAs for enhancing outperformance of DSSCs.

In this work, a novel route, i.e. hydrothermal vapor route, is put forward to realize crystallization of the as-anodic TNTAs film, and the resulting film with excellent crystallization and featured surface morphology were lift off from the Ti foil by chemical separation and transplanted onto the FTO substrate with TiO_2 sol paste, which can be used as front-side illuminated photoanode in DSSCs. To the best of our knowledge, there are no similar reports in DSSCs field. The effective characterization measurements are carried out to evaluate the performance of these photovoltaic devices, such as voltammetric test (J–V), incident photon to current conversion efficiency (IPCE), electrochemical impedance spectroscopy (EIS), and open circuit voltage decay (OCVD). The optimum PCE of our fabricated DSSCs can reach 8.11% when the ~34 μm TNTAs photoanode is used without any modification.

2. Experiment section

2.1. Preparation of TNTAs film on Ti foil

The highly oriented TNTAs were prepared through classical anodic oxidation in two-electrode configuration attached to a laboratory DC power supply (Model: GPR-30H-10D, GWINSTEK, Taiwan), with an anodization-polished Ti foil (purity 99.7%, substrate size 3 × 1.5 cm^2, thickness 0.127 mm, Aldrich) as the working electrode and a graphite flake as the counter electrode under the atmosphere environment. Firstly, the well-cleaned Ti foils were respectively anodized in mixed ethylene glycol electrolyte containing 0.25 wt% NH_4F and 1 vol% DI water under 60 V for ~1.5 h. Then, the preliminary TNTAs whose surfaces were covered with disordered debris were wholly removed by ultrasonication for ~10 min in diluted 10 wt% H_2O_2 aqueous solution to obtain the anodization-polished Ti foil. Subsequently, the secondary anodic oxidization was performed in the same experimental condition with only changing anodizing time to regulate the thickness of TNTAs. Finally, the as-prepared samples were washed by large amounts of ethanol, and dried for subsequent use.

2.2. Crystallization process of TNTAs film on Ti foil

Two different routes were applied to realize the crystallization of TNTAs film on Ti foil, and described in detail as follows:

Thermal annealing (TA): the amorphous TNTAs film was annealing at 450 °C in muffle furnace for 2 h at ramping rate of 2 °C/min and cooled down naturally, the resulting sample produced from this procedure was denoted as TA-450.

Hydrothermal vapor (HV): the amorphous TNTAs film was placed on top of the support in the interior of Teflon line (volume: 100 mL), which contained 10 mL DI water. The sealed liner was then loaded into a stainless steel autoclave and heated at different temperatures (160, 180, 200 °C) for 6 h, and cooled down by running water. The resulting samples produced from this procedure were dried at 50 °C overnight, and denoted as HV-160, HV-180 and HV-200, respectively.

2.3. Detachment process of TNTAs film from Ti foil

To lift off TNTAs film from the Ti foils, the crystalline TNTAs was then re-anodized in the same condition like mentioned above for 5 min to form a new layer of amorphous TNTAs between the crystalline TNTAs film and Ti foil. Afterward, the re-anodic sample was soaked in 33 wt % H_2O_2 solution for a certain time. When the whole film turned light yellow, the as-prepared samples were taken out immediately and rinsed with ethanol. After drying in air, the free-standing TNTAs would self-detach from the Ti foil.

2.4. Transplantation process of free-standing TNTAs film

To transplant the free-standing TNTAs film onto the FTO substrate, a viscous TiO_2 paste was prepared by mixing 1 mL titanium isopropoxide with 16 mL terpinol and 0.6 g ethyl cellulose under vigorous magnetic stirring at 80 °C until completely dissolved [23]. Then, an appropriate amount of the paste was spread onto FTO substrate by doctor-blade route as an adhesive layer. After that, the free-standing TNTAs film was carefully transferred to the paste-coated FTO substrate by tweezers, and the final front-side TNTAs