Effect of seed layer on growth of rutile TiO$_2$ nanorods

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Abstract. For achieving the high quality of titanium dioxide (TiO$_2$) nanorods, herein, we present a synthesis of rutile TiO$_2$ nanorods on a transparent conductive fluorine-doped tin oxide (FTO) glass substratewith seed layer by a two-step method. TiO$_2$ thin films were first precoated by spin coating and annealing, followed by the growth of TiO$_2$ nanorods with a hydrothermal method. The crystallographic nanostructures and properties of the nanorods were investigated. XRD results demonstrate that seed layer was tetragonal anatase TiO$_2$ structure while nanorods had tetragonal rutile TiO$_2$ structure. Since the hydrothermal technique was conducted in medium acid, structure of nanorods was induced to form in rutile phase. The major characteristic orientation of nanorods on the seed layers was (002) and minor in (101) planes. FE-SEM results show that seed layer enhances the process to achieve vertical-aligned orientation of the TiO$_2$ nanorods, which contribute to develop electron transport rate and could pay an important role inelectron transport layer in high-performance Perovskite solar cell.

1. Introduction

Among various semiconductor metal oxides, TiO$_2$ is a prime candidate for manufacturing chemicals on a large scale due to its high efficient photoactivity, stability and non-toxicity [1]. In recent years, TiO$_2$ has widely focused research in photovoltaic cells because of the wide band gap 3.0 eV for rutile and 3.2 eV for anatase. Only UV light or higher-energy photons can be absorbed, while a large portion of the visible and near infrared photo longer-wavelength photons cannot [2]. Especially, in Perovskite solar cells (PSCs), TiO$_2$ plays a key role as electron transporting layers (ETLs) receiving injected electrons from photogeneration in a Perovskite layer and transferring to collecting electrode [3]. Various observations report that TiO$_2$ nanorods (NRs) have capability more than conventional TiO$_2$ nanoparticles (NPs) since NPs consist of a great number of grain boundaries lead to energy loss because of electrons scattering in grain boundary regions [4-6]. Recently, among one-dimensional (1D) TiO$_2$ nanostructures, TiO$_2$ NRs exhibit the remarkable electron transfer properties such as high photoelectrochemical (PEC) performance and high electron life time because they provide the direct electron transport pathway [7]. Hence, TiO$_2$ NRs can be applied as ETLs in Perovskite solar cells. In practically substrate surfaces have significant role on architectures of NRs. Fluorine-doped tin oxide

(FTO) substrate with high surface roughness could provide poor vertical orientation of NRs. This results in lower short-circuit current in dye-sensitized solar cells (DSSCs) compared to DSSCs based on $TiCl_4$ seed layers (SLs) [8]. Therefore, this work aims to achieve highly crystallinity and crystallographic orientation of TiO_2 NRs using TiO_2 seed layers with minimal amount of harmful chemical such as hydrochloric acid (HCl).

2. Experimental details

2.1. Preparation of seed layer

FTO substrates were ultrasonically cleaned in 2% solution of alconox cleaning detergent and distilled water, de-ionized (DI) water, acetone and isopropanol for 15 min, sequentially. Next, the FTO substrates were flowed in nitrogen gas and cleaned with ultraviolet-ozone process for 30 min. The specific seed layers were coated on cleaned FTO by spin coating of 0.15 M titanium diisopropoxide bis(acetylacetonate) (TDB) in 1-butanal solvent at 3000 rpm for 30 s. The coated substrates were annealed at 125°C for 5 min. After that the films were deposited by another spin coating of 0.30 M TDB solution and annealed at 125°C for 5 min. The second spin coating process was repeated one more time. After spin coating, the seeded substrates were treated at 500°C for 30 min.

2.2. Synthesis of TiO_2 NRs

The hydrothermal process was carried out in Teflon liners (50 ml volume) contained in stainless autoclaves. In order to decrease amount of toxic chemical, deionized (DI) water and 37% by weight of hydrochloric acid (HCl) were mixed together at volume ratios of 2:1and stirred for 5 min. Then, 1.0% titanium (IV) butoxide (TBO) per solution was added into the mixture and stirred for another 5 min. After that, the FTO substrates with TiO_2 seed layer were placed in Teflon liners. The autoclaves were heated at 150°C for 1.5 h before they were flown with water for cooling down to room temperature. Then the FTO films were removed from the Teflon liners, rinsed with distilled water, and finally air dried under ambient conditions.

3. Results and discussion

In this work, FTO-coated glass with 562 nm mean thickness was used as substrate. Uniformly distributed TiO_2 seed layers (SLs) was coated on the FTO substrate consisting of nanoparticles with mean diameter and thickness of 27 nm and 101 nm, respectively. Figure 1.(a-b) shows the field emission scanning electron microscopy (FE-SEM) images of the FTO surface and TiO_2 SL surface. It revealed that the roughness on FTO surface was superior compared to that on the SL surface. This could result in TiO_2 NRs grown on the bare FTO showing terrible vertical orientation that some NRs almost collapsed and paralleled to the horizontal direction. The neighboring NRs collided with each other that could prevent the electron transfer (figure 1. (c,e)). On the other hands, SLs provide a lower surface roughness thereby oriented NRs arrays were obtained significantly. This led to an increase in density and vertical orientation of the NRs, which is expected to achieve a high electron transport as shown in (figure 1. (b,d)). The results of the study correspond with K. Hyun and B. Lyong Yang, showing that the seeded-FTO films with smaller roughness would benefit to grow denser nanorods [8]. Average diameter of the TiO_2 NRs on FTO was 41 ± 9 nm and that on SLs was 78 ± 20 nm. This represents that dimensions of the TiO_2 NRs grown on SLs are larger than those grown on bare FTO. This appearance can be seen clearly in 1.0% TBO (figure 1. (e-d)). This can be attributed to SLs providing smooth surface. Assisted by the smooth SL surface, it can promote nucleation of rutile TiO_2 leading to high vertical alignment of NRs and contributing to development of NRs in both height and width. XRD results in figure 2.(a) shows that all diffraction peaks of SLs agree well with the dominate (001) anatase tetragonal plane and small a (200) anatase peak. Even though SLs were anatase structure, the characteristic peaks of 1.0% TBO NRs on SLs demonstrate (101) and (002) rutile (figure 2.(a)). Because, during the particle agglomeration, the acidity of the reaction solution is suggested as a critical factor. HCl participates in hydrolysis by separating butoxy groups $[C_4H_9O]$ from Ti atoms and replacing with dissociated hydroxyl groups $[OH^-]$ in the solution. In addition, HCl takes responsible
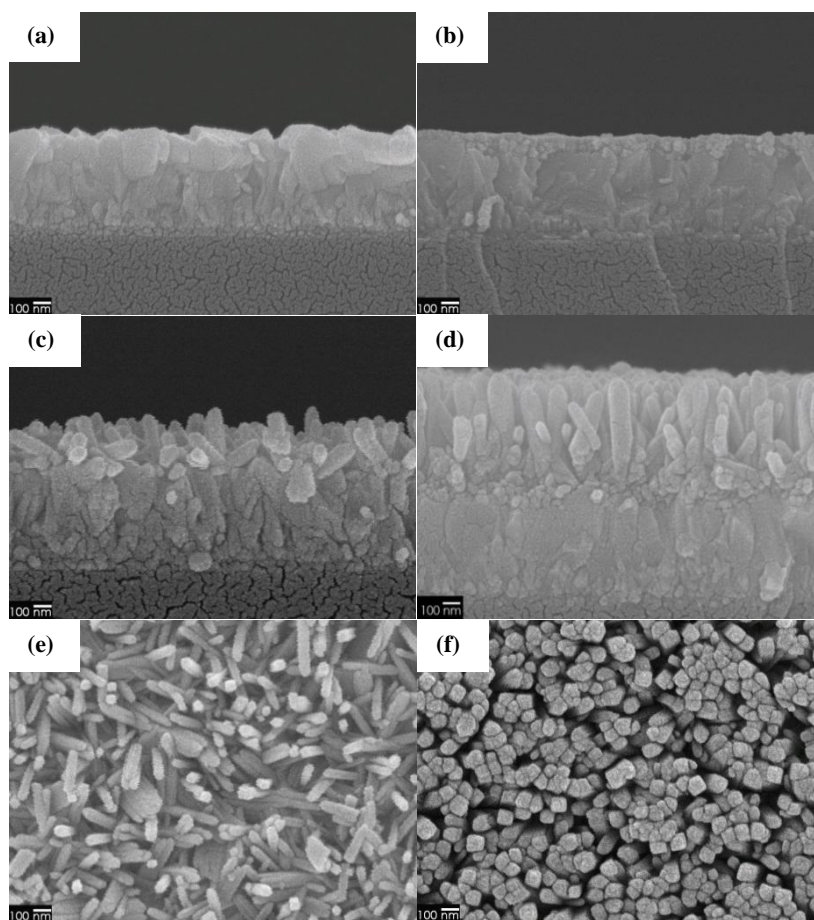
Figure 1. Cross section FE-SEM images of (a) FTO (b) seed on FTO (c) 1.0% TiO$_2$ NRs on FTO (d) 1.0% TiO$_2$ NRs on seed layer. (e) Top view FE-SEM images of 1.0% TBO NRs on FTO (f) Top view FE-SEM images 1.0% TBO NRs on seed layer.
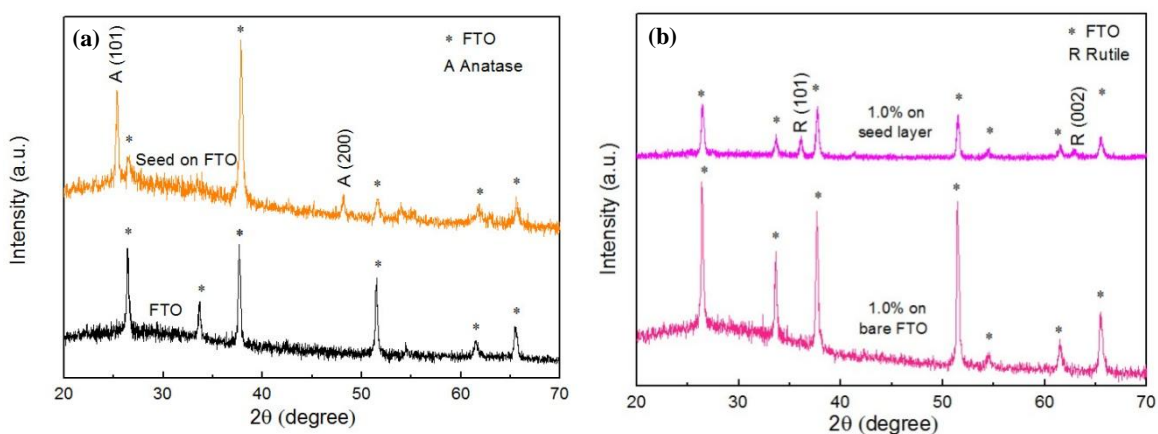

Figure 2. XRD pattern of (a) bare FTO and seed layer on FTO (b) 1.0% TBO TiO$_2$ NRs on bare FTO and TiO$_2$ NRs on seed/FTO.

to protonate OH$^-$ in Ti-hydroxo [9]. By the attribution of dehydration (elimination of water molecules), Ti-hydroxo could be combined into the precipitated crystal. Since rutile phase requires high degree of protonation of the TiO$_6$ octahedra to form their favourable dense orientation that means it desires advanced acid intensity to effectively catalyze the hydrolysis and dehydration reaction [9]. Moreover, characteristic anatase architecture is not stable under highly acidic conditions because of

strong repulsion between the protonated molecules within crystal structure [9]. Previous study reported that dominate crystal plane of NRs in length of 1-2 μm on seed layers was (002) and (101) for NRs on FTO. This indicated that seed layer provides the nucleation of high surface energy (002) plane of tetragonal rutile TiO_2 NRs [9, 10].

4. Conclusion

In summary, the vertically well-align TiO_2 NRs were successfully synthesized using hydrothermally grown on FTO substrate and on seed layers (SLs). SLs with a lower surface roughness contribute to orderly grown NRs in vertical. The oriented NRs were obtained significantly, which could lead to the improvement of electron transport. SLs can also improve TiO_2 NRs crystallinity providing tetragonal rutile TiO_2 with high density. The obtained TiO_2 NRs have pure rutile structure because the attribution of high concentration HCl in hydrothermal medium while SLs show anatase phase. This suggests that surface roughness and reaction medium have effects on TiO_2 NRs alignment and phase structure, respectively.

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