Bond Strength of TiO₂ Coatings onto FTO Glass for a Dye-sensitized Solar Cell

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Abstract

The bond strength of three types of TiO₂ coatings onto fluorine-doped SnO₂ (FTO) glass was investigated with the aid of a tape test according to ASTM D 3359-95. Transmittance was then measured using an UV-vis spectrophotometer in the wavelength range of 300 nm to 800 nm to evaluate the extent of adhesion of TiO₂ nanorods/nanoparticles on FTO glass. A sharp interface between the coating layer and the substrate was observed for single TiO₂ coating (TiO₂ nanorods/FTO glass), which may be detrimental to the bonding strength. In multicoating sample (TiO₂ nanorod/TiO₂ nanoparticle/TiO₂ nanoparticle/FTO glass), the tape test was not performed due to severe peeling-off prior to the test. On the other hand, the dual coating sample (TiO₂ nanorod/TiO₂ nanoparticle/FTO glass) showed minimum variation of transmittance (4%) after the test, suggesting that the topcoat adheres well with the FTO substrate due to the presence of the TiO₂ nanoparticle buffer layer. The use of a TiO₂ nanorod electrode layer with good adhesion may be attributed to the excellent dye sensitized solar cell performance.

Keywords : TiO₂ thin film, Transmittance, Nanorod, Nanoparticle, Bond Strength, Tape test

1. INTRODUCTION

One-dimensional nanostructures have been investigated extensively for their potential applications, such as electronics, optoelectronics, mechanics, catalysis, as well as biological and environmental systems because of their unique properties[1-4]. TiO₂ has been prepared by using numerous methods such as sputtering, sol-gel, spray pyrolysis, and metal-organic chemical vapor deposition[1-5]. Among the various synthetic methods, electrospinning (ES) is employed to synthesize fibular mesostructures for simplicity[6]. Despite these advantages, weak bonding strength between the nanofiber and the substrate limits its widespread use[1, 4]. The sintered TiO₂ nanofibers shrunk dramatically in the lateral direction and the layer peeled off[1]. This poor adhesion resulted in inferior device

performance[1, 4].

TiO₂ nanofibers were fabricated by drying electrospun TiO₂/polyvinylpyrrolidone (PVP) nanofibers for 5 h in air and subsequent annealing for 3 h at 500°C in air[3, 4]. As the temperature rose, an interesting phenomenon occurred, in which the fibers began to break apart because high temperature made the fibers as brittle as dry spaghetti noodles. The TiO₂ fibers without the TiO₂ buffer layer on glass did not show any bond strength[4]. In order to improve the bond strength, a TiO₂ buffer layer was spin-coated on the glass slide at room temperature prior to ES by using the same precursor solution. However, the bond strength increased only 3-10%, suggesting that the addition of the buffer layer in the middle of the coatings had only a modest effect on the bond strength[4].

The adhesion difficulties of longer nanofibers on fluorine-doped SnO₂ (FTO) glass can be solved by employing short nanorod powders. Fujihara et al.[1] developed a large-area (~20 cm²) of nanofibrous layers by spraying TiO₂ nanorods, obtained by the grinding of electrospun nanofibers, dispersed in suitable solvents on FTO glass and subsequent sintering. Such enhanced adhesion provides electrospun TiO₂ nanofibers the possibility of application in electronic devices[3].

Although the performance of dye-sensitized solar cells (DSSCs) using TiO₂ nanomaterials on FTO glass has been

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studied by numerous researchers due to the channeled electron transfer, no quantitative study for the bond strength is given[1]. Poor adhesion of nanomaterials with the conductive glass substrate imposes severe restrictions on the fabrication of DSSCs. In the present study, the bond strength of TiO₂ nanomaterials was investigated by using a tape test according to ASTM D 3359-95 to evaluate the extent of adhesion regarding the TiO₂ nanorods/nanoparticles on FTO glass[7-9]. The properties of TiO₂ nanorods were evaluated by using an UV-vis spectrophotometer, a scanning electron microscope (SEM), and a transmission electron microscope (TEM).

2. EXPERIMENTAL

The precursor solution was prepared from titanium tetraisopropoxide (Ti(OCH(CH₃)₂)₄, 98%, Aldrich, USA) in ethanol and acetic acid by stirring (0.14 g/mL)[11]. Polyvinylpyrrolidone (PVP, Mw=1,300,000, Aldrich, USA) dissolved in ethanol (0.09 g/mL) was added to the TiO₂ precursor solution by weight. The solutions were mixed and stirred for 1 h at room temperature. The precursor solution was then filtered by using a sintered glass filter(16-40 μm) to remove possible impurities in the solution. The ES apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22 gage metal needle, a grounded collector, and a high-voltage supply (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with current and voltage digital meters[10-13]. The solution was placed in a 5 mL BD Luer-Lok syringe attached to the syringe pump and fed into the metal needle at a flow rate of 0.5 mL/h. TiO₂ nanofibers were electrospun at an electric field of 1 kV/cm. The as-spun nanofibers were dried in air for 5 h to allow the hydrolysis of Ti (OCH(CH₃)₂)₄. Subsequently, annealing for 3 h at 500 °C in air at a heating rate of 1 °C/min was performed to remove the PVP and achieve the crystallization of titania[4,6]. Then, these fibers were ground mechanically in a pestle and mortar to produce TiO₂ nanorods[1, 11].

FTO glass was first surface cleaned by sonicating using distilled water, alcohol, and KOH (1 M), followed by rinsing and drying. The FTO glass (25 × 25 mm²) was used as a substrate. Three types of TiO₂ multilayers on the FTO glass were fabricated. Firstly, only a TiO₂ nanorod layer

was sprayed using a high volume low pressure (HVLP) gravity feed spray gun with a nozzle (Φ=1.0 mm) directly onto the FTO glass. During spray deposition, the FTO glass was maintained at a temperature of 75 °C. Secondly, the TiO₂ nanorod/nanoparticle layer on the FTO glass was deposited. The TiO₂ nanoparticle layer was first prepared by the spin coating technique (ACE-1020, Dong Ah Trading Corp., Korea). TiO₂ sol was first spin coated at 500 rpm for 8 s and then 3000 rpm for 30 s on the FTO glass. The TiO₂ nanorod powder slurry, dispersed in a mixture of ethanol and methanol (10 g/L), were sprayed subsequently on the TiO₂ sol layer. The substrate was placed on a hotplate at 75 °C. Lastly, a dense TiO₂ (*d*-TiO₂) underlayer was deposited on the FTO glass substrate by spray pyrolysis[1]. This was followed by spin coating of a diluted precursor solution (1 : 5 volume ratio in ethanol) at a speed of 1300 rpm for 10 s in order to form the ultrathin surface treatment layer (STL). The substrate was then placed on a hotplate at 75 °C. The TiO₂ nanorods dispersed in a mixture of ethanol and methanol were sprayed on the surface of the STL. Three types of TiO₂ nanorod layers on FTO glass, as summarized in Table 1, were then calcined for 1 h at 500 °C. The sintered TiO₂ nanorod layer was further solution treated with TiCl₄ (40 mM) for 30 min at 75 °C to provide improved connectivity between the nanorods, followed by calcination for 1 h at 500 °C[1-3].

Table 1. Three types of TiO₂ layers on the FTO glass

No.	1 st layer	2 nd layer	3 rd layer
sample 1	TiO ₂ nanorod	-	-
sample 2	TiO ₂ nanoparticle	TiO ₂ nanorod	-
sample 3	TiO ₂ nanoparticle	TiO ₂ nanoparticle	TiO ₂ nanorod

After the coating process was completed, the tape test was applied onto those materials in order to observe the adhesion strength qualitatively. The bond strength of the coatings was evaluated by a tape test according to ASTM D 3359-95[7]. An adhesive Scotch (3M) tape was applied onto the surface and rubbed to improve adhesion of the tape to the surface. The tape was then removed by pulling it off rapidly. The bond strength of the sample was then evaluated qualitatively using an UV spectrophotometer (V-570, Jasco, Japan) by examining the optical transmittance in the wavelength range of 300 nm to 800 nm[8, 9].

3. RESULTS AND DISCUSSIONS

The phase of the as-annealed fibers was previously reported to be a typical anatase phase [4, 11]. The morphologies of the as-spun and the as-annealed fibers were examined by using SEM, as shown in Fig. 1. The images show that the as-spun fibers with an average diameter of 180 nm have smooth and uniform surfaces with a random orientation. The SEM results revealed that the fiber diameter decreased from 180 nm to 100 nm after calcination at 500 °C, which is probably due to the decomposition of PVP and crystallization of TiO₂ [4, 6]. The TiO₂ nanorods were then produced by grinding the as-annealed fibers mechanically in a pestle and mortar, as depicted in Fig. 2.

Fig. 1. SEM images of nanofibers (a) before and (b) after calcination for 1 h at 500 °C.

Fig. 2. TEM image of nanorods.

The sintered TiO₂ nanorod layer on the FTO glass was further solution treated with TiCl₄ at 75 °C to provide improved connectivity between the nanorods, followed by calcination for 1 h at 500 °C. Fig. 3 shows the smooth surface of the porous TiO₂ nanorods filled with the TiO₂ nanoparticles after solution treatment. The cross-section of the sintered TiO₂ topcoat on the FTO glass or TiO₂ nanoparticle/FTO glass is shown in Figs. 4 and 5. A sharp interface (white line) between the FTO glass and the topcoat was visible for sample 1. In sample 1, the TiO₂ nanorods were sprayed directly onto the FTO glass, which was heated at 75 °C, without the TiO₂ buffer layer. The observed interface may be due to the absence of the TiO₂ buffer layer, probably leading to weaker bonding between the TiO₂ nanorod layer and the FTO substrate. On the other hand, the coatings having the TiO₂ nanoparticle buffer layer demonstrated the continuous interface. The observation of the discontinuous interface is possibly attributed to the presence of the TiO₂ buffer layer.

Fig. 3. SEM image of the surface of the TiO₂ nanorods/nanoparticles top coating layer.

Although a peel-off test using an adhesive tape showed that the TiO₂ nanorods adhere well with the substrate, sample 3 could not perform the tape test due to severe peeling-off prior to the test, as shown in Fig. 6. In the multicoat sample, adhesion failure occurred between the coats so that the adhesion of the coating system to the FTO glass is not determined. By contrast, two samples (Fig. 6(a) and (b)) adhere well to the FTO glass or the TiO₂ nanoparticle/FTO glass without peeling-off. In order to evaluate the adhesion, the difference in transmittance before and after detaching the Scotch (3M) tape was investigated. The tape was adhered to the coating by rubbing the entire surface area using constant pressure. Transmittance was measured using an UV-vis spectrophotometer in the wavelength range of 300 nm to 800 nm,

as shown in Fig. 7. The transmittance spectra were measured and examined at the wavelength of 550 nm. Transmittance of sample 1 rose from 2.4% to 18.8% after the tape test, indicating that the TiO_2 nanorod layer on the FTO glass was detached. Although the variation of transmittance of sample 3 (65.9% $\rightarrow$ 66.5%) was only 0.6%, the TiO_2 nanorod/ TiO_2 nanoparticle/ TiO_2 nanoparticle/FTP glass was already damaged significantly prior to the test. On the contrary, sample 2 showed the best adhesion (6.4% $\rightarrow$ 10.1%) among the samples investigated, suggesting that the TiO_2 nanorods adhere well with the TiO_2 nanoparticle/FTO glass. It is evident that the TiO_2 nanoparticle buffer layer is crucial to the bond strength of the TiO_2 coatings.

Fig. 4. Low magnification SEM images for the cross-section of the coatings on FTO glass ; (a) sample 1, (b) sample 2, and (c) sample 3, respectively.

Fig. 5. High magnification SEM images for the cross-section of the coatings on FTO glass ; (a) sample 1, (b) sample 2, and (c) sample 3, respectively.

Fig. 6. Optical photographs for the surface of the coatings on FTO glass before the tape test ; (a) sample 1, (b) sample 2, and (c) sample 3, respectively. Note that the coating area is $10 \times 10 \text{ mm}^2$.

Fig. 7. Transmittance spectra of the TiO₂ coatings on the wavelength range of 300 nm to 800 nm before and after the tape test.

In the present study, the thickness of the TiO₂ coatings investigated was less than 1 μm , which was insufficient for the DSSC. The TiO₂ nanoparticles/nanorods layer with a thickness of 15 μm to 20 μm on the FTO glass is known to be the best DSSC electrode with a high efficiency[1]. For the use of the TiO₂ nanorods with a good adhesion as the DSSC electrode, the TiO₂ nanorod layer should be deposited with a thickness greater than 15 μm . The results of DSSC performance constructed using a TiO₂ electrode layer with good adhesion are known to be excellent probably due to the minimization of electron back transfer[1]. The electrodes with good adhesion may reduce the electron back transfer between the FTO glass and the electrolyte, resulting in higher solar cell efficiency. However, it warrants further study.

4. CONCLUSIONS

The adhesion test of three types of TiO₂ coatings onto FTO glass was performed by using a tape test according to ASTM D 3359-95. Transmittance spectra were then examined in the wavelength range of 300 to 800 nm to evaluate the extent of adhesion of the TiO₂ nanorods/nanoparticles on the FTO glass. A sharp interface between the layer and the substrate was detected for the single TiO₂ coating (TiO₂ nanorods/FTO glass), resulting in weaker bonding strength. In the multicoating sample (TiO₂ nanorod/TiO₂ nanoparticle/TiO₂ nanoparticle/FTO glass), the tape test was not performed due to severe peeling-off prior to the test. On the other hand, the dual coating sample (TiO₂ nanorod/TiO₂ nanoparticle/FTO glass) revealed a minimum variation of transmittance (4%) after the test, suggesting that the topcoat adheres well with the TiO₂ nanoparticle buffer layer on the FTO substrate. The use of a TiO₂ electrode layer with good adhesion may provide excellent DSSC performance due to the minimization of electron back transfer.

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