Highly Laminated Electrospun ZnO Nanofibrous Film on the Transparent Conducting Oxide for Photovoltaic Device

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ABSTRACT:

The electrospinning technique is a revolutionary template-catalyst-free method that can generate 1D nanostructure with the tunability and the potential for the mass production. This approach received a great deal of attention due to its ability to give direct pathways for electrical current and has been utilized in various electronic applications. However, the delamination of inorganic electrospun film has prevented the intense utilization due to the thermal expansion/contraction during the calcination. In this study, we propose an electrical grounding method for transparent conducting oxide and electrospun nanowires to enhance the adhesion after the calcination. Then, we examined the potential of the technique on ZnO based dye-sensitized solar cells.

Keywords: ZnO, Nanowire, Electrospinning, Electrical grounding, DSSC

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1. Introduction

The dimensions of various nanomaterials have been tailored to modify the functionalities from zero dimensions to three dimensions.¹⁻³⁾ Matrices with nanoparticles or nanosheets provide a great surface area, which is relative to the volume in macroscale, so the system is favorable high reaction rates. However, the structures consisting of the nanoparticles have numerous grain boundaries, which scatter the charge carriers, so the electrical performance can be reduced in this fashion. Otherwise, the one-dimensional nanowire-based matrix, for example a carbon nanotube, induces the directional migration of the charge carriers, thus, it is suitable as an electrode for many electrical applications that require a noble property.

To fabricate one-dimensional materials, some methodologies have been developed, such as the VLS technique,⁴⁾ templating,⁵⁾ and self-assembly,⁶⁾ which are

complicate and inefficient in terms of productivity. Compared to the other methods, the electrospinning technique is a powerful approach with a template-catalyst free strategy that can fabricate highly continuous 1D nanostructures with delicately tunable morphology, and it can be easily scaled up for mass production.^{7,8)} In addition, many materials can be utilized through this technique, including not only inorganic, but also organic materials,⁹⁾ even for the nanotubes¹⁰⁾ and core-shell structures.¹¹⁾ The gel solutions that contain the sources for the nanowires are injected from the charged orifice to the oppositely charged target with the parameters of potential difference and injection rate.

Generally, inorganic materials have better properties than organic materials for electrical applications, and it involves a firing process to remove the solvent, which is for the viscosity of the gel solutions. However, the as-spun nanowires shrink and crack with the calcination on the glass substrate due to the thermal deformation of the nanowires, so the films become delaminated, which causes a serious decreasing of the

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electrical property. Thus, a great deal of research has been carried out to obtain inorganic electrospun films without shrinkage after heat treatment. Hot-pressing,¹²⁾ applying sublayer,¹³⁾ controlling thickness, and recollecting to the nanorod¹⁴⁾ have all been attempted, but these works could not be precisely controlled and were not reproducible.

Therefore, we report a unique method to fabricate highly laminated films without fractures on the transparent conducting oxide (TCO) with the electrospinning technique by grounding electrically. As the injection progresses, the gel solution is electrostatically charged by the orifice, so the adhesion to the TCO, which is oppositely charged, can be improved. In this report, we applied this idea to a ZnO based dye-sensitized solar cell (DSSC) to confirm the potential. This straightforward approach is very simple and easy to set up for mass production compared to the previously reported research, and it can facilitate the various applications for the electrospinning technique based process.

2. Experimental

The gel solution for the electrospinning was prepared by vigorously mixing 0.6 g of zinc acetate for the source of the ZnO nanowire, 0.5 g of polyvinylpyrrolidone (PVP) for the viscous solution, 2 g of deionized water, and 1.45 g of ethanol for the solvent. 0.5 ml of the solution was loaded to the syringe and injected under the conditions of 20 cm of distance to the target substrate, 15 V of operating voltage, and an injection rate of 1 il/min at room temperature. Fluorine doped tin oxide (FTO) coated glass for the TCO substrate of DSSC was placed on the stage of the electrospinner, and the Cu foil was connected between the FTO glass and the stage for the electrical grounding as shown in Fig. 1. The as-spun film on the FTO glass was heated to 500°C for 30 minutes. After the heating step, the electrospun ZnO electrode was trimmed to 0.27 mm² and immersed into the ethanol solution containing a 0.5 mM of N719 dye for 20 minutes to adsorb the sensitizer. The sample was rinsed with anhydrous ethanol to wash away the residual material, and was sealed using sealant, which has a width of 1.5 mm, with a drilled counter electrode coated with a drop of diluted H₂PtCl₆ solution (2 mg in 1 ml ethanol) and cured for 30 minutes at 400°C. The sealed cell was injected with a drop of electrolyte to the

Fig. 1. Schematic diagram representing the electrical grounding technique for the electrospinning method.

drilled hole and was sealed immediately by soldering a piece of slide glass/sealant. Finally, the contact area for the connection to the photovoltaic source meter was painted with a silver paste. The photovoltaic measurement was carried out for AM 1.5 condition.

3. Results and Discussion

The photograph of Fig. 2(a) and (b) represent the electrically-grounded sample and the ungrounded sample after the calcination, respectively, and the obtained films were quite different in terms of the adhesion on the FTO substrate. The film of the grounded sample was attached firmly on the substrate, unlike the ungrounded sample which was almost delaminated. The uniform distribution of diameter and the morphology of as-spun nanowires are shown in Fig. 2(c) and (d) without spherical beads, which can be found in some rough conditions. Because the as-spun wires contained polymeric binder, not only the ZnO source, so it showed smooth surfaces. However, the removal of the binder by heat treatment was essential to obtain the appropriate electrical property, so shrinkage occurred due to the difference of the thermal expansion/contraction between the electrospun nanowires and the FTO substrate, as Fig. 2(e) represents the topology after calcinations without electrical grounding. In Fig. 2(f), the cross-sections of fractured nanowires were observed and were seriously torn and delaminated from the substrate, which could induce a drop of electrical current. After the calcination, the surfaces of the electrospun

Fig. 2. Photographs showing the differences of the electrical grounded film (a) and the ungrounded film (b) for ZnO electrospinning on the FTO glass. In SEM images, the as-spun nanowires (c, d) showed smooth surface. The ungrounded nanowires (e, f) were fractured and delaminated into fragments, however the grounded nanowires (g, h) were highly laminated without defects.

nanowires became slightly rough, which indicates the local crystallization from the as-spun precursor. The diameters of the calcinated nanowires were decreased to below 200 nm with the decomposition of polymeric binder, which led to the peeling off of the film with the volumetric contraction. Fig. 2(g) and (h) shows the highly laminated morphology of the film with the electrical grounding, and no cracks or peeled fragments were observed from the grounded sample. The diameters of this case remained almost same as in Fig. 2(e) and (f), and it is obvious that the adhesion between the electrically-charged as-spun nanowires and the FTO substrate was dramatically improved by the grounding technique. In this way, it can be also applied to the organic materials only for the delamination issue, but not for the fracture.

Fig. 3. XRD spectra (a) showed the electrospun ZnO nanowires after the calcination had a common phase of wurtzite on the dashed line. The electrospun nanowire had a polycrystalline with multi grains in a single wire (b, c).

The measurement of X-ray diffraction is shown in Fig. 3(a), and we investigated whether the obtained film after the heat treatment had a typical wurtzite phase of ZnO as in previous studies.^{15,16)} The peak intensity of ZnO was lower than that of FTO, so it can be explained as the film had a great portion of pores relative to the total film thickness. In Fig. 3(c) and (d) of the transmission electron microscopic (TEM) image, the crystallinity of the electrospun ZnO nanowire can be identified, and it was represented for the polycrystalline phase from the images and the diffraction pattern as some grains existed in a single nanowire. Thus, we can speculate that the grounding method was effective for the combination of ZnO/FTO in regards to the electrospinning-based laminating issues, even though the calcination was sufficient to obtain the preferential phase.

The photovoltaic measurement is shown in Fig. 4. Despite of the solution of the peeling-off problem, the characteristic was not impressive because the short circuit current density (J_{SC}) and the open circuit voltage (V_{OC}) were poor with the limitations of the dye

Fig. 4. The photovoltaic characteristics and the J-V curve of the DSSC using the electrospun ZnO nanowire film as an electrode.

loading and the surface area for the ZnO based 1D nanostructure.^{17,18)} Future works can aim to optimize the photovoltaic characteristics,¹⁹⁾ and this work might be meaningful with the utilization of the electrical grounding technique, therefore, we can suggest other applications that are suitable with this method.

4. Conclusions

In conclusion, ZnO electrospun nanowires after calcination could be highly laminated without fracturing and peeling off by the enhanced adhesion between the nanowire and the substrate through the electrical grounding technique. This work was much more effective than the other related studies in terms of productivity. Many themes about the electrospinning technique for the inorganic/organic materials can be applied through these approaches, even though ZnO nanowire based DSSC was not fully optimized.

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