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Uniaxial Freezing, Freeze-Drying, and Anodization for Aligned Pore Structure in Dye-Sensitized Solar Cells

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A variety of methods are available for creating the titanium dioxide (TiO_2) semiconductor surface layer of dye-sensitized solar cells (DSSCs); however, many of them are used independently to create surface morphologies that are influenced by only one process. A series of experimental techniques are utilized, some not originally used for thin film preparation, to create a semiconductor surface that exhibits variations in morphology on the macro-, micro-, and nanoscales. The techniques used to create the micro- and nanostructures are uniaxial freezing, freeze-drying, and anodization or etching, combined with the macrostructural techniques of the doctor blade method, screen printing, and/or electrophoretic deposition. When several of these techniques are used together to create, and modify, a thin film for DSSC, these techniques can produce a TiO_2 semiconductor layer for DSSC that has very high current and voltage characteristics, and a surface morphology more complex than can be created by using any one of the techniques alone.

I. Introduction

Dye-sensitized solar cells (DSSCs) are comprised of three major and two minor components: the semiconductor base layer, the dye, the electrolyte, and the two electrodes, respectively. Titanium dioxide (TiO_2) plays a crucial role as the semiconductor base layer material, and its main structural function is to provide a substrate for organic dye attachment, and also to provide a barrier between the charge transfer electrolyte and the conducting glass anode (to prevent charge recombination—where electrons return to the electrolyte instead of traveling to the electrode). Electrochemically, the TiO_2 semiconductor accepts electrons injected by the organic dye, and transfers them to the conducting glass anode, with a negligible loss of energy.[1] Other semiconductors of similar nature (ZnO, etc.) can be used, but TiO_2 is the focus of most current research. This is due to the close match of the band gap of TiO_2 to energy of the electrons emitted by many of the metallo-organic dyes that are readily available on the market, and the ability of these dyes to attach with chelation.[2] Many methods are used to produce the TiO_2 surface for DSSCs, including electrophoretic deposition (EPD), screen printing, and doctor blade deposition. The goal of each of these methods is to produce a semiconductor layer whose surface maximizes the amount of dye that can attach, while minimizing the recombination losses.

The doctor blade technique was the first technique[3] used to create the semiconductor band gap layer of DSSCs, and is the least sophisticated. The technique consists of using a flat, sharp object (like a razor blade) or a round, thin object (like a glass stirrer) to lay a thin layer of slurry, with a thickness determined by a spacer. The simplest spacer is adhesive tape, which is between 8 and 10 μm thick on average,[4] and it is placed on opposite sides of the area where the film is to be laid, and the doctor blade is dragged across. The surface structure produced by this method is flat, with variations based on rolling technique, flatness of the spacing material, and position of the blade during the process. One of the drawbacks to this method is that there is limited control over the properties of the final surface and its microstructure, and there is no direct way to manipulate the morphology at the nanoscale. Another drawback is that the thickness of the film is directly related to the thickness of the spacers, and it is difficult to find appropriate spacing material with the desired thickness of 1–7 μm.[5] Overall, the doctor blade method is rather limited to produce the complex surface needed for DSSC to maximize dye attachment.

The second method to be discussed that is used to produce the semiconductor layer for DSSCs is screen printing.[6–9] This technique is used to deposit thin films based on applying a slurry to a designed pattern on a screen, where the slurry is pressed through the screen to land on a desired substrate. The thickness of the layer is determined by the viscosity of the slurry, and by the speed at which it is pressed through the screen. By laying thin layers, letting them dry, and then adding new layers on top, relatively complex structures can be produced, at the desired thickness. However, for more complex processes, many screens have to be used and the process can be very time consuming for thick or complex surfaces. Also, the highest resolution of screen printing is on the order of 100 μm, which means that any feature on the surface created by screen printing cannot be smaller than this scale. Considering that the dye molecules are only a few nanometers wide, this process does not increase the surface area enough to compete with other mechanisms for creating a textured surface, although screen printing can produce a much better surface than the doctor blade method.[10] Much research has been devoted to screen printing of DSSCs, as the process is carefully controlled and designed by creating the screens, and is used widely in industrial silicon-based solar cell production. It may be the easiest, and most cost-effective, method to transition existing solar cell facilities to production of the new types of cells.

The third method that is used for the creation of the semiconductor layer for DSSC is EPD. This method involves putting the desired particulate material in a solution (preferably with constant mixing to keep the particles in suspension), and creating an electric potential that drives the deposition of the material on the substrate. This process creates a varied surface texture. The deposition rate is determined by the materials properties. In many cases the created deposit is not structurally ordered. EPD creates a significant amount of porosity for dye attachment, but

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may create closed pores instead of open ones, which decreases the surface area as compared with ordered structures with controlled surface porosity.

Each of the three aforementioned methods has its advantages and disadvantages, but none come close to the ‘‘ideal’’ surface morphology—the one that maximizes the amount of dye that can attach to the surface while minimizing the distance the electrons have to travel to reach the conductive electrode.

II. Optimization of Surface Morphology

As mentioned above, the ideal morphology for the semiconductor layer of DSSC has a large surface area for dye attachment, but also does not impede electron flow to the conduction layer. However, a high surface area may cause electrons to travel farther to reach the electrode, and they run the risk of recombination. Given that the recombination time of the electron in DSSC is much lower than the injection time of the dye and the travel time through the semiconductor material, very complex surface morphologies can be created without a great risk of performance loss due to recombination.[11] Using a set of complementary methods, we present a technique for creating a varied surface morphology of TiO_2 that approaches the ‘‘ideal’’ surface structure. Using the doctor blade method, uniaxial freezing, freeze-drying, and surface etching (or anodization), we have been able to create a large amount of micro- and mesoscopic surface variation that drastically increases the surface area compared with simple doctor blade or EPD produced semiconductor layers (with no further surface modification). Each of the steps in the process creates a unique modification to the semiconductor, which combines with the others to produce a total increase in surface area. The most important methods used are those of freeze-drying and uniaxial freezing, due to their ability to affect the structure of a material on the nanoscale after a primary process of thin film creation has been used, and their previous lack of employment in the particular research area of semiconductor thin film layers for DSSC. These methods are able to optimize the surface of the material created using one of the bulk methods (screen printing, EPD, doctor blade, etc.).

Anodization has been used mainly to increase the layer of oxides on surfaces, to increase corrosion resistance, in industrial applications (particularly with aluminum) and recently has been shown to have unique effects on the surfaces of materials.[12]

Anodization is the process of passing an electric current through an electrolytic solution, with the object to be anodized serving as the anode, and with another conductor as the cathode. The electric current causes a reaction at both electrodes, with hydrogen being released at the cathode and oxygen at the surface of the anode. This produces a building of the oxide layer on the surface of materials that can oxidize, located at the anode.[13]

Many materials that form into oxides have a certain (passivation) thickness of oxide at the surface that develops spontaneously. The electrolytic solution used in this process is often an acid, which slowly dissolves the oxide layer, creating a porous structure that allows for the oxidation process to continue. The reaction rate is balanced so that the oxidation rate is similar to the corrosion rate by the acid bath. Without the application of the acid, the oxide would only form a passivation layer on the surface of the material. When the acid is used, the reaction can occur beyond the thickness of the passivation layer because the acid is etching deeper into the material, and allowing reactions to occur at the deeper sites. This allows a buildup of an oxide layer than can be several times thicker than the passivation layer.[14]

Oh and Jin[15] have used the anodization process on a thin sheet of titanium metal, to convert the material into a porous TiO_2. The titanium sheet is so thin that the acid can reach every part of the material as the pores develop, and therefore can convert the entire metal to the oxide. The process involves 30 min, and 20 V of dc current applied to titanium in a hydrofluoric acid bath. This extended time guarantees that the entire thickness of the material will be converted to oxide. The surface is not just converted to oxide, but as the acid etches the surface, it creates nanorods on the surface. This nano-morphology fits with our desire to create a macro-, meso-, and nanoscopic varied surface for dye attachment. Research has shown that the nanorods produced using this method are in the amorphous form, and sintering is necessary to produce the phase change from rutile to anatase that is required for DSSC.[16]

The results of this anodization method are a TiO_2 thin film with nanorods covering the surface, which is very similar to a TiO_2 thin film that has been deposited by doctor blade method and then etched with nanorods on the surface. The anodized film retains the bulk porosity and surface structure of the titanium metal film from which it was produced, while the doctor blade and etched film retains the bulk porosity from deposition, both of which are not well controlled (as mentioned previously as a drawback for the doctor blade method). This method of anodization (etching with electric current to produce thin films for DSSC) and the subsequent surface structure have been widely studied and the experiments were not repeated by us.[17] Experiments with DSSCs made in this manner show a significant improvement in the performance compared with nonanodized doctor blade solar cells.

The precursor material that we use is TiO_2, and not titanium metal, and therefore it does not benefit from the anodization procedure directly. Because there is no oxide to form, anodization of TiO_2 simply becomes etching by hydrofluoric acid. However, the anodization process by Jin *et al.*,[14] shows a particular surface morphology created by the hydrofluoric acid etchant. If we use the same acid solution, but without electric current, then we can expect a similar nanorod morphology. However, due to the lack of oxide formation at the surface in titanium oxide (versus pure titanium metal) and due to the higher reaction constants for TiO_2 in hydrofluoric acid (compared with titanium metal in hydrofluoric acid), the exposure time of the TiO_2 samples to hydrofluoric acid must be significantly shorter.

Also, Kitano *et al.*[18] have showed that hydrofluoric acid etching of TiO_2 increases the photoelectrochemical performance not only under UV but also visible light irradiation, with the HF-treated thin films having a larger surface area and higher donor density than nontreated films.

Freeze-drying has been used in other areas (mainly in the food industry and pharmacology), and has some history in materials research,[19,20] but has been gaining frequency of use in this field only in the past decade.[21–23]

Others have reported[24] on the morphology that uniaxial freeze-drying (a combination of uniaxial freezing and freeze-drying) can create, mainly macroscopically aligned channels. The orientation and properties of the channels may be controlled and tuned, depending on the placement of the freezing surface, the temperature gradient between the freezing surface and the top surface of the material, and the quality of the aqueous solution. These channels can be oriented in different directions, parallel or perpendicular to the substrate, depending on the shape of the cooling plate, and its contact with the glass substrate. One of the main factors controlling growth of these channels is the temperature gradient between the conductive plate immersed in refrigerant, and the medium surrounding the upper surface of the material. The temperature gradient is the driving force for ice crystal growth, and causes the ice crystals to form in a direction parallel to the heat flow, and perpendicular to the cooling surface. Figure 1 shows this in detail.

Freeze-drying is the sublimation of a frozen, aqueous solution, usually at low temperature and decreased pressure for water-based solutions (parameters vary depending on the liquid being used). For DSSCs and other materials, the aqueous solution is the semiconductor oxide slurry or gel, created and placed on the conducting glass substrate using some other method like doctor blade deposition, EPD, or screen printing. The oxide slurry is composed of water, the semiconductor oxide, a binding agent, and a dispersant. The conducting glass substrate, coated with the aqueous semiconductor oxide layer, is placed on a

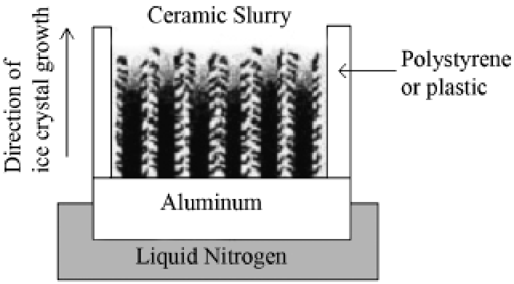

Fig. 1. Direction of ice formation during the uniaxial freezing process that creates the aligned pores.

thermally conductive plate (in our case, aluminum), as shown in Fig. 1. The plate is surrounded with a refrigerant, such as liquid nitrogen, with the bottom of the sample in contact with the plate and the upper surface in contact with the air atmosphere, which cools the semiconductor oxide layer rapidly (depending on the refrigerant used) and causes the formation of ice crystals in a direction parallel to heat flow.[23] Once the aqueous semiconductor oxide layer is frozen, the layer and substrate are freeze-dried, to remove the water, leaving only empty channels in a porous material. A semiconductor oxide surface layer can be calcined or sintered normally after freeze-drying has finished, to remove the rutile phase in TiO_2. Freeze-drying is necessary to compliment the uniaxial freezing process, as normal melting of the water in the slurry destroys the fragile structure of the pores in the material.

Gratzel (who pioneered the DSSC technology)[25] has suggested that the desirable morphology of the films should have mesoporous channels, or nanorods, aligned in parallel to each other and vertically with respect to the glass current collector. This would facilitate pore diffusion, give easier access to the film surface avid grain boundaries and allow the junction to be formed under better control.[25] Neither the doctor blade method nor EPD creates a varied morphology as described here, but rather a smooth layer with a high surface roughness. Screen printing has a potential for creating aligned channels, but only through careful creation of the screens and printing of multiple layers.[26] Only by creating the base layer of the semiconductor with one of these three methods, and then modifying the surface with the two optimization methods (uniaxial freeze-drying and anodization) can we create a morphology that approximates Gratzel's ideal.

III. Experimental Procedure

For the uniaxial freeze-dried TiO_2 DSSC samples, 20 nm average particle size powder (Evonik Degussa Aeroxide P25, Evonik Degussa, Essen, Germany) was added to water, in a mole ratio of about 1:5, followed by magnetic stirring for 15 min. A drop of Triton X-100 was added to the water/TiO_2 mixture before stirring.

Dispersions of TiO_2 P25 in H_2O were applied to FTO conductive glass (2.5 cm^2 area) by the doctor blade technique, using transparent tape as a spacer material, to deposit a thin film (slurry) onto the one conductive side of the FTO glass substrate.

A polystyrene container was used to create a bath of liquid nitrogen (for rapid freezing), with an aluminum plate partially immersed (but not covered) in the liquid nitrogen. When the aluminum plate reached a suitably cold temperature (as verified by infrared temperature measurements), the FTO glass coated with the thin film slurry was placed directly onto the exposed surface of the aluminum plate, with the nonconductive surface of the glass of the sample touching the plate and the thin film surface of the sample exposed to air. After 2 min, the thin film was completely frozen on the glass substrate, and the combination of thin film on substrate was placed in the freeze-dryer at $-50°C$ and 0.3 μbar for 24 h.

After removal from the freeze-dryer, the thin film on substrate was dried, and sintered, by heating at 450°C for 30 min. Immediately after, the thin film on substrate was sensitized by dipping into a 0.5 mM solution of N719 dye (acquired from Solaronix, Aubonne, Switzerland), in ethanol, and held in solution overnight at room temperature.

For normal (nonuniaxial) freeze-dried DSSC samples, the thin film slurry is applied to the substrate in the same manner as mentioned above. However, the thin film-coated substrate is placed directly into the liquid nitrogen bath for freezing, rather than being placed on the aluminum plate. The sample is removed from the liquid nitrogen bath and placed in the freeze-dryer, sintered, and soaked in solution using the same process as mentioned above for uniaxial freeze-dried DSSCs.

Sandwich-type solar cells containing the P25 TiO_2 film on the FTO glass substrate, with a graphite-coated FTO counter electrode, were created for making photocurrent and photovoltage measurements. The electrolyte consisted of $0.05M$ I_2, $0.5M$ KI in ethylene glycol, and the dye was N719 (mentioned above). Ethylene glycol (reagent grade) was from Sigma Aldrich (St. Louis, MO) and used as received.

For the anodization, a solution of $1M$ HF (Fisher Scientific, Pittsburgh, PA) was diluted with deionized water, for a total volume of 100 mL. The DSSC samples were immersed completely in the etching solution for 4 min, after which they were gently rinsed with DI water and dried in a vacuum furnace for 2 h.

For solar testing, the samples were placed under two fluorescent bulbs, calibrated to the AM 1.5 standard. A UV filter was used to recreate solar conditions.

For the SEM images of the uniaxial freeze-drying effects, each of the samples was coated with epoxy, to minimize damage during cutting and polishing.

IV. Discussion

The freeze-drying technique can be utilized for a large variety of different material systems. For the band gap semiconductor for DSSC, the dimensions are very small (thickness <10 μm, 1 cm^2 area or less), and it is difficult to understand the complex effects of each of the individual techniques utilized in this research.

According to Deville's comprehensive review of freeze-casting, experimental results show that structures with porosities of 25%–90% can be achieved with freeze-casting methods (such as uniaxial freezing).[27] This fits perfectly with the desired goal of 40%–60% porosity for DSSC, as stated by Gratzel and others.

The factors that influence the ice crystal structure of the frozen material, and pore structure of the finished solid, include the solvent, particle size, temperature gradient, and several other factors. Deville's review work, and another of Deville's works,[28] partially elucidate the relationships between several of these factors and the ice front velocity (the speed at which the "front" of freezing travels as a freeze-cast material is frozen), specifically an inverse proportionality between velocity and lamellae thickness (the thickness of the ice channels, which later become pores), initial particle size of the solute, and temperature gradient during freezing. Reevaluating these parameters in terms of lamellae thickness (rather than ice front velocity), we find a proportional relationship between lamellae thickness and both particle size and temperature gradient. Although ice front velocity is a difficult parameter to measure, and the entire process is very complex and the influence of each parameter is not known, the importance, and relevance, for our research is that Deville has shown that a higher temperature gradient and a smaller particle size of powder in the slurry are directly proportional to the size of the channels in the material. Because we use 20 nm average particle size powder, and a high temperature gradient (due to the use of liquid nitrogen), we can be certain that any channels formed during freezing are on the micrometer scale based on Deville's empirical plots (for 100 and 400 nm alumina) and SEM confirmation, and therefore contribute directly to enhancing the DSSCs microstructure. Although no particle size to

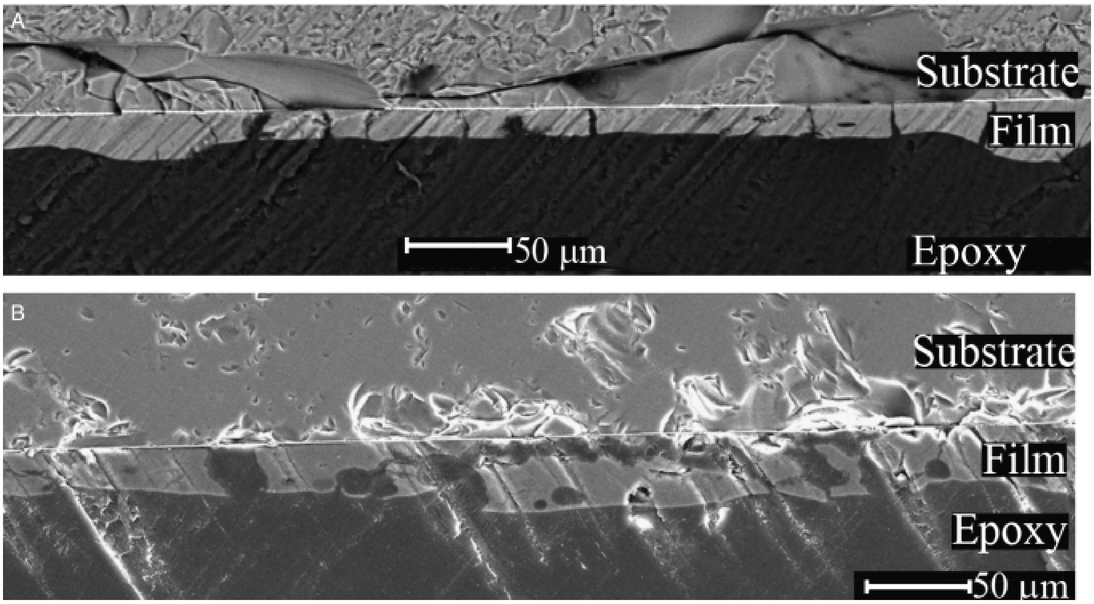

Fig. 2. (A) Cross section of a doctor blade deposited cell; (B) cross section of a similar cell after the freeze-drying process. Note the increased pore structure for the freeze-dried sample. The imperfections in the freeze-dried image are due to the fragile titanium dioxide fragmenting during cutting that scratched the sample.

lamellae thickness plots are available in Deville's review, we feel confident using the plots for 100 and 400 nm alumina particles as a rough basis, because in the equations he presents, properties of the solute material are significantly less important than particle size, and our particles are an order of magnitude smaller than those of alumina.

Based on this research, freeze-drying of the TiO_2 surface layer produces a porous, beneficial surface for dye absorption and electron transport. However, the results for these thin films are not similar to those seen in bulk structures. Because the TiO_2 surface layer is so thin (<20 μm), the temperature gradient is higher, but the ice crystals cannot grow as uniformly in the solution. This is compared with those samples of larger height, such as bulk zirconia samples from the literature where the temperature gradient is lower, but the distance for crystal growth and development is much larger.[22] Figure 2 shows a cross section of a standard doctor blade deposited TiO_2 layer compared with a freeze-dried TiO_2 layer. The upper portion of each image, which is designated by a nearly horizontal line in the sample, is the glass substrate on which the TiO_2 layer is attached, while the lower portion of the image is the epoxy coating that allowed for cutting of the fragile thin film. These samples were produced in the traditional manner (with the addition of uniaxial freeze-drying to the latter), using the doctor blade deposition method, as indicated in some early works by Gratzel.[29] The freeze-dried layer shows a much higher surface area, and much higher porosity than the doctor blade sample. The doctor blade sample only has channels from the surface to the conducting glass substrate, most likely due to cracking during drying. The freeze-dried sample has a varied pore structure throughout the TiO_2 film. Despite the fact that the images are cross sections, given the extremely varied shape and size of many of the pores, it is likely that most of them are open, which would allow for more dye attachment.

Figure 3 shows a comparison between the surface of a uniaxial freeze-dried DSSC and one produced using EPD (from a previous Gratzel work).[30] The higher variation of the surface and increase in surface area is apparent in the uniaxial freeze-dried image (right) versus the EPD sample (left). This increased surface roughness is clearly due to the optimization of the surface by uniaxial freeze-drying, as the method used (doctor blade) to create the thin film produces less roughness of the surface than EPD. Besides the surface roughness, the overall porosity of the freeze-dried sample is higher, with smaller interconnects between regions of particles, and larger pores.

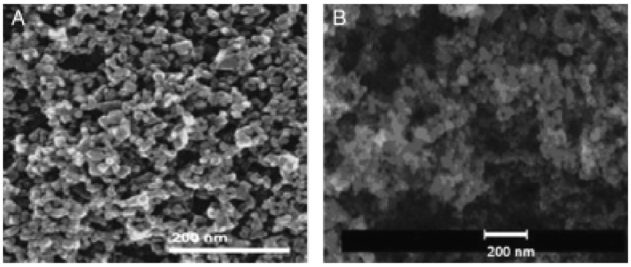

Fig. 3. (A) Electrophoretic deposition dye-sensitized solar cell (DSSC) produced by Gratzel,[30] and (B) uniaxial freeze-dried DSSC produced in the framework of the present research. Scale bar = 200 nm.

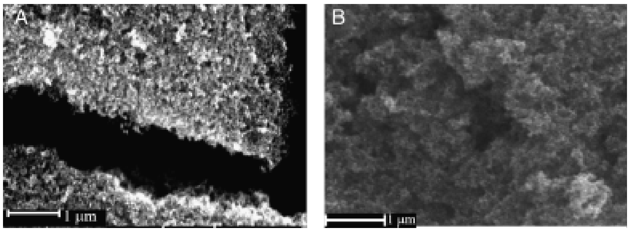

Fig. 4. (A) Uniaxial freeze-dried dye-sensitized solar cell (DSSC) without etching, and (B) after etching for 4 min. The large gap in the left image is where a scratch was created for white-light profilometry measurements.

Figure 4 shows a comparison between a uniaxial freeze-dried DSSC surface before etching with hydrofluoric acid, and one after etching. The nonetched sample shows a large amount of surface variation, while the etched sample has that same variation, along with nanorods that have been etched into that surface. This addition of the etching of nanorods provides an additional area for dye attachment.

Analysis of the freeze-dried cell's performance shows a significant increase over traditional doctor blade deposition methods. Figure 5 shows an *I–V* curve for the uniaxial freeze-dried, and etched solar cells, and two different conventional doctor blade solar cells. The current increased a maximum of 70%, while the maximum voltage increased 20% in the freeze-dried solar cell, compared with doctor blade. The current increased a maximum of 200%, while the maximum voltage increased 100% in the freeze-dried and etched solar cell, compared with the doc-

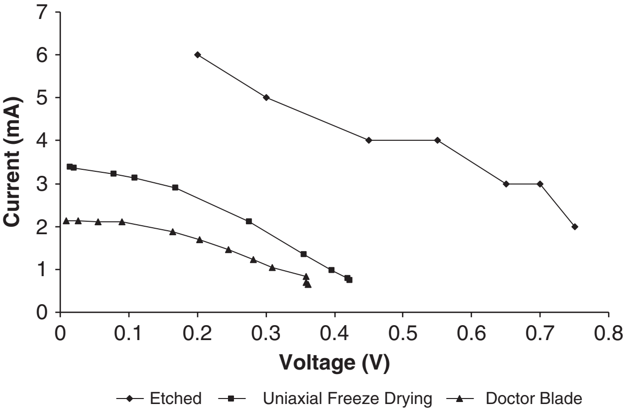

Fig. 5. The freeze-dried solar cell with aligned pore structure shows significant improvement over conventional doctor blade deposited cells.

tor blade. These current and voltage results are comparable to some of the better results produced by Gratzel; however, due to the large size of these cells (approximately 4 cm^2), the current density J_{sc} is only about half of the calculated maximum.[31] Also, the current–voltage curve does not show the traditional shape and stability of current across different voltages that is normally seen, and this may be due to the choice of electrolyte.

There are other methods for introducing nanorods to the surface of the TiO_2 layer.[32] The implementations of these methods show that introducing the extra surface area of the nanorods greatly improves the performance of the DSSCs. Another possibility for further investigation is starting this same solar cell production process with titanium powder, then using doctor blade, etc., and freeze-drying to create the thin film, followed by anodization and then sintering. The different starting materials and reversal of the order of sintering and anodization steps may produce different results.

After taking all of these processes into account, and comparing them with samples produced without them, we can directly see the influence of each process. The uniaxial freeze-dried specimens have a higher, and more varied porosity than either the standard nonfrozen doctor blade or the nonuniaxial frozen specimen. The beneficial effects of the etching, and increased surface area on the nanoscale, can be seen when comparing the surface structure of the nonetched specimen with the etched specimen. Although it is difficult to quantify the effects of each process on the current and voltage characteristics, it can be seen that the effects of each process are cumulative and provide a substantial benefit for the DSSC performance.

V. Conclusions

Using the techniques of uniaxial freezing, freeze-drying and anodization, or etching can introduce a nanoscale variation on the semiconductor surface layer of DSSC, which have their macroscopic and microscopic surface structure created by another method, such as the doctor blade method, EPD, or screen printing. Utilizing these techniques, we have been able to produce a DSSC with high current and voltage characteristics. Further examination of the parameters that affect the nanostructure properties (such as pressure and temperature during freeze-drying, or pH and duration of etching) will allow for fine tuning and order to be introduced, to achieve the goal of the more efficient surface structure, which maximizes the amount of dye that can attach to the surface while minimizing the distance the electrons have to travel to reach the conductive electrode.

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