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ELECTROSPUN PHOTOVOLTAIC CELLS

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ABSTRACT

Electrospinning is a simple technique to form high surface area membranes using large static electric potentials. An application, taking advantage of such a high surface area, is a dye-sensitized photovoltaic cell, wherein a chromophore molecule absorbs light before being oxidized to generate a photocurrent. We report functioning photovoltaic cells made from polyacrylonitrile fibers infused with the azo-dye, Congo Red in a liquid-junction cell assembly. Cell performance of the electrospun cells compared favorably to cells made by spin-coating thin films of polyacrylonitrile and Congo Red. Also reported are the effects of adding nanoparticles of titanium dioxide to the cells. Finally, the maximum amount of dye that can be incorporated into a fiber is presented.

Key Words: Electrospinning; Photovoltaic cell; Congo red; Nanofiber

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INTRODUCTION

Electrospinning

Electrospinning has been studied since the 1930s[1] and has recently been employed to produce fibers for a number of polymers, including polyethylene oxide,[1,2] poly(p-phenylene terephthalamide),[3] and calf thymus DNA.[4] In electrospinning, a polymer solution or melt is placed in the proximity of a charged electrode from a DC power source such that the species present in the solution become charged. At a critical potential, the binding forces within the solution are overcome and a fine jet of solution sprays from the solution surface to the nearest electrically grounded object.[2]

As the jet travels from the source to the grounded target, the solvent evaporates and charge on the remaining jet repels itself to split the jet into finer and finer subsequent jets in a behavior termed splay.[2] More recent studies suggest the instability of the charged solution in the electric field causes the jet to elongate forming a thinner fiber.[5] If the distance from the source to the target is great enough such that the solvent evaporates sufficiently, a fiber remains. The fibers then adhere to the target in a random arrangement and dissipate any residual charge.

The polymer solution, or spin-dope, must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric field. The solution must also have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the solvent has evaporated.[6]

Dye-Sensitized Photovoltaic Cells

Dye-sensitized photovoltaic cells differ from conventional semiconductor photovoltaics, in that the role of photon absorption is performed exclusively by the dye molecule while the role of charge carrier separation is performed by another species in the cell, other than the dye.[7] The most successful dye-sensitized photovoltaic cell work has been conducted using a dye adsorbed onto a porous matrix of semiconductor titanium dioxide (TiO_2).[7–11] In such a cell, the dye molecule absorbs a photon thereby exciting a valence electron to a higher, previously unoccupied, molecular orbital. This excited electron possesses an energy within the conduction band of the TiO_2 particle, thus, the electron is driven to transfer from the dye to the TiO_2 by enthalpy.[8] Once in the conduction band of the titanium dioxide layer, the electron is easily transferred to an electrode and through a circuit to perform work. At the counter electrode, electrons are typically transferred to an electrolyte in solution or gel that carries the electrons back to the dye molecule, reducing it back to its ground state.[8] The maximum voltage possible from the cell is determined by the difference between the electric potential of the conduction band in the semiconductor particle and the redox chemical potential of the electrolyte.[7] The maximum current possible from the cell can be determined by dividing the maximum voltage by the internal resistance of the cell.[7]

In these dye-sensitized photovoltaic cells, it is necessary to sinter TiO_2 nanoparticles around 450°C to form a porous structure over which the dye can be adsorbed.[7] It is believed this porosity of the substrate has a beneficial effect on the photo-response.[7] The particles are sintered onto an indium tin oxide (ITO) or a tin dioxide (SnO_2) layer on a glass slide. Tin dioxide and ITO are useful in that they are transparent conductors in the visible spectrum, and can be used as the top electrode in the cell permitting photons to reach the dye inside and conducting electrons out of the cell and into a circuit. Sintering is necessary to ensure good contact between the TiO_2 electron acceptor material and the ITO electrode and to maximize the surface area of the dye/TiO_2 interface, the TiO_2/ITO interface and the dye/redox electrolyte interface.[7] Close contact ensures that the electrons are able to move between each of the layers. A rough surface enables more dye molecules to be in contact with both the titanium dioxide particles and the redox electrolyte, thus permitting more dye molecules to contribute to the power output of the cell.

EXPERIMENTAL

Electrospinning Apparatus

The electrospinning apparatus used consisted of a DC power source (Gamma High Voltage Research, Inc. Model HV ES 30P/100), where the charged electrode wire was immersed in a polymer solution. The polymer solution was drawn into a disposable glass pipette mounted a few degrees down from a horizontal position. It was necessary to angle the pipette so that the solution would collect at the tapered end rather than drip out of the wide end of the pipette where the electrode wire was inserted. A second ground wire from the power source was attached to a conducting target where the fibers were collected. The electrospinning target used in making the photovoltaic cells was indium tin oxide (ITO) coated onto glass slides, with a surface resistance of approximately 25 ohms per cm^2.

Spin Dope Solutions

Spin-dope solutions of polyacrylonitrile (PAN) (average molecular weight 80,000 d) and the azo-dye Congo Red were prepared in N,N-dimethyl formamide (DMF). Some solutions additionally contained titanium dioxide nanoparticles (Degussa Titandioxid P25). It was necessary to stir or agitate, with ultrasound, the solution shortly before electrospinning to keep the nanoparticles from settling on the bottom on the vial. The solution was electrospun onto a glass slide coated with indium tin oxide (ITO) such that the ITO was in contact with the membrane. Prior to spinning, the ITO glass slide was cleaned in a solution of equal parts ethanol, chloroform, and acetone. It was then soaked in a 5% by weight aqueous sodium hydroxide solution for one hour to impart a slight charge on the surface. All chemicals were used as received. All other chemicals were obtained from Aldrich.

Photovoltaic Cell Assembly and Characterization

All photovoltaic measurements were made using a liquid junction cell. In the cell, the polymer/dye coating was applied to an indium tin oxide (ITO) coating on a glass slide that was suspended in a 0.5 M aqueous solution of potassium chloride (KCl). The top of the slide was cleared of any membrane and remained above the surface of the KCl solution. An electrode was then connected to the ITO coating of the slide. The counter electrode consisted of a platinum wire immersed in the KCl solution. The cells being measured were not protected from ambient light in the room.

Electrical current from the photovoltaic cell was routed through a current amplifier (Stanford Research Systems, Model SR570 Low Noise Current pre-amplifier) and connected to an oscilloscope (Hewlett Packard Model 54510B Digitizing Oscilloscope 300 MHz, 1 G Sa/s). A 50 Watt halogen light source (Newport Corporation, Model NRC 780 Lamp Supply) was used to illuminate the liquid cell. An UV filter (420 nm cutoff) was installed on the lens of the light source as was an adjustable aperture set to one square centimeter. A shutter (Uniblitz, Model T 132 Shutter Driver/Timer) was placed between the light source and the cell to control the light exposure. The shutter signal was also routed to the oscilloscope so that both light exposure and photo-response were visible on the same screen. The oscilloscope was connected to a PC so that the signal data could be downloaded and plotted elsewhere.

It should be noted that the light source would illuminate the sample with a light intensity of about 10 milliwatts per cm^2. Light intensity of the lamp was determined by measurement with a digital power meter (Newport, Model 815 series). The standard light source for flat panel photovoltaic cells is Air Mass 1.5, or AM 1.5, which corresponds to a light intensity of about 100 milliwatts per cm^2.[12]

The dye content in the cells was measured by directly inserting the membrane/ITO slide into a photospectrometer (Perkin Elmer UV/vis/NIR Spectrometer Lambda 9). The surface concentration[7] of the dye was found by dividing the absorbance at 498 nm by the extinction coefficient of 40.1 cm^2 per mol.

Since Congo Red was found not to absorb at 900 nm, this wavelength was selected as a convenient point to use in correcting for light scattering losses of the fibers. The measured absorbance was thus corrected by subtracting the absorbance at 900 nm from all absorbances. Note that this correction was not entirely accurate across the whole spectrum as it assumes equal scattering losses for all wavelengths. Raleigh's law, however, states that the intensity of scattered light scales with the inverse of wavelength. In addition, the fiber diameters, in the range of 100 to 500 nm would tend to scatter light with wavelengths in this range. That these two sources of error would compensate each other is, perhaps, too much to hope for. However, presuming the scattering at 900 nm is representative for the scattering at all visible wavelengths is both convenient and not an unreasonable approximation.

RESULTS AND DISCUSSION

Electrospun Cells

A total of fourteen electrospun cells were prepared by electrospinning the spin dope directly onto ITO coated glass. Samples 1–6 and 13–14 were made from Congo Red and PAN dissolved in DMF. Samples 7–12 were made from Congo Red, PAN, and TiO_2 nanoparticles in DMF. All of the samples were electrospun at 10–12 kV potential for about one minute. The electrospun membrane formulations, the measured dye content, and the steady-state photocurrents (corrected for light scattering) are shown in Table 1. A representative current profile from sample 3 is shown in Fig. 1.

Spin-Coated Cells

A total of five spin-coated cells were prepared on ITO coated glass. Three of the cells (samples 1–3) used a solution of Congo Red and PAN in DMF; the remaining two cells (samples 4–5) contained Congo Red, PAN, and titanium dioxide nanoparticles. Table 2 shows the formulations, the measured dye content, and the steady-state photocurrents for all five spin-coated cells.

All five samples show a surge in reverse current at every change in light status (on and off) that was not observed in any of the electrospun cells. Figure 2 shows the photocurrent response of sample 5 and is typical for all five spin-coated samples. When the cell was first exposed, a surge in current was observed followed quickly by a reversal in current and a gradual increase to an illuminated steady-state current. When the light was removed, a surge

Table 1. Dye Content and Photocurrents from Electrospun Cells Corrected for Light Scattering

Sample Number	Wt% PAN	Wt% CR	Wt% TiO_2	Absorbance at 498 nm	Surface Dye Conc. (mol/cm^2)	Photo-current (nA/cm^2)	Current per mol of Dye (nA/mol)
1	10	3	0	0.0574	0.0143	0.60	41.92
2	10	3	0	0.1566	0.0391	0.75	19.20
3	10	3	0	0.2705	0.0675	1.20	17.79
4	10	3	0	0.1347	0.0034	2.00	595.40
5	10	3	0	0.1177	0.0030	0.62	211.23
6	10	3	0	0.6015	0.0150	5.30	353.33
7	10	3	1	0.0453	0.0113	0.35	30.98
8	10	3	1	0.0827	0.0206	0.70	33.94
9	10	3	1	0.0952	0.0237	1.06	44.65
10	10	3	1	0.1008	0.0251	0.86	34.21
11	10	3	1	0.2201	0.0055	4.05	737.87
12	10	3	1	0.2895	0.0072	2.36	326.89
13	5	5	0	0.0026	0.0006	1.63	2506.25
14	5	5	0	0.0578	0.0144	7.34	509.23

in current in the same direction to the exposed, steady state current was observed quickly followed by a reversal in current to a dark, steady state current. The surges in current were attributed to the low porosity of the films that hindered the charge carriers in the electrolyte from reaching and reducing the oxidized dye molecules at the ITO surface. This type of current surge was not observed in the cells made from electrospun membranes.

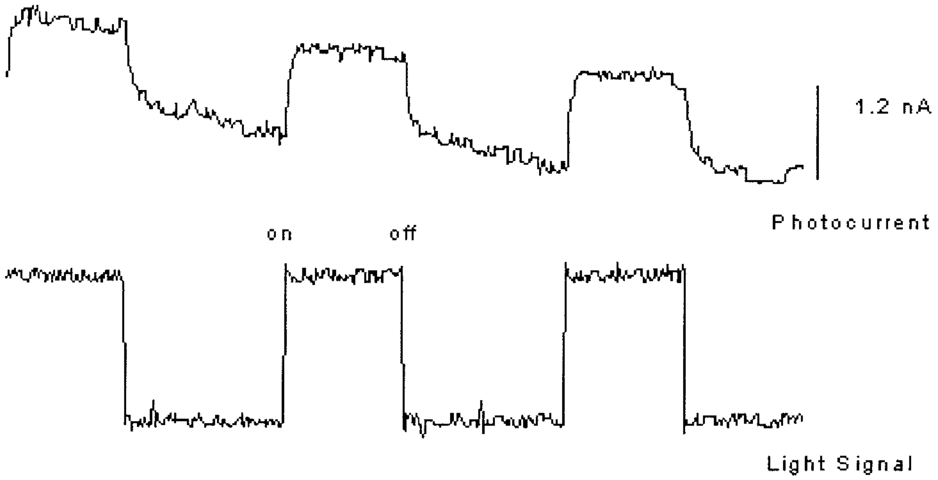

Figure 1. Photocurrent response for sample 3, representative of all electrospun cells.

Table 2. Dye Content and Photocurrents from Spin Coated Cells

Sample Number	Wt% Congo Red	Wt% TiO_2	Wt% PAN	Absorbance at 498 (nm)	Surface Dye Conc. (mol/cm^2)	Photo-current (nA/cm^2)	Current per mol of Dye (nA/mol)
1	1	0	3	0.31	0.08	9.65	123.28
2	1	0	3	0.34	0.09	16.25	190.53
3	1	0	3	0.33	0.08	3.44	41.67
4	1	0.3	3	0.55	0.14	4.50	32.55
5	1	0.3	3	0.63	0.16	5.30	33.47

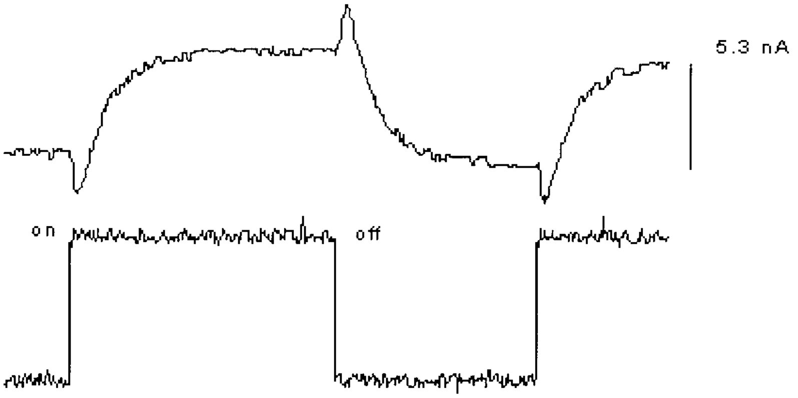

Figure 2. Photocurrent response for sample 5, representative of all spin-coated cells.

Electrospun vs. Spin-Coated Cell Performance

In the case of cells made without TiO_2, the mean current per mol of dye was 294.43 nA per mol for electrospun cells and 118.49 nA per mol for spin coated cells. Similarly, for cells containing TiO_2, the mean current per mol of dye was 201.42 nA per mol for electrospun cells and 33.01 nA per mol for spin coated cells. A t-test (13) of the data sets for electrospun and spin coated cells showed a statistically significant difference in both the cells with and the cells without TiO_2. Thus, we conclude an advantage in cell performance in the electrospun cells over the spin-coated cells, despite large variances in both data sets.

Effect of TiO_2

The effect of added titanium dioxide in the electrospun fibers seems to be negligible. The mean current per mol of dye for fibers with no added TiO_2

(samples 1–6) was 294.42 nA per mol while the mean for fibers with an addition of 7 wt% (1 wt% in solution) (samples 7–12) TiO_2 was 201.42 nA per mol. As can be seen in Table 1, the variation among the samples was quite large and the results highly dependant on the assembly of the cell. Consequently, it would be unreasonable to conclude the effect of additional TiO_2 was detrimental to cell performance, as the two means suggest.

A simple t-test (13) was performed to evaluate the significance of the two sets of data: current per mol of dye with and without added TiO_2. As a result of the large standard deviation in each set, the t-test results indicate no statistically significant difference in the results of both experiments. Thus, we conclude there was no effect on the photocurrent of the cell as a result of adding TiO_2 into the fiber. We suspect the reason for this was that the TiO_2 particles in the spin dope were coated with dye molecules but were, for the most part, isolated from each other and from the ITO electrode in the cell. Electrical connectivity between the particles and the electrode was likely insufficient to facilitate additional electron transfer.

Maximum Dye Content

Knowing that more dye generally yielded a larger photo-response in the cell, a series of solutions was prepared to determine the maximum dye content in electrospun fibers. The solvent weight percentage was held constant at 90% since a spin dope of 10 wt% polyacrylonitrile in DMF was known to spin well. The proportions of dye and polyacrylonitrile were varied within the 10 weight percent fraction. No TiO_2 was added to any of these solutions. The electrospinning results for the various dye:polymer ratios are shown in Table 3. Electrospun membranes were characterized as either fiber or droplets, by optical microscopy, and by attempts to remove the membrane from the target. Fibrous membranes were readily peeled off in a single piece, while droplets could only be scraped from the surface.

As shown in Table 3, fibers were formed for very high dye to polymer ratios in the spin-dope. The maximum ratio was 7.2:2.8 dye to polymer, by

Table 3. Electrospinning Results for Dye:Polymer Ratio Variations

Wt% PAN	Wt% Congo Red	Wt% DMF	Electrospinning Result
5.0	5.0	90	Fibers
4.0	9.0	90	Fibers
3.3	6.6	90	Fibers
2.8	7.2	90	Fibers
2.0	8.0	90	Droplets
1.6	8.4	90	Droplets

weight. This resulted in a polymer fiber that was 72%, by weight of small dye molecules, and only 28%, by weight of polymer, presuming all solvent was driven off. It is not inconceivable that higher dye:polymer ratios are possible. These membranes were, however not tested for photoresponse due to the tendency of the dye, and thus the whole fiber, to dissolve in the electrolyte. The lower dye concentrations measured contained enough polymer to remain intact upon immersion in the aqueous electrolyte solution.

That it was possible to make an electrospun membrane with such a high dye content as demonstrated was remarkable, yet it fits in well with the theory of electrospinning. Viscosity, coupled with charge density, is responsible for preventing the jet of solution from collapsing into droplets before the solvent has evaporated and formed a fiber.[6] In a pure polymer solution, the viscosity would result only from the concentration of the polymer. In the solutions presented, viscosity is a function of both the polymer and the dye concentrations.

The extent, to which dye molecules may be substituted for polymer, is not, however, without limits. A solution of pure dye would likely not form an electrospun fiber, yet solutions where dye is present in a 7 to 3 ratio to polymer, readily form fibers by electrospinning. Since the solution with 8 wt% dye, 2 wt% PAN in DMF, did not form electrospun fibers, the minimum amount of polymer required for fiber formation is suggested to be higher.

Electrospinning of pure PAN in a DMF solution was found to be limited to concentrations of 5 wt% polymer, or greater. This was true even at higher potentials than the 10 to 12 kilovolts required for 10 wt% PAN solutions to spin well.

CONCLUSION

Functioning photovoltaic cells have been constructed using electrospun membranes of a polymer/chromophore blend and liquid electrolyte. Photocurrents in the nanoampere range were measured. The electrospun cells produced a photocurrent that was significantly higher than the current produced by a spin-coated thin film of the same materials.

The difference in cell performance with the addition of titanium dioxide nanoparticles was not statistically significant. This was attributed to poor connectivity among the nanoparticles and between them and the electrode.

It was possible to make nanofibers consisting of less than 30% by weight of polymer and 70% by weight of Congo Red dye. While these fibers were impractical in the liquid junction cell studied, it is believed that a higher concentration of dye should be able to generate a larger photoresponse. Studies to measure the photoresponse of these high dye-content electrospun cells are currently underway.

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