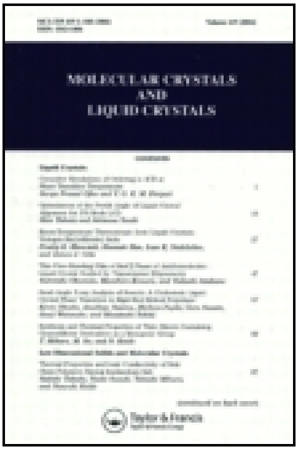

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Effect of Electrolyte in Electrospun PEO/TiO_2 Composite Fibers

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Effect of lithium perchlorate and TiO_2 particles on electrospinning of polyethylene oxide was studied to fabricate TiO_2 electrodes for dye-sensitized solar cell. Fibers were analyzed with optical microscope and scanning electron microscope. Optimum amount of salt content induced stable fiber formation.

Keywords: electrospinning; lithium perchlorate; polyethylene oxide; titanium dioxide

INTRODUCTION

Electrospinning of polymer nanofibers attracted significant attention during the last several years as a simple and straightforward method to produce long polymer fibers with diameters in the range of 20–2000 nm, which are of interest in many applications, reinforcements in nanocomposites [1], nanowires and nanotubes [2], and tissue engineering [3]. Fibers are collected as a non-woven membrane, which has a very large surface area due to the small dimensions of the fibers [4].

Grätzel et al. [5] has reported dye-sensitized photovoltaic cells that greatly benefit from a large interfacial area between a chromophore

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and a nanoporous titanium dioxide (TiO_2) layer. It has been a problem to use a liquid electrolyte because of solvent evaporation and leakage of electrolytes. It is practically beneficial to replace liquid electrolytes with polymer electrolyte [6], which still has a lack of pore filling because of interconnected structure of titanuim dioxide (TiO_2) particles. Electrospun TiO_2 fibers to overcome these problems has been reported from different groups by using polyethylene oxide [4], poly(-acrylonitrile) [7], and poly(vinyl pyrrolidone) [8], which were used as a vehicle to obtain TiO_2 fibers.

It has also been known that the addition of salts into polymer solution results in a higher charge density on the surface of jet during electrospinning, producing more electric charges by the electrospinning jet. Sodium chloride and lithium chloride have been used successfully to fabricate fine electrospun nanofibers [9]. The effect of lithium perchlorate, which may increase the conductivity of polymer solution, was studied in the electrospinning of polyethylene oxide/TiO_2 composite material in this work. Electrospun fibers were characterized to find the optimum condition for nanofiber fabrication with SEM and optical microscope.

EXPERIMENTAL

Polyethylene oxide (M_v 900,000), ethanol and lithium perchlorate ($LiClO_4$) were purchased from Sigma-Aldrich. TiO_2 was obtained from Degussa. Polymer solutions were made of polyethylene oxide (4 wt%) dissolved in 50 mL cosolvent of ethanol and deionized water in a 6:4 ratio by volume, followed by adding lithium perchlorate (0, 1, 10, 100 mmol) and 3 wt% of TiO_2. The polymer solution was vigorously stirred before electrospinning.

A schematic diagram of the electrospinning apparatus is shown in Figure 1. The electrospinning system used in this work was composed of a syringe and needle, a high-voltage source, a ground electrode and a high voltage supply. The needle was connected to the high voltage supply, which generates DC voltages up to 30 kV. The resulting electrospun fibers were collected on a glass slide mounted on an electrically grounded target for use in an optical microscope and a scanning electron microscope.

Optical microscope images were taken through a Leica DMRB microscope using a 40X objective with phase-contrast and captured with digital camera. Scanning electron microscopy (SEM) was carried out using XL 30 Siron D1578 SEM from FEI with XL Docu software for imaging and measurement of diameter. All samples were coated with gold before scanning. Diameters in this study were measured 30 times and averaged.

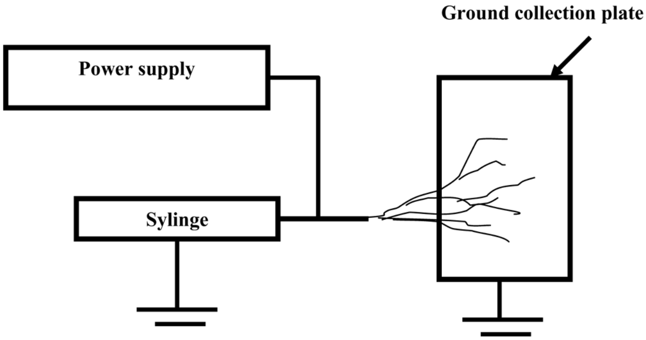

FIGURE 1 Schematic diagram of the electrospinning apparatus.

RESULTS AND DISCUSSION

Electrospun fibers containing $LiClO_4$ with or without TiO_2 particles are studied. Solutions used in this work are listed in Table 1. Electrospinning was performed at 19 kV with a distance of 15 cm. Syringe pump was used to control eluting rate with a rate of 0.7 mL/h. Different concentrations of PEO solution were electrospun. Beads were found from the electrospun fibers with 3 wt% PEO solution and too much viscosity was observed with 5 wt% PEO solution in a cosolvent system. Electrospun fibers from 4 wt% PEO solution showed less beads indicating appropriate concentration for electrospinning.

Effect of $LiClO_4$ and TiO_2 particle was studied in standard 4 w% PEO solution by changing concentration of $LiClO_4$ with and without 3 wt% TiO_2 particle. Stable jet and fibers without forming beads were observed from 4 wt% PEO solution without $LiClO_4$ as depicted with optical microscopic images in Figure 2(a). It was found that 1 mmol $LiClO_4$ enhances stable fiber deposition on a target, which makes more electrostatic interaction between ejected fibers and target electrode (Fig. 2(b)). Jet stream recombination induced unstable fiber formation with 10 mmol $LiClO_4$ solution (Fig. 2(c)), which was also observed with 100 mmol $LiClO_4$.

TABLE 1 Composition of Polymer Solutions

PEO (wt%)	$LiClO_4$ (mmol)	TiO_2 (wt%)	PEO (wt%)	$LiClO_4$ (mmol)	TiO_2 (wt%)
4	0	0	4	0	3
4	1	0	4	1	3
4	10	0	4	10	3
4	100	0	4	100	3

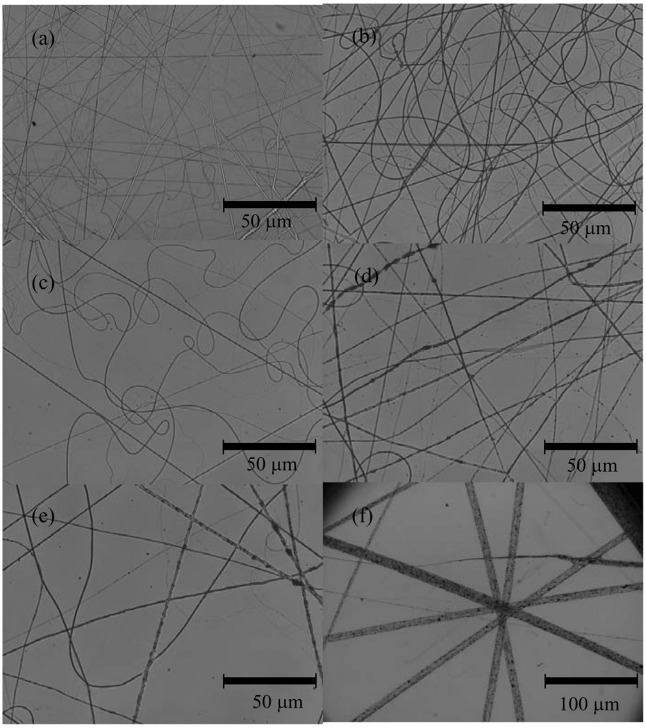

FIGURE 2 Optical microscope images of electrospun fibers: (a) No $LiClO_4$ (50 X); (b) 1 mmol $LiClO_4$ (50 X); (c) 10 mmol $LiClO_4$ (50 X); (d) No $LiClO_4$, 3 wt% TiO_2 (50 X); (e) 1 mmol $LiClO_4$, 3 wt% TiO_2 (50 X); (f) 10 mmol $LiClO_4$, 3 wt% TiO_2 (25 X).

Electrospun fibers from PEO solution with 3 wt% TiO_2 particle showed thicker fibers containing little bumps along fibers, which are different from beads. They were groups of TiO_2 particles on fibers indicating that TiO_2 particles were not homogeneously dispersed in PEO matrix in Figure 2(d). It was observed that 1 mmol $LiClO_4$ also enhances fiber deposition on the target electrode. Electrospun fibers from the solution containing 10 mmol $LiClO_4$ were combined during electrospinning process as already observed from the sample containing $LiClO_4$ without TiO_2 particles. Fibers from 100 mmol $LiClO_4$ showed thicker diameter contains TiO_2 particles in fiber matrix.

SEM study showed more detail results about electrospun PEO fibers. SEM images of electrospun fibers without electrolyte ($LiClO_4$) were depicted in Figure 3. The concentration of $LiClO_4$ did not significantly affect diameter of fibers between 0 mmol sample (Fig. 3(a)) and 1 mmol sample (Fig. 3(b)) with diameters of 378 nm and 384 nm

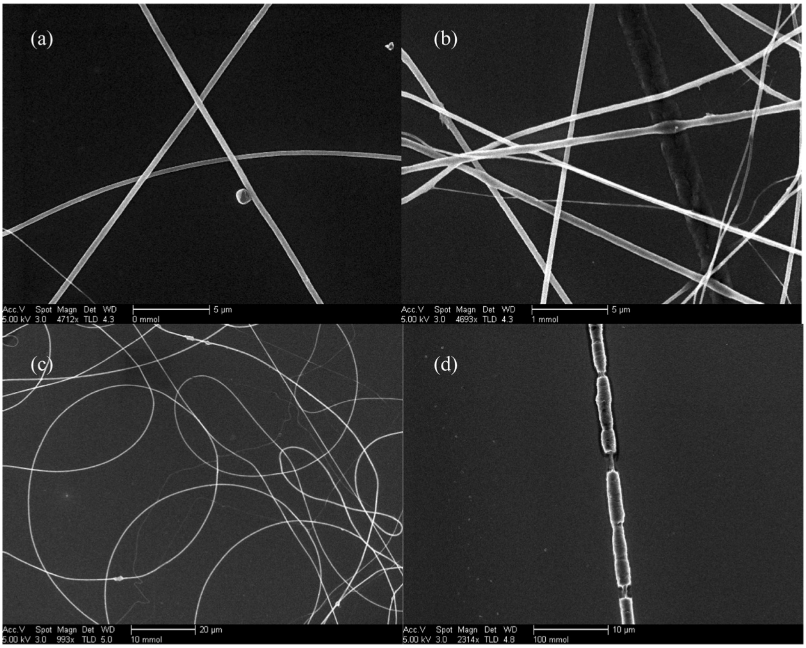

FIGURE 3 Scanning electron microscope images of electrospun fibers without TiO_2 particles: (a) No $LiClO_4$; (b) 1 mmol $LiClO_4$; (c) 10 mmol $LiClO_4$; (d) 100 mmol $LiClO_4$.

respectively. Circled fibers were observed from 10 mmol sample with a diameter of 400 nm in Figure 3(c). It was confident that the addition of $LiClO_4$ was not a significant factor to change diameter of fibers upto 10 mmol sample. Figure 3(d) shows fibers containing 100 mmol $LiClO_4$. Fiber was not continuous, indicating that too much salt content reduces molecular interaction between polymer chains. The diameter of fibers from 100 mmol sample was approximately 1 µm.

Fibers with TiO_2 particles were illustrated in Figure 4. TiO_2 particles were found as bumps along fibers from 0 and 1 mmol samples with diameters of 167 nm and 234 nm respectively, as described in Figure 4(a,b), indicating that TiO_2 particles were not dispersed homogeneously in the entire fiber matrix. Fibers from 10 mmol sample show thicker diameters (1.09 µm) in Figure 4(c), which was observed from 100 mmol sample without TiO_2 particles. Content of TiO_2 particles may increase jet combining in the process of electrospinning including the effect of $LiClO_4$. It was also observed that high content of $LiClO_4$ induces thick and non-continuous fiber formation (2.7 µm)

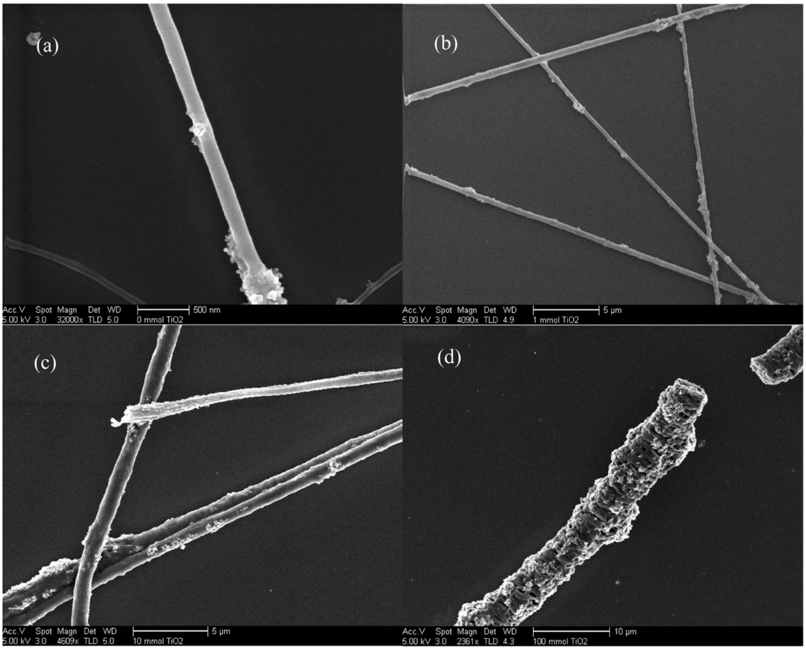

FIGURE 4 Scanning electron microscope images of electrospun fibers with TiO_2 particles: (a) No $LiClO_4$; (b,c) 1 mmol $LiClO_4$; (d,e) 10 mmol $LiClO_4$; (f) 100 mmol $LiClO_4$.

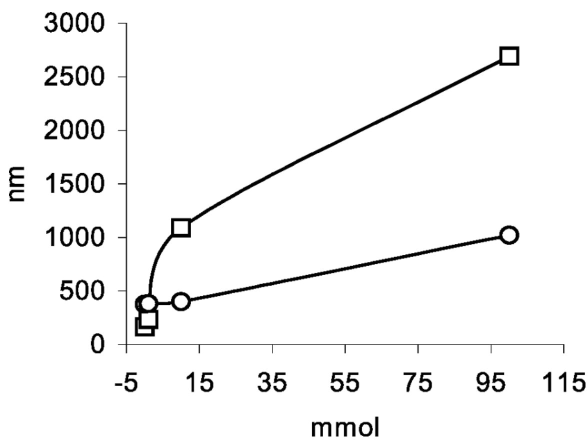

FIGURE 5 The effect of lithium perchlorate concentration in PEO solution with (open square) and without TiO_2 particles (open circle).

in Figure 4(d) as observed from 100 mmol sample without TiO_2 particles. Effect of $LiClO_4$ is described in Figure 5. Diameters increase from the samples with TiO_2 particles. Diameter change was not significant in 0, 1, and 10 mmol samples without TiO_2 particles, compared to those with TiO_2 particles.

CONCLUSION

Electrospun fibers containing $LiClO_4$ with or without TiO_2 particles are studied. PEO solutions containing $LiClO_4$ and TiO_2 particles showed an increase of fiber diameter. Optimum amount of $LiClO_4$ induces stable fiber formation. Too much salt content induces an increase of diameter and non-continuous fiber formation. Fiber combining was observed during electrospinning process from the samples containing 10 mmol of salt or more.

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