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# Advances in Nanofiber composites and Thermosets

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**Abstract**

—Advancement is a result of recurring efforts beyond expectation‖. Nanofibers are an exciting materials defined as fibers having diameter less than or equal to 100 nm. When we deal with Nano-level the conditions required are different compared to micro-level. The dispersion of nanofiller is difficult because of orientation effect and less aspect ratio. Nanofibers exhibit special properties mainly due to extremely high surface to weight ratio compared to other nonwoven fibers. Low density, large surface area to mass, high pore volume, and tight pore size make nanofiber appropriate for making membranes as filtration applications. Those properties will be helpful in ameliorating the conventional solar cells, supercapacitors and battery separators. The most important property; which is high surface area makes it worthful in applications described above.

**Keywords**- Nanofibers composites, solar cells, super capacitors, reducing noise pollution, battery separators, etc.

## Introduction

Nanofiber is a continuous fiber which has a diameter in the range of billion with diameter in nanometer range. Many types of polymers can be processed into nanofibers of 50 to 1000 nanometers in diameter, several orders of magnitude smaller than conventional fiber spinning. [1, 2]. Nanofibers have large surface area, high porosity and small pore size. The huge surface area available on nanofibers makes it very suitable for new technologies which require smaller and smaller environments for chemical reactions to occur. Increasing the surface area speeds up a chemical reaction. They can be produced by melt processing, interfacial polymerization, electrospinning, antisolvent induced polymer precipitation and electrostatic spinning. [3]. More than 30 polymers, including polyethylene oxide, DNA, polyaramids, and polyaniline can be electro spun into fibers using their polymer solution and melts. These fibers can be made of variety of organic (nylon, polyester, acryl) or biological polymers (proteins, collagens). Smallest nanofibers made today are in range of 1.5 and 1.75 nm. Researchers have developed piezoelectric nanofibers that are flexible enough to be woven into clothing. The fibers can turn normal motion into electricity to power your cell phone and other mobile electronic devices. Small device lengths have the potential to result in improved charge collection without sacrificing collection efficiency. Increasing charge collection efficiency could lead to improved device efficiency and the simple fabrication method could result in lower cost and ease of scaleup. This can be achieved by using photovoltaic cells from conjugated polymer nanofibers [4]. Nanofiber is a continuous fiber which has a diameter in the range of billion with diameter in nanometer range. Many types of polymers can be processed into nanofibers of 50 to 1000 nanometers in diameter, several orders of magnitude smaller than conventional fiber spinning. [1,2]. Nanofibers have large surface area, high porosity and small pore size. The huge surface area available on nanofibers makes it very suitable for new technologies which require smaller and smaller environments for chemical reactions to occur. Increasing the surface area speeds up a chemical reaction. They can be produced by melt processing, interfacial polymerization, electrospinning, antisolvent-induced polymer precipitation and electrostatic spinning. [17]. More than 30 polymers, including polyethylene oxide, DNA, polyaramids, and polyaniline can be electrospun into fibers using their polymer solution and melts. These fibers can be made of variety of organic (nylon, polyester, acryl) or biological polymers (proteins, collagens). Smallest nanofibers made today are in range of 1.5 and 1.75 nm. Researchers have developed piezoelectric nanofibers that are flexible enough to be woven into clothing. The fibers can turn normal motion into electricity to power your cell phone and other mobile electronic devices. Small device lengths have the potential to result in improved charge collection without sacrificing collection efficiency. Increasing charge collection efficiency could lead to improved device efficiency and the simple fabrication method could result in lower cost and ease of scaleup. This can be achieved by using photovoltaic cells from conjugated polymer nanofibers [5].

## Applications of Nanofiber Composites

### Solar Cells

The first piece of crystalline silicon solar cells with 4.5% conversion efficiency, which opened up a new era in the use of solar energy [6]. Since then, the solar energy technology development has gone through three stages: monocrystalline and polycrystalline silicon solar cells, amorphous silicon thin film solar cells, and the third generation solar cells referring to new concept solar cells with high conversion efficiency such as the dye-sensitized solar cells and hybrid solar cells. While many advances have been made in photovoltaic devices, efforts still need to be made to dramatically improve the conversion efficiency of photovoltaic cells. One efficient strategy is the introduction of new structured materials like electrospun nanofiber materials.

***Dye-Sensitized Solar Cells***

- ***Photo anode***

Dye-sensitized solar cells (DSSCs) can directly convert light into electricity with the help of a photosensitizing dye. A typical DSSC consists of three primary components: a photo anode, a counter electrode, and an electrolyte. A photo anode is composed of a transparent conducting glass coated with a porous semiconductor film, and the photosensitizing dye is adsorbed on this semiconductor film. In DSSCs, once the photo sensitizer absorbs photons, the photoelectrons first move into the conducting band of the semiconductor from the photosensitizer and is collected on the photo anode. The photoelectrons are transferred to the counter electrode through the external circuit to form current. In this process, the maximum light absorption and efficient charge transport affect the overall photoelectric conversion efficiency. Hence, the photo anode plays a vital role. Electrospun metal oxide nanofibers as a thin film coated with photo anode have been a hot research topic due to their high specific surface area and 1D fibrous morphology. The high specific surface area enhances the absorption of photosensitizing dye. In contrast to those sintered nanoparticles, 1D fibrous morphology has lower grain boundaries attributes to its improved interconnectivity and high surface areas, which leads to better charge conduction and reduced charge-carrier recombination[7,8]. In addition, the large and controllable pore sizes of electrospun NFs contribute to the penetration of viscous polymer gel electrolyte [9].

$TiO_2$ anatase NFs prepared by electrospinning is effectively used as photo anode material [1012]; Major problem is their poor adhesion to conductive substrate. Many effective methods are adopted to solve the problem, such as converting electrospun nanofibers into nanorods [13], using hot press pretreatment [14], and introducing ultrathin surface treatment layer (STL)[15]. Nanofibers are uniformly dispersed in amorphous carbon matrix. Post treatment of the electrospun composite nanofiber at $500^0$C under 10% $H_2$/Ar mixture gas atmosphere. Additionally, efforts are also done onto $TiO_2$ composites (especially for NPs incorporated in NFs), which are employed as a photo anode of DSSCs because, when NPs are integrated in electrospun NFs, the NPs enable the NFs/mats excellent performance [16]. For example, Freestanding nonwoven composite of hybrid nanofibrous $TiO_2/SiO_2$ mat and $TiO_2$ nanoparticles. The DSSC based on this composite photo anode attain a power conversion efficiency of 6.67$\pm$0.33% on FTO/glass substrate. It is believed that the $TiO_2$ nanoparticles elevate the dye loading, while the $TiO_2$ NFs improve the electron transport and the $SiO_2$ NFs provide the mechanical strength and flexibility [17]. An innovative coexistence of $TiO_2$ NPs/NFs comprising both smaller-, larger-diameter electrospun $TiO_2$ NFs and $TiO_2$ NPs, which served as a photo anode of DSSCs [18]. The power conversion efficiency (PCE) reached 8.40%, which could be explained by the following effects. First, the $TiO_2$NF packed with highly crystalline $TiO_2$ grains not only could provide a large surface area to improve photon absorption but also could escalate the transport and collection of electrons. Second, the bigger-diameter fiber layer could work as the lightscattering that reduces the transmission of incident light and makes the use of light repetitively and thus increases the photocurrent density [19].

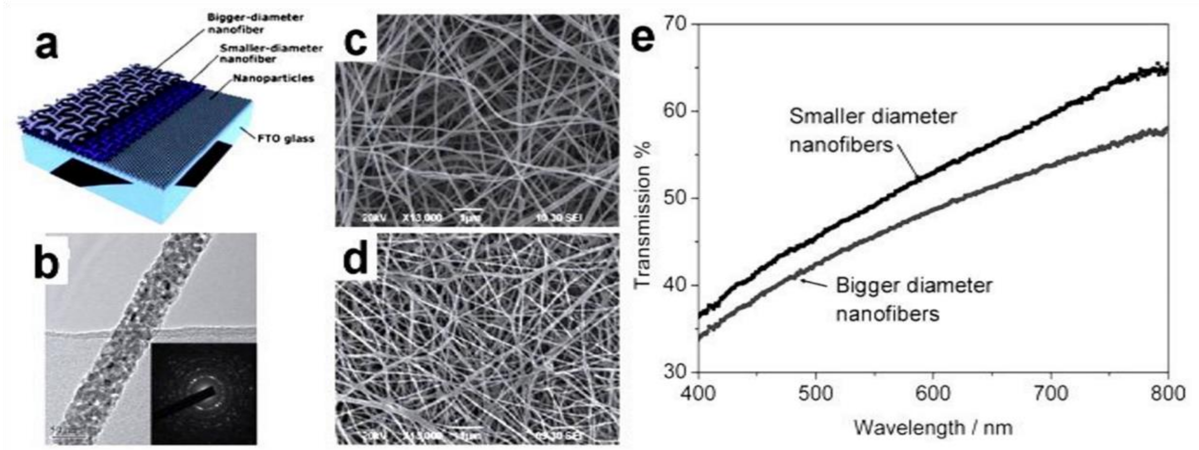


Figure. 1 SEM images of the bilayer $TiO_2$ nanofibers photo anode of a dye-sensitized solar cell

**Counter Electrodes**

In DSSCs, the counter electrode (CE) plays a role in transmitting and collecting electrons and the catalytic activity of CE affects the device's internal series resistance, resulting in a change of fill factor [20]. Traditionally, counter electrode in DSSCs is platinum (Pt) due to its high electro catalytic activity and high photovoltaic performances with $I_3^-/I^-$ redox couples [21]. As we know, Pt is expensive and the long-term stability of the DSSCs based on Pt CE is unsatisfactory due to the corrosive redox couple. In order to overcome these problems, many studies have been carried out on alternative counter electrodes such as carbonaceous materials (graphite [22], mesoporous carbon (C)[23], and CNTs[24]) that are integrated into transition metal compounds to replace Pt[25]. The short circuit current density (Jsc) and open circuit voltage (Voc) of such CNFs based cells were comparable to that of Pt-based cells, but the efficiency was different [26]. The relatively lower performance of the carbon NFs based cells is mainly attributed to their lower fill factor (FF) caused by high series resistance, which was probably improved by fabricating thinner and highly porous CNFs in order to reduce the thickness of the CE. Synthesized electrospun CNFs/Pt nanocomposites combining with different amounts of Pt nanoparticles [27]. DSSCs fabricated with CNF/Pt nanocomposites (with 40 wt% Pt nanoparticle) exhibit much better FF, and photo conversion efficiency (4.47%) than do those with CNF only and CNF/Pt nanocomposites do (with 20 wt% Pt nanoparticles). This is because the presence of welldistributed Pt nanoparticles on the CNFs improves the electro catalytic activity with the electrolyte. Recently, Fabricated kieserite $Cu_2ZnSnS_4$ (CZTS) NFs by electrospinning process [28]. Using cellulose acetate solvent counter electrode, DSSCs achieve higher conversion efficiency than Pt-based CE due to lower interfacial recombination between the counter electrode and electrolyte and lower series resistance. And the photovoltaic performances of electrospun nanofibers counter electrodes mentioned above are summarized in Table 1.

Table 1: Photovoltaic parameters of the DSSC devices with respect to different counter electrodes made of electrospun nanofibers obtained under air-mass (AM) 1.5 illumination at 100 mW/cm$^2$.

| COUNTER FIBER (Ω/ (V) (MA/CM$^2$) FF H ELECTRODE DIAMETER CM$^2$) (%) (NM) | | | | | | |
|---|---|---|---|---|---|---|
| PTNFS | 40–70 | 71 | 0.81 | 12.3 | 60.4 | 6.0 |
| CNFS | 250 | 15.5 | 0.76 | 12.6 | 0.57 | 5.5 |
| CNFS + PTNPS | 140–160 | NA | 0.66 | 13.54 | 49.81 | 4.47 |
| $CU_2ZNSNS_4$NFS | 30–40 | 69 | 0.574 | 8.42 | 65 | 3.9 |

DSSCs Electrolytes. Although the power conversion efficiency (PCE) of DSSC based on liquid electrolyte has surpassed 11% [29], the leakage and volatilization of liquid electrolytes result in a poor long-term stability, thereby restricting the practical application of DSSCs. To address this issue, inorganic or organic hole conductors, ionic liquids, and polymer gel electrolytes have been investigated as replacements for liquid electrolytes in DSSCs [30]. It is worth noting that polymer gel electrolyte employed in quasi-solid-state DSSCs has attracted wide attention from researchers due to their high thermal stability, good permeability into the mesoporous $TiO_2$ electrode and the counter electrode, and high ionic conductivity [31]. The commonly used polymer gel electrolytes for quasi-solid-state DSSCs include Polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), and poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP), among which, PVDF-HFP exhibits relatively high stability and ionic conductivity at room temperature. However, the major drawbacks of these polymer gel electrolytes are complex preparation technology and lower PCE. To overcome these problems, electrospun polymer gel electrolytes membranes have been examined. For instance, fabricated electrospun PVDF-HFP nanofibers films and spin-coated PVDF-HFP films that were applied to the polymer matrix in polymer electrolytes for DSSCs [32]. The experimental results have shown that the DSSC devices using electrospun PVDF-HFP nanofiber films exhibited higher PCE than that of DSSC devices using spin-coated PVDF-HFP films because of their high porosity and electrolyte uptake and 1D fiber morphology. It was evident that, with increasing the ionic conductivity of electrospun PVDF-HFP nanofiber films, the photocurrent density of DSSC devices decreased. Therefore, it indicates that photocurrent density and efficiency of DSSC using electrospun PVDF-HFP nanofibers in electrolytes are not necessarily proportional to the ionic conductivity in electrolytes. In addition, PVdF-PAN-$V_2O_5$ electrolyte nanofiber membrane by electrospinning technique and such composite nanofiber membrane based DSSCs showed a potential of 0.78 V, a FF of 0.72, and a current of 13.8 mA cm$^{-2}$ at an incident light intensity of 100 mW cm$^{-2}$leading to a photovoltaic efficiency of 7.75%. It has been demonstrated that such improved photovoltaic performances can be attributed to the high liquid electrolyte uptake resulting from the excellent porosity of composite nanofiber membrane [33].

***Super capacitors (SCs)***

Super capacitors are considered to be one of the most promising new energy storage devices in many areas such as transportation, electricity, communications, defence, consumer electronics, and other applications due to their high power performance, long cycle life, and low maintenance cost. Depending on different energy storage mechanisms, SCs can be classified into pseudocapacitors (PCs) and electrical double layer capacitors (EDLCs). PCs store energy based on fast reversible surface redox reactions, whereas EDLCs store energy using ion adsorption and desorption at the electrode and electrolyte interface. Recently, novel carbon-based materials with rational design of material composition, size, and morphology have been explored for highperformance EDLCs. Electrospinning is perhaps the most facile route to prepare the highly porous nanofibers. Thus, electrospun carbon NFs from polymer precursors such as polybenzimidazole (PBI), PAN, and PI have triggered widespread investigations. And these electrospun CNFs can be utilized as electrode for EDLCs after undergoing the process of stabilization, carbonization, and activation, in which the surface area and porosity of the NFs can be improved. Some studies have also investigated ZnCl2 [34], silver [35], and nickel [36] as additives to the precursor solution in order to enhance the capacitance of electrospun nanofiberbased EDLCs. It has been found that the addition of ZnCl2 has a great influence on fiber morphology and the specific capacitance of carbon NFs containing 5 wt% ZnCl2 reaches to the highest value of 140 F/g when compared to those containing 1 wt% and 3 wt% ZnCl2. Furthermore, the coaxial electrospinning technique has been the research hotspot due to its advantage of material preparation. An and Ahn [37] prepared coaxial NFs with different morphologies using PVP-doped Sn and a PVP/PAN mixture as inner and outer solution, respectively, by the method of electrospinning combined with the reduction of H2. The electrochemical test has shown that the capacitance of capacitor reaches maximum on the condition that the mass fraction of Sn is 8% in the PVP solution. And it is believed that this enhanced electrochemical performance is ascribed to the synergistic effect of active sites on the surface of fibers and pore structure after the reduction of H2.

$RuO_2$ and $V_2O_5$ have also attracted much attention as PCs electrode materials because of their electrochemical stability, high electrical conductivity, and capacitances. For instance, Choi et al. [38] prepared electrospun Pt NFs to support the deposited hydrous $RuO_2$ over layers and found that the resulting composite electrode showed good performance with a capacity loss of only 21.4% passing from 10 to 1000 mV/s. Lee et al. [39] reported that the RuO2–Ag2O composite

NWs electrode produced from electrospinning exhibited high capacitance of 173.25 F/g at 10 mV/s and excellent retention of capacitance up to 97% after 300 cycles. However, considering the high cost and toxicity of Ru, researchers recently have focused on conducting polymers such as PANI, polypyrrole (PPy), and poly-p-phenylene (PPP) as electrode materials for PCs. PANI is currently the most promising candidate due to its low cost and high electrical conductivity. Researchers have prepared [40] electrospun PANI NF and found that the specific capacitance and rate performance of PANI NFs are much higher than that of PANI powder.

***Reduction of noise pollution***

Noise pollution can have a serious impact on human health, including noise-induced hearing impairment and disruption of rest. Loud interior noise levels within airplanes are a major issue for pilots, crew members, and travelers. Aircraft manufacturers are eager to decrease the amount of noise in the fuselage and are looking at new methods and materials. They especially want to find engineered compounds that reduce sound and are also lighter weight, which provides the added benefit of reduced fuel consumption.

Electrospun nano composite fibers are lightweight, dimensionally stable, porous, flexible, and can absorb high, medium, and low frequencies. The researchers manufactured high-surface-area microscale and nanoscale electrospun fibers using three different polymers: polyvinylpyrrolidone, polystyrene, and polyvinylchloride. These polymers were dissolved in appropriate solvents and electrospun at various electrospinning conditions. The two-microphone transfer-function method of the B&K impedance tube was used to determine the acoustical properties of the electrospun fibers at different frequencies. [41]

Test results showed that the absorption coefficients of the fibres (200 nm to 7 µm) were significantly enhanced at the nanoscale. This may be the result of the higher surface area of fibers providing more interaction with sound waves/air molecules (nanofiber surface areas can be up to 10,000 times greater than for microfibers).

The diameter of the traditional acoustical fibers is in the range of micrometers (5-100µm), whereas nanofibers have diameters ranging from 10 nm to 500 nm. Nanofibers have special characteristics such as large specific surface area, high porosity, flexibility, and extremely low weight. These outstanding properties are helpful in obtaining preferable acoustical damping performance.

Traditional sound absorption materials include foams, fibers, membranes, perforated panels, etc. These materials have good noise reduction abilities at the high frequency range, but exhibit few sound absorption properties in the low- and medium-frequency range (250-2000 Hz) in which human sensitivity to noise is fairly high. ―Therefore materials with excellent noise reduction properties in the low- and medium-frequency range are highly desirable in the acoustical purposes. Multi-polymer solutions can be electrospun simultaneously to fabricate various membranes for the sound absorption.

***Battery separators***

Separators play a key role in all batteries. The main function is to keep the positive and negative electrodes apart to prevent electrical short circuits and, at the same time allow rapid transport of ionic charge carriers needed to complete the circuit during the passage of current in an electrochemical cell. Separators should be very good electronic insulators and have the capability of conducting ions by either intrinsic ionic conductor or by soaking electrolyte. They should minimize any processes that adversely affect the electrochemical energy efficiency of the batteries. [42]

A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes. A variety of separators have been used in batteries over the years. Starting with cedar shingles and sausage casing, separators have been manufactured from cellulosic papers and cellophane to nonwoven fabrics, foams, ion exchange membranes, and microporous flat sheet membranes made from polymeric materials. As batteries have become more sophisticated, separator function has also become more demanding and complex.

Common PP and PE separator membranes can be replaced with a nanofiber separator made from PVDF, PVDF copolymers and PAN. These Nano-fibrous separators meet the most important battery separator performance requirements such as[43]:

- Chemical stability
- Tensile strength (acceptable for winding machines)
- Thermal stability (less than 5% shrinkage after 60 min at 90 °C (in a vacuum))
- Thickness (dimensional stability)
- Porosity (greater than 40%)
- Pore size and pore size distribution (uniform pore distribution to avoid performance loss arising from non-uniform current densities) Enabling construction of a battery with superior parameters. ❖ **This technology enables the manufacture of cost effective separators through**
- Lower consumption of polymer material due to the lower basis weight of the membrane
- Significant increase of battery power density
- Higher charge and discharge rate
- Increase in battery life

**Conclusion:**

We have studied role of nanofibers in various applications but still there is incomplete information about some cases such as conversion of nano-fibers to nano-rod and this study helps to illuminate technologists and researchers to carry out detailed study on them. Use of nanofibers in different fields is still burgeoning and eventually will help to satiate various necessities of society.

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