Materials design and processing development of electrospun nanofibers for energy conversion systems

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2018

Electrospinning is a nanofiber fabricated technique that has been discovered for more than three centuries and was first patented in 1900 by John Cooley.[1] Regarding to its advantages over other methods of nanofiber fabrication such as drawing, phase-separation, and self-assembling, this technique was widely researched and applied with many industrial applications.[2] The electrospinning is a continuous and cost effective process to obtain very fine nanofibers with high porosity, high surface area-to-volume ratio and well-ordered of alignment structure that tailorable mechanical properties of the nanofibers. Different polymers were used as precursor solutions to suit with their applications such as polyacrylonitrile (PAN)[3-5] and polyvinylpyrrolidone (PVP)[6] for production of carbon nanofibers; poly(methyl methacrylate) (PMMA),[7,8] polystyrene (PS),[9] polyethylene oxide (PEO),[10] or other transparent polymers for optically active materials and tissue engineering scaffolds.

During the electrospinning process, the polymer solution is fed to a syringe pump and then injected into the liquid jet through a small diameter needle upon applied the external voltage. Therefore, there are many factors that affected to the morphologies and final properties of the obtained nanofibers; both internal factors (*e.g.* type and molecular weight of polymer, concentration of polymer solutions, dielectric constant and evaporation rate of the solvent)[11-13] and external factors (*e.g.* collecting distance, pumping flowrate, applied voltage, and ambient conditions).[14-18] These selected materials and

electrospinning parameters are important to stabilize the conical-like shape of an injected polymer solution at the end of the needle (*viz.* commonly known as a Taylor cone) and balance the forces occurred in the electrospinning process.[19]

Different methods of electrospinning including of direct electrospinning which is used single nozzle to produce the solid nanofibers, emulsion electrospinning and coaxial electrospinning which could produce the nanofibers which more unique properties such as composite nanofiber, porous nanofiber, core-shell nanofiber, and hollow nanofiber.[20] Among these methods, the coaxial electrospinning is wider used because of its advantages in term of size-controllability, tunable core-shell structures, and homogenous preparation of the nanofibers.[21,22]

In this work, the nanofibers with adjustable properties were prepared *via* electrospinning technique by optimization of their precursor solutions, improvement of electrospinning equipment (*viz.* the coaxial nozzle), and incorporation of some functional materials such as the fluorescent dyes and a chiral polymer. The research aims to apply the electrospun nanofibers (ENFs) in the energy conversion applications including the production of carbon nanofibers (CNFs) for electrode materials of secondary battery and fluorescent-chiral nanofibers for optical applications such as wavelength conversion materials and polarizing filters.

In the first phase, the core-shell nanofibers or hollow carbon nanofibers (HCNFs) were fabricated by coaxial electrospinning of polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA) solutions. Optimum range of the viscosity ratio of PAN (outer)/ PMMA (inner) solutions was clarified to obtain good core-shell morphology. Moreover, the balance levels of the inner-to-outer nozzles were studied to obtain unique properties of the HCNFs such as high specific surface area, high crystallinity, and high electrical

conductivity. In the second phase, the nanofibers with optoelectronic properties were prepared by incorporation of two cationic fluorescent dyes and an anionic chiral polymer by single nozzle electrospinning. Well-alignment of the dye molecules, including of pyrene and/or porphyrin, and the naturally-occurring chiral polymer (hyaluronic acid) obtained by electrostatic stretching during the electrospinning process could be confirmed by better photoluminescent (PL), polarization, and circular dichroism (CD) properties. The FRET energy transfers in the ENFs from pyrene to porphyrin (or a fullerene derivative, PCBM) were studied in the last part of this work.

For the CNFs production, suitable combination of fluid viscosities, in terms of viscosity ratio of outer/inner polymer solutions, through the use of PAN (outer fluid) and PMMA (inner fluid) solutions as a model system. The viscosity of each of polymers was adjusted by varying the concentration of the polymer solution. The SEM images of the core-shell nanofibers reveal that continuous nanofibers with small amount of beads morphology could be obtained in the range of studied PMMA and PAN concentrations. Core-shell structures of the obtained nanofibers could be clearly distinguished, as confirmed by the observation of TEM images with high resolution. It was found that the core-shell structure was tunable by adjusting the viscosity ratio of outer/inner solutions. With increasing the viscosity ratio of PAN/PMMA, the total diameter and the wall thickness were increased, while the core diameter seems almost constant. Non-uniform core-shell structures were observed at low viscosity ratio of outer/inner solutions due to the shell solution viscosity was too low to stabilize the core-shell morphology. When increasing the viscosity ratio of outer/inner solutions, the shell solution not only was more stable but also obstructed the flow of the core solutions out of the spinneret, resulting in the smaller core diameter

of the fibers. From this work, the viscosity ratio of outer/inner solutions used to prepare the uniform core-shell structure was optimized to be in the range of 1.22 to 2.82.

By using the suitable viscosity ratio of the polymer solutions, this research has further study about the effect of the balance level of inner and outer nozzle ends on the physical and electrical properties of the HCNFs, which were obtained from carbonization of the core-shell nanofibers of PMMA and PAN. In this experiments, the inner nozzle was set to three levels; (i) normal coaxial nozzle (*viz.* inner and outer nozzle-ends are balanced in the same level) (ii) inward coaxial nozzle and (iii) outward coaxial nozzle. As-spun core-shell nanofibers from three different levels of the inner and outer nozzle-ends were carbonized by oxidative stabilization of the nanofibers at 250 °C for 30 min in air, then calcined at 800 °C for 1 h in nitrogen, and finally heated up to 1000 °C in nitrogen for another hour to obtain the HCNFs.[23]

As results of the nanofiber morphologies obtained from SEM and TEM images, fiber diameters were decreased with some surface roughness after carbonization process in all three set-up levels of the coaxial nozzle. From the TEM images, hollow morphologies could be clearly observed and they also revealed that the HCNFs produced from outward coaxial nozzle show some non-uniform core/shell structure due to an instability of the jet solution during electrospinning. However, this structure may have benefits for some physical properties such as increasing of the specific surface area as confirmed by the N_2 adsorption measurement.

The N_2 adsorption isotherms show that all HCNFs samples show higher N_2 adsorbed volume as compared to that of the normal CNFs, which was produced by single nozzle electrospinning of only PAN solution. The HCNFs produced from the outward coaxial nozzle reveal the largest surface area of 278.56 m^2 g^{-1}, which is 1.69 times larger than

that of the CNFs. This value is also larger than those of the hollow carbon nanofibers fabricated by the same bi-component system of PMMA and PAN reported previously.[24] However, from the XRD and Raman patterns, the HCNFs produced from the normal coaxial nozzle exhibit higher degree of graphitization and crystallinity as compared to that of the HCNFs produced from the inward and outward coaxial nozzles. This result might be derived from the better orientation of graphitic plane that obtained by the smoother flow of both outer and inner polymer solutions from the same comparative levels of outer/inner nozzles. From the XRD patterns, broad C(002) peaks were observed at 2θ around 24-26°, which indicate that the highly amorphous region in the structure of the obtained carbon nanofibers. Not only quite broad C(002) peaks, all samples show large interlayer distance (d-spacing or $c/2$) than those of graphitic carbon (0.335 nm) and turbostratic carbon (0.344 nm).[25] This result suggests that the HCNFs and CNFs from the present work can be classified as amorphous carbon with quite low crystallinity. However, this enlarged interlayer distance of the carbon nanofibers was suitable with some applications such as electrode material for secondary batteries since it provide high initial Coulombic efficiency, excellent rate capability, and stable cycle-ability.[26]

In addition, the conductivity measurement of all obtained CNFs and HCNFs was carried out using two-electrode cells. It was found that all HCNFs show relatively lower electrical conductivity as compared with the CNFs (electrical conductivity = 376 S m^{-1}). However, among the hollow nanofibers, the HCNFs produced from the outward and the normal coaxial nozzles show higher electrical conductivity almost two orders of magnitude that of the inward one. This results implied that both specific surface area-to-volume ratio and the crystallinity (or graphitization degree) affected to the electrical conductivity of the obtained HCNFs. The high electrical conductivity of the HCNFs

produced from the normal coaxial nozzle (648 S m^{-1}) was resulted from its high degree of crystallinity. On the other way, the high electrical conductivity of the HCNFs produced from outward coaxial nozzle (675 S m^{-1}) was resulted from its high porosity and surface area which decreased the contact area or resistivity between metal electrode and the HCNFs during conductivity measuring experiment.

For another application of the nanofibers in photoexcitonics field was explored by incorporation of fluorescent dyes and a chiral polymer into the ENFs prepared by single nozzle electrospinning. The fluorescent dyes have photosensitizing moieties which can re-emit the light through the irradiation of light for excitation. They typically have π-conjugated planar or cyclic structures, which can absorb and emit the specific wavelength of the light when they are excited. Two types of small molecules of pyrene and porphyrin were used as fluorescent dyes in this work. Pyrene is one of polyaromatic hydrocarbons (PAHs), which has large Stokes shift, high quantum yield and long lifetime, and its fluorescence emission spectra are very sensitive to the environment (*e.g.* solvent polarity, temperature). Most interesting fluorescence property of pyrene is to form excimers when the two molecules of the dyes have got closer to the optimum distance for a coupling mechanism.[27] On the other hand, porphyrin is another widely investigated dye that has been used in excitonic studies through UV-vis spectroscopy, PL, and CD spectroscopic analyses. Porphyrin molecules often exist in an aggregated forms through strong intermolecular hydrogen-bondings or π-π interactions. Their stacking forms are well-known as J-aggregates and H-aggregates,[28] which can be distinguished from each other by the different spectral shift in their UV-vis absorption spectra.

Some naturally produced-polysaccharides have been well-known for their chiral formation such as hyaluronic acid (HA), chitosan, L-glutamic acid and polynucleotides.

Their CD induced helical conformation has been studied in many reports.[29-33] HA is also one of interesting chiral polysaccharides that has been utilized as a scaffold for some dyes through the electrostatic molecular interactions.[34]

In this experiments, the ENFs of cationic fluorescent dyes; 1-pyrenemethylamine hydrochloride (PyrMA) and/or $\alpha,\beta,\gamma,\delta$-tetrakis(1-methylpyridinium-4-*yl*)porphyrin *p*-toluenesulfonate (TMPyP), and a complimentarily anionic chiral polysaccharide (HA) were prepared by single nozzle electrospinning with the assistance of a transparent supporting polyethylene oxide (PEO) solution. For comparison, the thin film (fabricated by spin-coating method) and solution samples were prepared to compare their optical properties against the obtained ENFs such as UV-vis absorption, PL emission, and CD.

From the results of UV-vis, PL and CD spectra of the samples prepared with different methods, the electrospinning technique offers better alignment of the dye molecules and chiral polymer chain inside the fiber in nanoscale and also macroscopic alignment of each fibers in the same direction. From these specific properties, the ENFs of the PyrMA have their pyrene excimers emission intensity higher than the same molar ratio of samples in their solution and thin film. While, the ENFs of the TMPyP show much stronger tendency to form higher aggregated state (J- and H- aggregates). Moreover, both of the ENFs of PyrMA and TMPyP show small red-shift in their absorption spectra and strong apparent CD intensities as compared to their solution and thin film. However, the intensity of apparent CD in this work was proved to be mainly resulted from linear dichroism (LD) and linear birefringence (LB) obtained by the macroscopic alignment.

In addition to preparation methods, the effects of the concentration of the dye were studied in term of molar ratio of [Dye]/[HA] ranging from 0.5 to 4. From the PL spectra, it was observed that the excimer to monomer emission of PyrMA ($I_{exc(457)}/I_{mon(397)}$) ratio

was increased dramatically and saturated after increasing the concentration of the dye more than [PyrMA]/[HA] = 1. In the same way, apparent CD intensities of the ENFs of TMPyP was increased proportionally with increasing the concentration of the dye. While, for the ENFs of PyrMA, the maxmum CD intensity can be obtained at the [PyrMA]/[HA] = 2. This result implies that the one-to-one interaction between positive and negative charge of the excimers of cationic pyrene and anionic chiral HA polymer. Therefore, the excess amount of dye could not amplify the CD properties, in other words, the excess amount of dyes was aligned randomly (*viz.* isotropically) as monomer and/or dimer.

For studying the effects of HA to induced circular dichroism (ICD) properties, the ENFs and solution without HA (or dyes) were prepared and their CD spectra were measured as the control experiments. From the apparent CD spectra, all of the solution samples exhibit no trace of apparent CD in the visible region assigned from the two dyes. Whereas the ENFs of PEO-HA-dye for both pyrene and porphyrin exhibit the strong CD apparently in the visible region as compared to the intensity in the UV region originated from chiral HA. The important issue to be noted is that true CD intensity, which is the CD regardless of artifacts from LD and LB that can be calculated according to the theoretical approach suggested by Buffeteau and co-workers,[35] could be observed only in the presence of HA. Thus, the results confirmed the role of HA to amplify the ICD of the obtained nanofibers.

The ENFs of PyrMA and TMPyP were further studied for the FRET in the dyad (mixed dyes of PyrMA-TMPyP) system, and the triad (mixed dyes of PyrMA-TMPyP-PCBM) system by extending their preparation *via* electrospinning process. By using the advantages of electrospinning process, which is well-known technique to obtain the fine nanofibers with well-ordered orientation of the molecules inside its one-dimensional

structure.[36] The smaller diameter of nanofibers is favorable for fluorescent sensing applications.[37] The FRET efficiency (E_{FRET}) then was determined by the fluorescence quenching of the emission of the donor molecules.

In the dyad system, the different steps of electrospinning method, *viz.* pre-mixed and post-mixed methods, were studied to compare the effect of contact (or interaction) on the E_{FRET} of these mixed dye ENFs. It was found that the ENFs of PyrMA-TMPyP prepared from both two methods reveal the absorption bands of both pyrene (332 and 347 nm) and porphyrin (Soret band at 433 nm and small Q-bands from 490-610nm). For the fluorescence emission spectra, the ENFs of PyrMA-TMPyP prepared from pre-mixed method reveal higher quenching efficiency of pyrene excimer emission as compared to the post-mixed method, along with higher intensity of porphyrin emission band.

From the excitation spectra of the ENFs of PyrMA-TMPyP measured by the emission wavelength of PyrMA (donor) and TMPyP (acceptor) revealed that the ENFs of mixed dyes can be excited by both FRET from the excited pyrene molecules (mainly the amount of pyrene excimer is larger than the monomer) and direct excitation of the acceptors simultaneously. To avoid the cross talk phenomena, the energy transfer from PyrMA to TMPyP were studied by excitation at the donor's absorption wavelength of 342 nm. The E_{FRET} calculated from the ENFs fabricated by electrospinning of pre-mixed method are as high as 95.9%, much higher than the post-mixed method, due to its higher contact points between two fluorescent dyes.

For the ENFs of PyrMA-TMPyP-PCBM triad system, it was observed that the PCBM cannot be quenched by the donor than TMPyP (only 93%). The mechanisms of FRET are assumed to be direct energy transfer from PyrMA to PCBM without transfer *via* TMPyP. This is due to the PCBM absorption band was mainly overlapped with the excitation

wavelength of PyrMA and the emission of the PyrMA monomer and excimer, but almost being not overlapped with the TMPyP emission band. Other reasons for lowering the FRET to PCBM might be the combinations of dipole moment, distance, and affinity of PCBM with PyrMA and/or TMPyP. Improvement of the FRET from donor to acceptor in the fine nanofibers of both dyad and triad systems was suggested to be resulted from the alignment and confinement effects (confining the dye molecules in the condense space of small diameter of the ENFs ~400 nm) *via* the electrospinning process.

In summary, the nanofibers prepared through the electrospinning process provide some unique properties to be applied in the energy conversion system. Since one dimensional nanostructures provide materials with a very high surface area and adjustable properties that can be obtained by using various precursors and the improvement of the electrospinning process. In addition, a better orientation of the molecules inside their nanostructures of the ENFs, which had been obtained by electrostatic stretching in the fabrication process, can offer better polarization, PL and CD properties for application of photoexcitonic devices. The FRET in the ENFs is also interesting issue to be considered, even though, the FRET still has not smoothly been occurred in the selected dyad and triad system. Those findings will bring useful information to find the suitable couples of the fluorescent dyes for the better applicable energy conversion devices.

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