Environment-Sensitive Nanofibers and Anchoring of Dyes

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In this paper a new type of multilayered hollow nanofibers was fabricated through the combination of the layer-by-layer technique and the electro-spinning method by removal of the template nanofibers. The morphology of the obtained nanofibers was observed when they were treated in different environments; *i.e.* different pH solutions and heating conditions. The ability to carry a dye in the obtained hollow multilayer nanofibers was probed and the result shows that the obtained nanofibers can anchor dyes effectively.

Key Words: Layer-by-layer, Electrospinning, Hollow nanofibers, Polyelectrolyte.

INTRODUCTION

Recently, nanofibrous webs have gained great attention due to the lower diameter of their fibers than that of webs of fibers fabricated by conventional spinning techniques and resulting in high surface areas per unit volume, small pore structure, *etc.*[1]. Generally, nanofibers can be made by the electro-spinning method, with the setup shown in **Scheme-I**. In the electro-spinning process, a high voltage is used to create an electrically charged jet of polymer solution or melt, which dries or solidifies to leave a polymer fiber[2,3]. One electrode is placed into the spinning solution/melt and the other is attached to a collector. An electric field is supplied to the end of a capillary tube that contains the polymer fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion causes a force opposing the surface tension[4]. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone[5]. With increasing field, a critical value is attained when the repulsive electrostatic force overcomes the surface tension and a charged jet of fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes a whipping process[6] wherein the solvent evaporates, leaving behind a charged polymer fiber, which lays itself randomly on the grounded collecting metal screen. In the case of a melt, the discharged jet solidifies when it travels in the air and is collected on the grounded metal screen. Hollow nanofibers have two times surface areas per unit volume than the normal nanofibers. Considering its wide application, there

has been much effort on developing various techniques to fabricate hollow nanofibers[6].

The layer-by-layer fabrication technique based on electro-static forces is a controllable approach for surface coating of fibers with a designable layer structure, defined wall thickness and diameter. With this method a variety of polyions, including synthetic and natural materials, have been used to construct polyelectrolyte multilayer microcapsules which provide hollow capsules with special functions, such as catalysts, reaction cages, controlled permeability and drug carriers. In the past, we have reported on the fabrication of hollow multi-layered nanofibers by the combination of the layer-by-layer technique and the electrospinning method and their application[7-12]. The fabrication procedure is illustrated in **Scheme-II**. Although nanofibrous mats consist of many fibers, the formation of only one fiber and its' cross-section diagram is illustrated in **Scheme-II** so that one can easily understand the procedure.

In this paper, we report the morphology change of the obtained multilayered nanofibers in different pH solutions and higher temperature, then study its application as dye carrier.
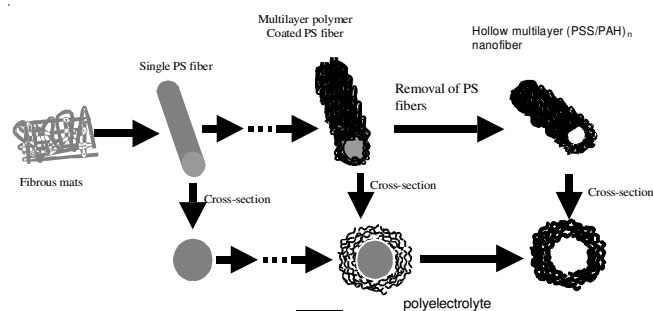
EXPERIMENTAL

The sources of the chemicals were as follows: poly(styrene-sulfonate, sodium salt, PSS) (M_w 70,000), poly(allylamine hydrochloride, PAH) (M_w 70,000), polystyrene and tetrahydro-furan (THF) were from Aldrich. All these materials were used as-received. Sodium chloride and acid blue were bought from Saiji Co. Positively charged melamine formaldehyde particles

(MF particles) with a diameter of around 4.34 ± 0.08 mm were obtained from Microparticles GmbH, Berlin.
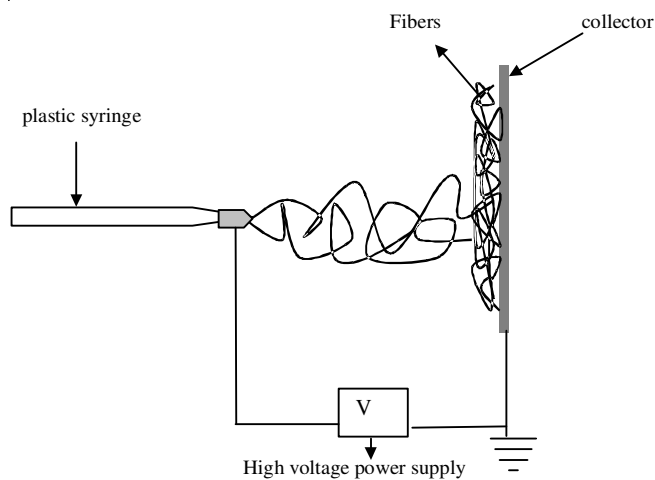
**Scheme-I:** Diagram of electro-spinning device

Scheme-II: Scheme for the fabrication of the multilayer hollow fibers

The water used in all experiments was prepared in a three-stage Millipore Milli-Q plus 185 purification system and had a resistivity higher than 18.2 MΩ × cm^{-1}.

Fabrication of the polystyrene nanofibrous mats by electrospinning method: Polystyrene nanofibrous mats were prepared from tetrahydrofuran/N,N-dimethylformamide (DMF) (1:1, v/v) mixed solution and polystyrene polymer. As a typical procedure, 9.32 mL of THF/DMF solution containing 1.5 g of polystyrene (M_w = 185,000 g/mol) was mixed for 2 h to get a viscous gel. It was quickly loaded into a syringe equipped with a five gauge stainless needle which was connected to a high-voltage supply capable of generating voltages up to 23 kV. The feeding rate of the precursor solution was controlled using an automatic syringe pump. The plate used as the collector was placed 15 cm from the tip of the needle for the collection of the nanofibers. The solution on the tip of the needle was ejected as fibers under a strong electric field towards the collector. Details of the fibrous preparation method are described by Gu *et al.*[13].

Construction of hollow multilayered polyelectrolyte nanofibrous mats: poly(styrene sulfonate) and poly(allyl-amine hydrochloride) (PAH) polyelectrolyte solutions used for building the multilayers were prepared in Milli-Q water with a concentration of 1 mg/mL in 0.5 M NaCl aqueous solution. A polystyrene fibrous mat was selected as template and immersed into poly(allylamine hydrochloride) solution

and poly(styrene sulfonate) solution, alternatively. In every step, 30 min was left for adsorption followed by rinsing by abundant water. When five [(PAH/PSS)₂/PAH] layers were finished, the multilayer polymer coated polystyrene fibers were immersed into THF (2 mL) solution and left 15 min to remove the polystyrene core. In order to remove the excess solution, the sample was centrifuged at 5,000 rpm for 5 min and then washed with THF three times. Finally, the sedimented material was dispersed in water for the next measurement; there were very small agglomerates of fibers at the bottom and some very small pieces of them in the supernatant. The chemical structure of the obtained fiber is shown in **Scheme-III**.
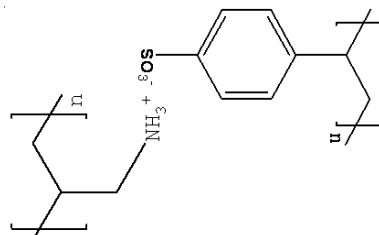
Scheme-III: Chemical structure of the obtained PSS/PAH hollow fiber

Polyelectrolyte capsules prepared through layer-by-layer adsorption: Multilayered assembly was accomplished by the adsorption of the polyelectrolytes on MF particles at a concentration of 1.0 mg/mL in 0.5 mol/L NaCl aqueous solution. Oppositely charged polyelectrolyte species were subsequently added to the suspension followed by repeated centrifugation cycles. After the intended layer numbers [(PSS/PAH)₄] were adsorbed, 0.1 mol/L HCl was used to remove the core (MF particles) and hollow polyelectrolyte shells were obtained. Poly(styrene sulfonate) was used to form the first layer and the outermost layer was poly(allylamine hydrochloride).

Heating treatment of the obtained multilayered poly-electrolyte capsules and hollow multilayered polyelectro-lyte nanofibers: A drop of the obtained capsules and the fibers were placed on aluminum foil respectively, then treated at 60 ℃ for 3 h in oven.

Measurements by scanning electron microscopy: PS/(PAH/PSS)₂/PAH fibrous mats and the (PAH/PSS)₄ capsules were prepared to observe with scanning electron microscopy S-3000N (HITACHI, Japan).

Anchoring of acid blue dyes onto the multilayered nanofibers: The dye solutions were prepared is 10 mg/100 mL aqueous solution. The dyes were absorbed onto the hollow multilayered nanofibers by dispersing them in dye solutions for 12 h at room temperature (300 K) and then removing the nanofibers from the solution. The optical properties of the dye solution before and after absorbing on the nanofibers were studied by absorption spectra using the UV-visible spectro-photometer (U-4100, Hitachi).

RESULTS AND DISCUSSION

According to our previous work, negatively and positively charged polymer can be alternatively assembled on colloidal particles[10,13,14]. Multilayered polyelectrolyte microcapsules were derived by removal of the colloidal particles[10]. In this experiment, a similar method was employed to form multilayer

polyelectrolyte films on nanofibers[15]. Fig. 1 shows the poly-styrene fibers obtained from the electro-spinning device and used as templates in our study. The morphologies of the (PAH/PSS)₂/PAH film coated polystyrene fibers are shown in Fig. 2. Fig. 2a shows that the morphologies of the fibers were retained after coating with five PAH/PSS layers, which means that the multilayered polyelectrolyte films were primarily formed on the surface of the nanofibers. Fig. 2b is the high magnification image of Fig. 2a. The surface became rougher after coating which means that multilayered films were successfully deposited on the fibrous surface. In our previous report, we used Fourier transform infrared spectrometry to confirm this process[15].
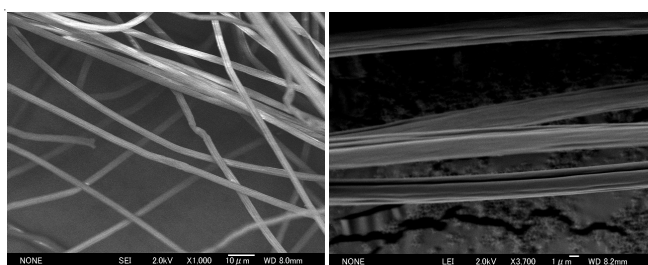

Fig. 1. SEM image of polystyrene electrospun nanofibers: a) low magnification; b) high magnification
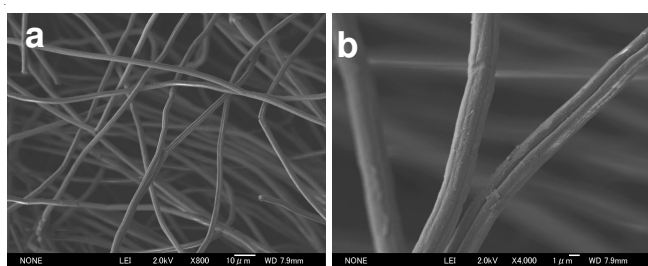

Fig. 2. SEM image of polystyrene fibers coated with (PAH/PSS)₂/PAH layers: a) low magnification; b) high magnification

Polystyrene fibrous mats coated with (PAH/PSS)₂/PAH were then treated with THF to remove the polystyrene fiber and re-dispersed in water. The mats were dried. Fig. 3 shows the SEM images of the obtained hollow polyelectrolyte nanofibers with low and high magnification. They collapsed during the sample preparation because of the solvent evaporation. According to our previous report, hollow multilayered polyelectrolyte capsules obtained by the layer-by-layer method will collapse when they are dried because of the inner solvent evaporation. This is consistent with the results obtained here. The hollow multilayered microcapsules obtained by layer-by-layer technique have a similar phenomenon, too[13]. Such collapse was caused because the shell was too thin to support itself and the surface tension made them collapse during the inner solvent evaporation. If the thickness of the shell is increased, a round tubular shape can be obtained, as we reported previously[15].

The outstanding advantage of the layer-by-layer technique is that the shell thickness can be tuned with a precision of nanometers[7-10]. The previous publications on the fabrication of multilayered hollow microcapsules disclosed the relation-ship between the properties and the surface charge, morphology,

elasticity, conductance, permeability, *etc.*[13,16-20]. It was also reported that the microcapsules' properties can be changed by exposing to a higher temperature, different pH solutions, which the capsules were dispersed in, solutions with different polarities and different ionic strength[18-20]. In all of these cases, the strength of the intermolecular interaction between the oppositely charged polyelectrolytes changes dramatically, resulting in a denser or looser arrangement of the layers. A basic understanding of the multilayered structure and its control during layer formation in order to tailor specific properties is required for all potential applications. In this paper we describe the influence of the temperature and pH solutions on the obtained multilayer hollow nanofibers. Fig. 4a and b show the SEM images of the obtained hollow polyelectrolyte nanofibers with low and high magnifi-cation after they were treated at 60 ºC for 3 h. Compared with Fig. 3, the fibrous film becomes opaque. Fig. 5 shows the diffe-rence before and after the microcapsules were treated at 60 ºC for 3 h. After heat treatment, the capsules' sizes deswelled from 4.5 mm to 1.4 mm, the shells of the capsules changed from transparency to opacity and the capsule morphologies from the collapsed and form to a round shape. Heat treatment results in the deswelling of the capsules and the nanofibers. A possible reason is that a substantial amount of water was contained in the multilayer polyelectrolyte layers during the preparation, which was already partially confirmed by FTIR spectra in the previous publications. The water amount in the PAH/PSS multi-layer films was as high as 42 % confirmed by small-angle neutron scattering measurements on coated colloidal particles[21,22]. The water contained in the multilayered films can be divided into two parts: one part filled up the pores and small voids of the multilayered film; the other part is the absorbed water. The observed denser structure of the multilayered hollow nanofibers and the capsules after heat treatment might be due to the polyion layers' interpenetration and coiling. So, part of the water losses from the multilayered polyelectrolyte films[21-23].
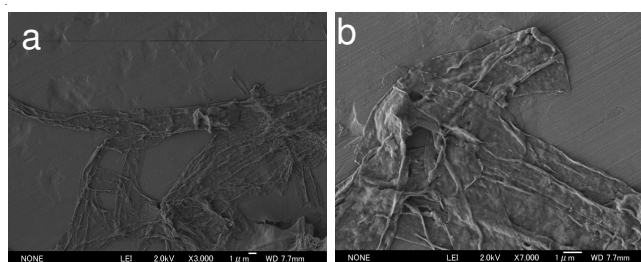

Fig. 3. SEM image of the obtained (PAH/PSS)₂/PAH multilayer hollow nanofibers: a) low magnification; b) high magnification
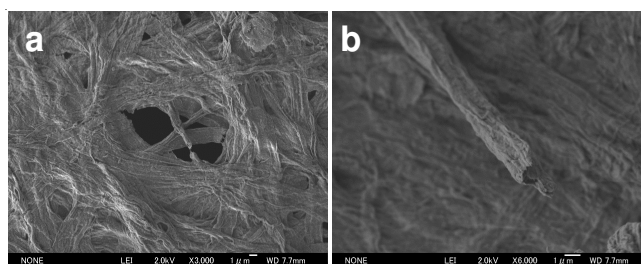

Fig. 4. SEM image of the obtained (PAH/PSS)₂/PAH multilayer hollow nanofibers treated at 60 ºC, 3 h: a) low magnification; b) high magnification
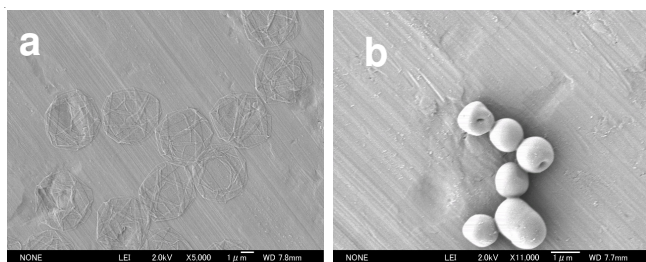
Fig. 5.   Control experiment, the SEM image of multilayer microcapsules (PSS/PAH)$_4$ were treated at 60 ºC, 3 h: a) before heat treatment; b) after heat treatment

The level of swelling of the polyelectrolyte multilayers in aqueous environments is a critically important parameter when considering their use as functional biomaterial coatings and/or vehicles for controlled drug delivery[24,25]. Here we studied the obtained hollow nanofibers' behaviour in different pH solutions. Fig. 6a shows SEM images of the obtained multilayered nanofibers, which were treated by 1 M NaOH solutions. Comparing it with the Fig. 3, one can find after being treated with NaOH solution, the fibrous film became highly opaque and the tubular structure appeared again. Fig. 6b shows in the SEM image of the hollow fibers, which were treated with 1 M HCl solution. The fibers were fused if their contacts and the diameter of the fibers shrank dramatically. The average diameter was about 150 nm. According to a previous report on the effects of the pH on PAH/PSS multilayer films[26], a possible mechanism of the pH influence on the multilayered film is the disruption/reformation of hydrophobically associated poly(allylamine hydrochloride) domains. Manifestations of this influence include the ability of a multilayer to exhibit a molecular memory effect, which is a simple consequence of a broad, well-defined swelling-deswelling hysteresis loop. In the case of PAH/PSS multilayers, the poly(styrene sulfonate) chains kinetically inhibit the reformation of the hydrophobic domains established during assembly and as a result, over short time periods, the deswelling transition takes place at a pH much higher than the swelling transition[26,27].
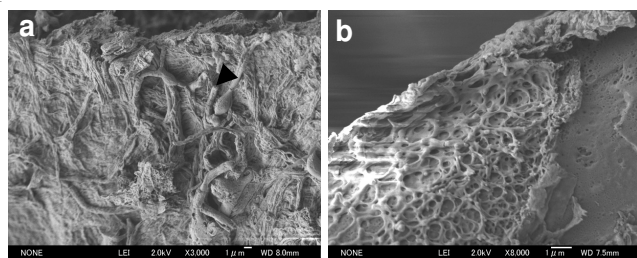

Fig. 6.   SEM image of the obtained (PAH/PSS)$_2$/PAH multilayer hollow nanofibers treated with different pH solutions; a) 1 M NaOH; b) 1M HCl

Because the hollow nanofibers have high surface areas per unit volume, one of their main applications is as carriers[1-3]. In order to test the carrier ability, we used acid blue: 0.1 g polystyrene template nanofibers were used to prepare multilayer hollow nanofibers; then the obtained fibers were immersed into the dye solution. UV-visible absorbance of the solutions were measured before and after the hollow multilayered nanofibers immersion are shown in Fig. 7. After the

nanofibers were removed from the solution, part of the dye was removed too. The volume of the dye solution was 10 mL. According to Beer's Law[28]:

$$A = \varepsilon bc$$

where, ε is a constant of proportionality, called the absorbtivity, b is the path length, c is the concentration and A is the absorbance. The hollow nanofibers obtained by starting with 0.1 g polystyrene fiber can carry 0.5 mg acid blue. Comparing with the traditional mesoporous material[29,30], the hollow multilayer nanofibers have higher ability to carry dyes.
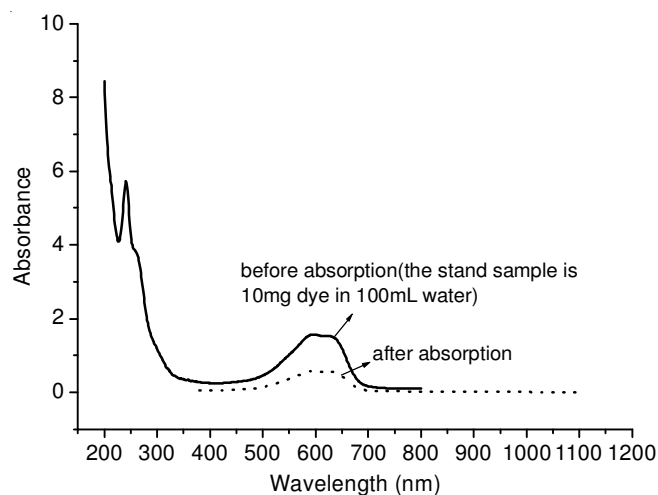

Fig. 7.   UV-spectra of the acid blue solution before and after the dyes were anchored on the fibers

Conclusion

In this paper, a new type of multilayered hollow nanofibers was obtained by the combination the electrospinning method with the layer-by-layer technique. The obtained multilayered hollow nanofibers can change their morphology when in different environments; for example, different pH solutions or heat treatment. SEM was employed to show the differences before and after the treatment. For heat treatment, the possible mechanism is that part of the water loss is from the multilayer films. For different pH solution treatment, it is because the polymer chains rearrange in different pH solutions. Because the hollow multilayered nanofibers have high surface areas per unit volume, acid blue was used to study their carrying ability; the results showed that the obtained nanofibers have a high ability to carry the dye, This is very important for their potential applications in catalysis, biosensors and dye-sensitized solar cells.

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