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Rose thorns-like polymer micro/nanofibers via electrospinning and controlled temperature-induced self-assembly

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ABSTRACT

Novel rose thorns-like nanofibers, composed of polyarylene ether nitriles (PEN) “rose stems” and iron phthalocyanine (FePc) “thorns”, are prepared by combining electrospinning and controlled temperature-induced self-assembly. After removing solvent and subsequent temperature treatment, the FePc sheath structure changes from bead structure to rose thorns-like structure. The unique nanoscale architecture can be finely controlled by the processing time and temperature. The length of “thorns” on the “rose stems” can change from several nanometers to decade micrometers. The driving force for the morphology changes comes from self-assembly of FePc, including the π – π supramolecular interaction between aromatic cores and the cooperative complexation of metal ions between peripheral crown ether moieties. This novel structure, rendering a 3-D feature, can offer potential in a number of applications, including nanoelectronics.

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1. Introduction

In the last decade, electrospinning has revived as a fascinating choice to assemble polymer nanofibers with various morphologies and functionalities due to its simplicity and cost effectiveness, along with environmental benignity [1–4]. The unique structural features, such as high surface-area-to-volume ratio, extremely long length, and complex porous structure, etc., of electrospun nanofibers make them suitable for various applications, including drug delivery [5], sensors [6], catalyst support [7] and tissue engineering [8]. Nanofibers made from simple electrospinning usually exhibit a solid interior and smooth surface. However, recent demonstrations imply that nanofibers with unique secondary (e.g., core/sheath, hollow, and porous structures) can also be prepared if appropriate processing parameters or new designs of spinnerets are employed [3]. For example, Wei et al. observed the formation of core-sheath structures when a solution containing polyaniline

(PANI) and polycarbonate (PC) nanofibers, was electrospun into thin fibers [9]. Li and co-workers prepared hierarchically ordered polymer nanofiber structure (nanofiber shish kebab (NFSK)) by combining electrospinning and controlled polymer crystallization methods [10]. Zhang and co-workers prepared the PAN-PPy core-sheath composite nanofibers by a judicious combination of electrospinning technique and surface-initiated polymerization processes using Fe^{3+} as an oxidant. And the PPy sheath structure changes from particle-like, fibrillar, to continuous coating with increase in Fe^{3+} content [11]. Herein, we report a novel thorns-like structure nanofibers by combining electrospinning and the subsequent temperature-induced self-assembly processes [12,13].

Phthalocyanines (Pcs), with applications ranging from voltaic devices, compact-disc coatings, to photodynamic therapy [14–16] can be self-assembled into columnar structures to form lyotropic and thermo-tropic liquid-crystalline phases and highly ordered thin films able to self-assemble into stacks through π – π supramolecular interaction [17]. The intermolecular interaction can be enhanced due to these ions complex between the crown

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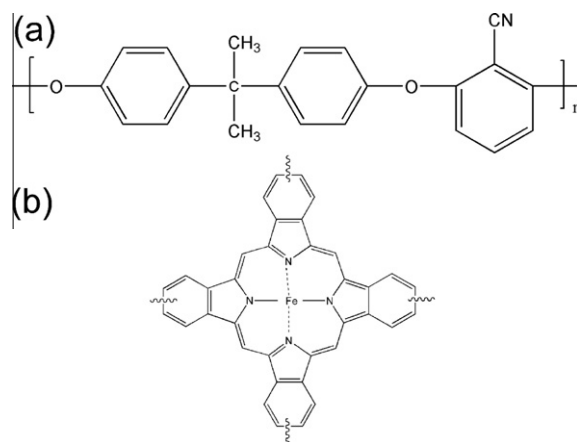
ether fragments. In this way fine tuning of the self-assembled architecture at the molecular level is possible and results in dramatic structural changes at the mesoscopic level [14]. Thus, we electrospun polyarylene ether nitriles (PEN)-iron phthalocyanine (FePc) rose thorns-like structure composite nanofibers by the self-assemble into rod-like structure feature of FePc.

In this article, polyarylene ether nitriles (PEN), as a kind of high-performance engineering material, were chosen due to their outstanding properties such as radiation resistance, high thermal and thermo-oxidative stability, good mechanical properties and chemical inertness. Therefore, PEN composites are very attractive in aerospace, industrial and automotive area where elevated temperature and aggressive chemical environment are often encountered [18–21]. Thus, through combination the PEN and FePc, we prepared the PEN/FePc composite nanofibers by electrospinning. And the surface morphologies of the prepared nanofibers changed from core-sheath structure to rose thorns-like structure after the removing solvent and subsequent temperature treatment. The preparation process of rose thorns-like nanofibers is shown in Fig. 1. Furthermore, the size of “thorns” can be controlled by the processing time and temperature, respectively.

2. Experimental

Polyarylene ether nitriles (PEN) were provided by Union Laboratory of Special Polymers of UESTC-FEIIYA, Chengdu, China. It is a copolymer derived from 2,6-difluorobenzonitrile with bisphenol A (BP-A) and resorcinol (RS) with the inherent viscosity of 1.22 dL/g (in N-methylpyrrolidone, 0.005 g mL⁻¹). N,N'-Dimethylformamide (DMF, 99%), was purchased from Tianjin BODI Chemical Company. Iron phthalocyanine polymer (FePc) was prepared in our lab [22]. Scheme 1 shows the molecular structure of PEN and FePc.

The PEN solution was prepared by dissolving 2 g PEN in 15 mL DMF then the same quality of FePc (2 g) was added into the solution. Prior to electrospinning, the mixtures were stirred for 2 h to obtain the homogeneous co-dissolved spinning dopes. They were then carefully placed into a 50 mL syringe which included a metallic needle with



Scheme 1. The molecular structure of (a) PEN and (b) FePc.

an internal diameter of 0.5 mm. Electrospinning was carried out under a fixed electric field of 25 kV/15 cm. The feeding rate of the solutions was controlled at 1 mL h⁻¹. The electrospun PEN/FePc composite nanofibers were accumulated on an aluminum foil surface and collected as a fibrous mat. Additionally, the PEN fiber prepared in the same way was electrospun as a contrast sample.

Collected nanofibers membranes were immersed in water overnight to replacement off solvents. Subsequently, the membranes were placed in oven at 80, 100, 120, 150 and 160 °C for 2 h, respectively to remove any trace solvent that may be present in the nanofibers membranes. Then, the membranes were heated to 180, 200, 210, 230 °C for 4 h, respectively.

The morphology of electrospun PEN/FePc nanofibers and the corresponding rose thorns-like nanofibers via the range of temperature treatment were evaluated using scanning electron microscopy (SEM) (JSM, 6490LV). The surface tension of solutions was measured by a dynamic contact angle analyzer (KRÜSS GmbH, model DSA-100) at room temperature. The viscosity measurements were performed at room temperature in a stress-controlled rheometer (TA Instruments AR-2000) using primarily cone and plate geometry. Reproducibility of these solution

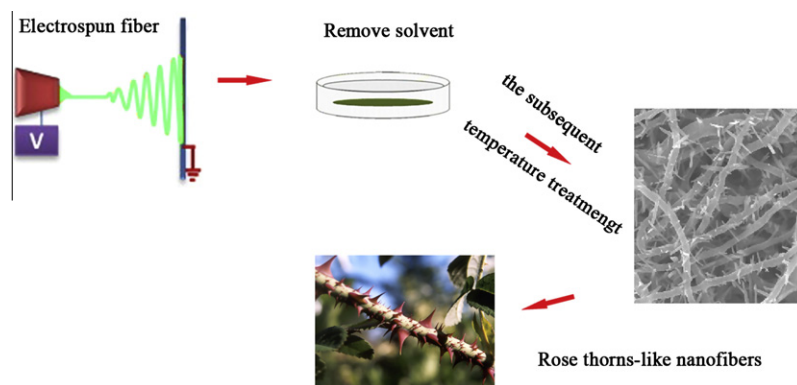


Fig. 1. The preparation process of rose thorns-like nanofibers.

properties was assessed by conducting all measurements on at least five samples.

3. Results and discussion

As we know, in the electrospinning process, the whipping motion of the electrospinning jet results in drawing of the fibers. This increase in the surface area of the jet, leads to rapid solvent evaporation at a time scale down to the millisecond range [23]. For the spinning solution containing different materials, the rapid evaporation of solvent will take the polymer blend solution through the phase boundary into the two phase regime [24]. Thus, during the solvent evaporation, the low molecular weight FePc (from Table 1) can provide the system lower viscosity and higher mobility of molecules, which can overcome the viscous friction of the mixture, promoting the migrating and coarsening to form phase separation. Furthermore, in the case of pipe or capillary flow during the electrospinning process, the system will attempt to attain a state of minimum energy dissipation. This causes the lower viscosity fluid (FePc) to migrate to locations of highest shear rate, which are located at the walls. Thus, the lower viscosity

Table 1

The physical properties of polymers.

	Surface tension (mN m ⁻¹)	Viscosity ^a (PaS)
PEN	37.96	1.17
FePc	51.37	0.022

^a Shear rate is about 1.5 S⁻¹.

fluid will attempt to encapsulate the higher viscosity material to form core (PEN)–sheath (FePc) structure. A typical SEM image (Fig. 2c and d) exhibits that there are many distinct FePc bead or agglomerates wrapping the electrospun PEN nanofiber surface, not a continuous and elongated fibrillar sheath structure. Additionally, the prepared composite fiber diameter increases and the surface morphology are rougher compared with the PEN fibers (Fig. 2a and b). The presence of FePc-bead structures could be attributed to the high-surface tension of FePc molecules as shown in Table 1, which can drive the FePc molecules into spherical droplets forming beads rather than fibers for minimization of surface area [25]. Furthermore, work by Mead and co-workers [9] has demonstrated that polymers with a high number of entanglements or high-molecular weight tend to form fibers not beads, in the

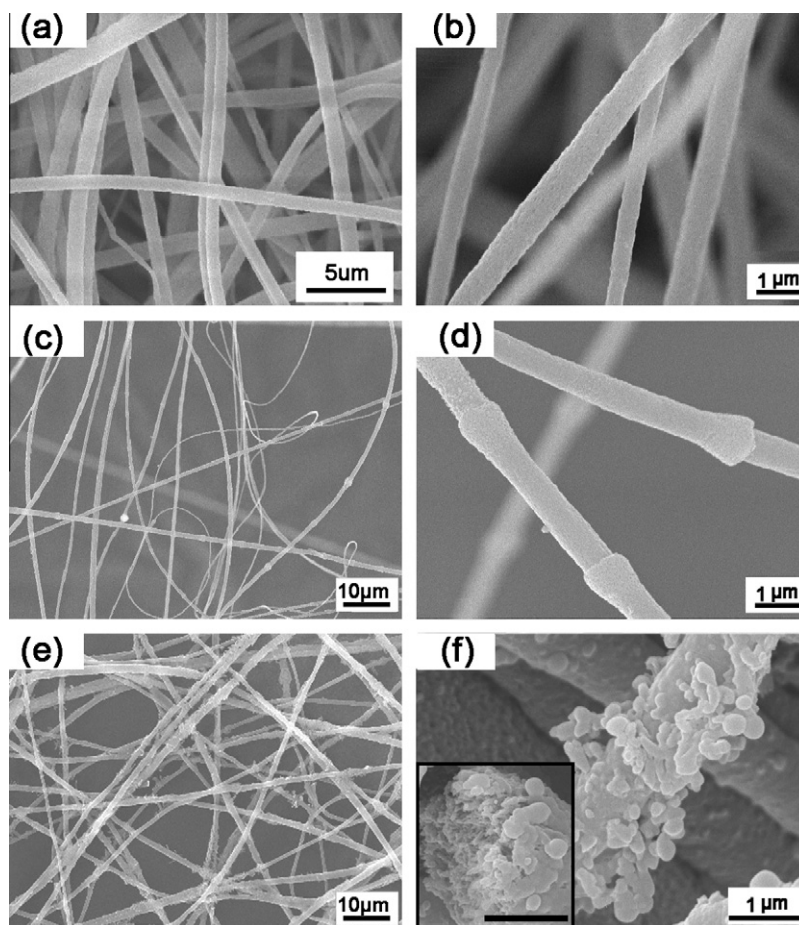


Fig. 2. SEM of images of electrospun PEN fibers (a, b), (c, d) composite PEN–FePc fiber and cross-sections of the composite fiber shown in the inset, composite fiber immersed in water (e, f).

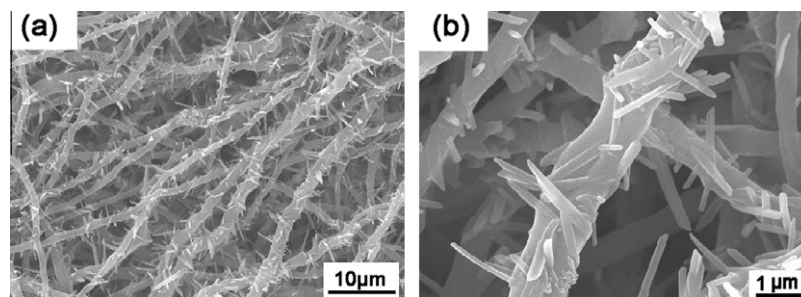


Fig. 3. SEM of images of rose thorns-like micro/nano fibers treated at 180 °C, 4 h.

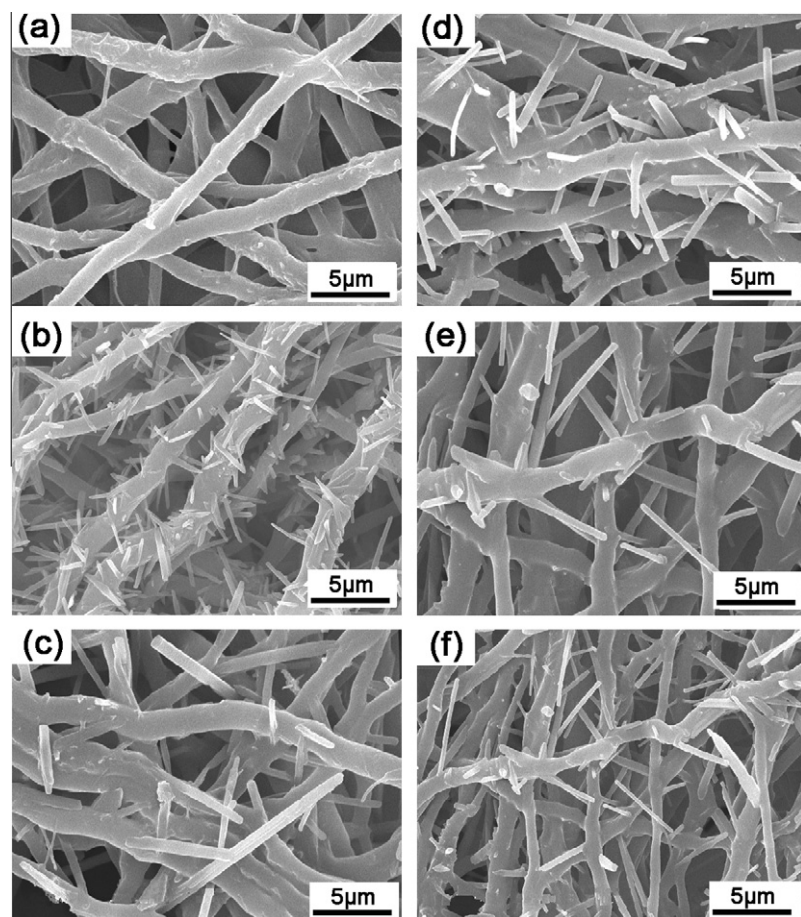


Fig. 4. SEM of PEN-FePc nanofibers at different temperature treatment (a) 150 °C, 4 h (b) 180 °C, 4 h (c) 230 °C; and at different time treatment at 200 °C (d) 2 h (e) 4 h (f) 6 h, respectively.

electrospinning process. Thus, the low molecular weight FePc tended to form beads. From Fig. 2e and f, more obvious FePc-bead structures are observed, and structural heterogeneity exists in the cross-section of the composite fibers (Fig. 2f, inset). The bead-like FePc is formed on the surface of fiber.

In addition, there are many “nanoknots” linking the nanofibers together. The formation of this structure would most likely be due to the insufficiently fast stretching during the whipping and bending process of the jet. Then, the

nanofibers membranes were treated via a range of temperature treatment from 80 to 160 °C to remove any trace solvent. After that, the membranes were heated to 180 °C. The FePc sheath structure changed from bead-like to rose thorns-like without any change of the PEN core structure (Fig. 3a and b). These special structures are attributed to the self-assemble into nanoribbon of phthalocyanines through π - π supramolecular interaction between aromatic cores and the cooperative complexation of metal ions between peripheral crown ether moieties [13,17,26].

Furthermore, the morphology and size of the “thorns” on fiber surface can also be finely controlled by the processing time and temperature, respectively. Here we report the influence of growth temperature and time on the morphology of PEN/FePc nanofibers at the temperature range from 150 to 230 °C and 2 to 6 h at 200 °C, respectively. The representative SEM images in Fig. 4 show the rose thorns-like morphology can change with increasing growth temperature. With the temperature increasing from 150 to 230 °C, the lengths of “thorns” on the fibers surface are 0.4–1, 1–4, 6–15 μm, respectively (Fig. 4a–c). The lengths of “thorns” also increases from 3–7, 4–8 to 4–10 μm with the processing time increase from 2 to 6 h at 220 °C (Fig. 4d and f). We can conclude that the FePc “thorns” are longer and less in numbers when the temperature is higher. The driving force for the self-assembly of FePc comes from interactions between the phthalocyanine molecules. First, π – π stacking of the Pc rings is the most important interaction to form the fibers. The phthalocyanines, as we have known, are macrocyclic π -conjugated compounds consisting of 18- π electrons in the center, which makes the macromolecules in the structure aggregate easily. The second interaction is the π – π tight packing between the cooperative complexation of metal ions between peripheral crown ether moieties [27]. The subsequent temperature treatment increases the motion velocity of the molecules which can increase the probability of interaction between molecules. As a result, the self-assembly speed of the FePc molecules becomes high. Thus, higher temperature and longer time leads to the formation of the long and crude FePc “thorns” as shown in Fig. 4c. At lower temperature, the slower self-assembly of the FePc molecules results in the formation of the thin and short “thorns” as shown in Fig. 4a. These self-assembly nanofibers membranes provide an elegant way of controlling the composition of the resulting assemblies and the surface morphology of the nanofibers. The control of FePc assembly on surfaces is of critical importance in the design and construction of functional devices with less expensive, finely controlled, which are distinct from conventional thin films process such as vacuum deposition [28] and Langmuir–Blodgett techniques [29].

The unique rose thorns-like architecture can be easily tuned for the application purposes and better than the nonwoven nanofibers. Firstly, the “rose thorns” provides much higher specific surface areas compared with nanofibers, which renders a 3-D feature to the 1-D nanofiber because the 2-D rose thorns-like structure are perpendicular to the nanofiber axis. This kind of unique “rose thorns” structure possessed a more open structure because the “thorns” serve as the spacers that keep the nanofibers apart, leading to a wider tuning window for the porosity control. Secondly, as fiber reinforced polymer (FRP) composite materials, this rose thorns-like structure can enhance nanofiber–matrix interfacial adhesion, offering great potential in enhancing mechanical properties of engineered composite materials. Furthermore, the phthalonitriles have a number of exceptional properties and offers promise as matrices for advanced composite applications [30,31], it provides a platform for incorporating different functionalities into nanoscale polymer fibers in the rose

thorns structure. And the electrical and magnetic behaviors and optical properties of the FePc can be maximized by combination of electrospinning technique.

4. Conclusion

PEN–FePc composite nanofibers membranes with a rose thorns-like structure were prepared by combining simple electrospinning and the subsequent temperature-induced self-assembly processes at low cost. It was found that the surface morphologies of the prepared nanofibers changed from core-sheath structure to rose thorns-like structure after the removing solvent and subsequent temperature treatment. The unique nanoscale architecture, like the conventional plant-rose thorns, can be finely controlled by the processing time and temperature. The lengths of “thorns” on the “rose stem” changed from several nanometers to decade micrometers. The driving force for the morphology changes comes from self-assembly of FePc, including π – π supramolecular interaction between aromatic cores and the cooperative complexation of metal ions between peripheral crown ether moieties. This novel structure which renders a 3-D feature can find wide applications in the fields of sensors, catalyst support, nanoelectronics, and tissue engineering.

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