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Full Length Article

Necklace-like fiber composite membrane for high-efficiency particulate matter capture

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ABSTRACT

The necklace-like fiber membranes are fabricated using electrospinning technique for high-efficiency PM (particulate matter) capture. Poly-*N*,*N*′-[(4,5-dihydroxy-1,2 phenylene)bis(methylene)]bisacrylamide (POHABA) nanospheres as "pearls" are embedded in poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP) matrix substrates to make necklace-like fibers. The reason for choosing POHABA nanospheres is due to their broad-spectrum inhibitory effect on bacteria. The diameters of three POHABA nanospheres are controlled to be 190 ± 50, 364 ± 39 and 467 ± 65 nm, respectively. The necklace-like structures become more pronounced with the increase of POHABA diameter. The $PM_{2.5}$ removal efficiencies of PEO necklace-like fiber membranes obtained with electrospinning time of half an hour are in the range from 88.0 to 92.5%. Under the same fabrication conditions, the PEO/POHABA-467 fiber membrane displays better capture efficiency than that of PVP/POHABA-467 fiber membrane. Using thicker PEO/POHABA-467 filter membrane (electrospinning for one hour), excellent removal efficiency of $PM_{2.5}$ (99.2%) is achieved, which is better than that obtained from other membranes and even commercial QMA filter (Whatman). The necklace-like fiber membranes have a great potential in the fields of aero filter and mask.

1. Introduction

Necklace-like nanostructures have drawn considerable attention owing to their enhanced extraordinary chemical and physical properties [1–4]. Because of structural defects and synergetic effect of beads and chains, the necklace-like materials exhibit much higher activities than pure beads or chains. The necklace-like structures were formed by various methods, such as electrospinning [5], hydrothermal process [6], microwave heating approach [7], and facile magnetic field-induced method [8] etc., among which the electrospinning is the simplest and cost effective technology. The membranes made by electrospinning technique were composed of various structures ranging from nano to micro scales with many advanced functions and applications [9–12]. The membranes usually act as a barrier separating two distinct phases for filtration and separation applications [13–16]. Recently, the air pollution from particulate matter (PM) caused serious problem to human health and daily life in China [17–22]. The necklace-like fiber membrane may find great use in this area.

PM is a mixture of various sized inhalable particles associated with potentially toxic chemicals, including heavy metals [23,24], inorganic anions [25], organic carbon [26] etc. Exposure to PM even at low concentrations below the health-based guidelines (European Union air quality limit values: PM_{10} (40 $\mu g/m^3$) and $PM_{2.5}$ (25 $\mu g/m^3$)) also could increase the risk for lung cancer [27]. However, the survey suggests that there are few studies on fabricating air filters for PM [28–31], which were made by polyacrylonitrile fibers [28], carbon fibers [29], polyimide-nanofiber [31] and nanofibrous Metal Organic Framework fibers [30]. The membranes capable to effectively remove PM are still highly demanded.

Herein we used the electrospinning method to make necklace-like poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP) fibers containing poly-*N*,*N*′-[(4,5-dihydroxy-1,2-phenylene)bis(methylene)]bisacrylamide (POHABA) nanospheres which were confirmed to be broad-spectrum inhibitors. The membrane made from those fibers exhibited remarkable removal efficiency for $PM_{2.5}$ and PM_{10}, which indicates that the necklace-

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like fiber membrane has great potential in the fields of aero filter and mask.

2. Materials and methods

2.1. Synthesis of POHABA nanospheres

The details for POHABA nanospheres synthesis were described elsewhere [32]. In brief, a mixture of 0.2 mol *N*-methylolacrylamide (98%, Aladdin), 0.1 mol catechol (99%, Aladdin), 3.75 mL sulfuric acid (95.0–98.0%, Sigma-Aldrich) and 50 mL ethanol (≥99.8%, Sigma-Aldrich) were under stirring for 8 days at room temperature. A white monomer called *N*,*N*′-[(4,5–dihydroxy-1,2-phenylene)bis(methylene)]bisacrylamide (OHABA) precipitated. The product was washed by distilled water and recrystallized by ethanol, and then dried in a vacuum desiccator. A certain amount of OHABA dissolved in 10 mL ethanol at 70 °C was mixed with 0.1 g 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%, Aladdin) for 10 h to fabricate POHABA nanospheres. The product was washed by ethanol for 3 times and dried in a vacuum desiccator for future use.

2.2. Electrospinning of PEO/POHABA and PVP/POHABA nanofibers

POHABA nanospheres were dispersed in ethanol or distilled water by 60 min sonication prior to mixing with the polymer solutions. The PEO or PEO/POHABA precursor solutions were prepared by dissolving 0.12 g poly(ethylene oxide) (PEO, Mv ~900,000, Aldrich) in 2 mL distilled water containing 0 or 0.5% (w/v) POHABA nanospheres at room temperature with overnight stirring. Similarly the PVP/POHABA precursor solutions were prepared by dissolving 0.2 g poly(vinylpyrrolidone) (PVP, Mw ~1,300,000, Aldrich) in 2 mL ethanol with 0 or 0.5% (w/v) POHABA nanospheres at room temperature with overnight stirring. These solutions were subsequently placed in a 1 mL syringe with a metallic needle of 0.9 mm inner diameter. The electrospinning was carried out with flow rate of the solution to be 0.5 mL/h, the tip-to-collector distance to be 20 cm, and the applied voltage to be 15 kV. The aluminium foil was used to collect the electrospun fibers. The electrospinning device was composed of a syringe pump (Model: KDS 101, KD Scientific) and a high voltage power supply (Spellman High Voltage Electronics Corporation, MP Series).

2.3. Characterization

The morphologies of the POHABA nanospheres were determined by AFM (Bruker Corp., Santa, Barbara, CA). The morphologies of the nanofibers were determined by SEM (FEI MAGELLAN 400, 30 kV and FEI Quanta 200FEG, 20 kV) and TEM (Tecnai G2 Spirit, 120 kV). The removal efficiency of $PM_{2.5}$ and PM_{10} was measured by NOVA PM sensor SDS011 (Nova Fitness Co., Ltd.).

3. Results and discussion

By adjusting the ratio of *N*,*N*′-[(4,5–dihydroxy-1,2-phenylene)bis(methylene)]bisacrylamide (OHABA) and 2,2′-Azobis(2-methylpropionitrile) (AIBN), the size of POHABA particles were controlled. Fig. 1 shows the AFM images of POHABA nanospheres synthesized by varying the mass ratio of OHABA and AIBN. With the ratio of OHABA and AIBN to be 1:8, the mean diameter of POHABA is 190 ± 50 nm, as shown in Fig. 1a–c. They are in spherical shapes. When the ratios are 1:2 and 1:1, the diameters of POHABA became 364 ± 39 nm and 467 ± 65 nm respectively. According to their sizes, they are named as POHABA-190, POHABA-364 and POHABA-467 respectively. In the insets of Fig. 1b, e and h, the height profiles are given according to the corresponding AFM images. The average heights shown in Fig. 1k were ~142, 328 and 437 nm, respectively, which are similar to the mean diameters in Fig. 1j. Because of the good dispersibility and uniform size, the spheres were spontaneously arranged as monolayer on mica plate. Every three adjacent spheres form an approximate equilateral triangle. Three angles were drawn in Fig. 1a, d and g to show this. The two joint edges were marked as a and b, which formed angle α. The edges and angles were measured as statistical data shown in Fig. 1l. Edge a (~182, 352 and 461 nm) and b (~182, 349 and 456 nm) of the same sample are almost equal. The angle α was 55, 58 and 58° with the error bar of 12°, 4° and 3°, respectively. The above mentioned data also confirm the uniformity of POHABA nanoparticles. POHABA nanospheres have great advantages including antimicrobial ability, low toxicity and easy to synthesize. In the follow-up experiment, the POHABA nanospheres were used to form necklace-like fibers, which hold great promise in antimicrobial field.

Upon electrospinning, the fibers combined with nanospheres were expected to be necklace-like fibers. Fig. 2 shows the morphologies (SEM and TEM images) and statistical diameter analysis of pure PEO and PEO/POHABA fibers. Base on the statistical analysis of the pure PEO fibers (Fig. 2a and b), PEO/POHABA-190 fibers (Fig. 2d and e), PEO/POHABA-364 fibers (Fig. 2g and h) and PEO/POHABA-467 fibers (Fig. 2j and k) SEM images, the mean diameter of pure PEO fibers and PEO/POHABA fibers (the flat parts) were found to be 302 ± 34, 319 ± 43, 315 ± 58 and 343 ± 46 nm shown in Fig. 2m, n, o and p (the gray and the black curves), respectively. The combination of POHABA nanopheres didn't affect the PEO electrospinning. By comparison, the mean diameters for the raised parts of PEO/POHABA fibers were found to be 382 ± 46, 422 ± 43 and 512 ± 42 nm shown by blue curves in Fig. 2n, o and p, respectively. As the diameter of nanospheres increased, the difference between thinner and raised parts (63, 107 and 169 nm, respectively) increased, and the necklace-like structure became more obvious. Because of the strong electron etching during TEM measurement, the fibers measured using TEM are thinner than SEM. The representative individual TEM images are shown in Fig. 2c, f, i and l, respectively. In Fig. 2c, the TEM images of pure fibers are shown. In Fig. 2f, i and l, the spheres in fibers can be clearly seen.

Another polymer, PVP, was used as bulk solution for electrospinning. Fig. 3 shows the morphologies and statistical diameter analysis of pure PVP and PVP/POHABA fibers. Base on the statistical analysis of the pure PVP fibers (Fig. 3a and b), PVP/POHABA-190 fibers (Fig. 3d and e), PVP/POHABA-364 fibers (Fig. 3g and h) and PVP/POHABA-467 fibers (Fig. 3j and k) SEM images, the mean diameter of pure PVP fibers and PVP/POHABA fibers (the flat parts) were found to be 536 ± 44, 568 ± 51, 572 ± 80 and 558 ± 55 nm, respectively. Because the pure PVP fibers are thicker than pure PEO fibers, the necklace-like structures are not as obvious as PEO fibers. In Fig. 3e, the PVP/POHABA-190 fibers are similar to the pure fibers in Fig. 3b. The mean diameters of raised parts of PVP/POHABA-364 and PVP/POHABA-467 fibers were found to be 618 ± 61 and 633 ± 34 nm, respectively. The difference between the flat and raised parts is very small (46 and 75 nm, respectively). The representative TEM images are shown in Fig. 3c, f, i and l, respectively. The electron transmission for PVP fibers is not as easy as PEO fibers. Therefore, for the thicker fibers, as shown in Fig. 2i and l, we can only see the raised parts rather than nanospheres. For the thinner fibers (Fig. 2f), the black nanospheres were imaged.

As shown in Fig. 4a, the PEO membranes are fibrous and porous, and POHABA nanospheres were embedded in the fibers. Due to the physical barriers and adhesion, PM particles were captured by the PEO/POHABA-467 fiber membrane as shown in Fig. 4b. The fog was deliberately generated from PROTECT 600i™ (Protect A/S Denmark) and were collected in two conical flasks. The two conical