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Highly permeable cellulose acetate nanofibrous composite membranes by freeze-extraction

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ABSTRACT

Ultrafiltration is widely used in waste water treatment and has become more crucial with increasing concerns in the living environment. Here we demonstrate a facile method to prepare 10 nm-diameter cellulose acetate (CA) nanofiber dispersions from very dilute CA solutions via freeze-extraction, and further fabricate nanofibrous composite membranes for ultrafiltration. The nanofibrous composite membranes are fabricated by directly filtering the dispersions on a CA microfiltration membrane (support), on which an ultrathin free-standing nanofibrous layer is formed. This layer, acting as a separation layer, has a uniform porous structure and ultrahigh porosity of up to 71%. The as-prepared membranes present ultrahigh water permeability and high efficient separation performance for ultrafiltration. The membrane with a 458 nm-thick nanofibrous layer has ferritin rejection of 90.7% and water flux of 3540 l m^{-2} h^{-1} bar^{-1} that is almost 10 times greater than that of most commercial membranes. These newly developed CA nanofibrous composite membranes have a great potential application in various separation processes.

1. Introduction

Ultrafiltration is important and widely used in water treatment, food industry and life science, and has become more crucial with increasing concerns in the living environment. However, most commercial membranes have a low porous separation layer and a large flow resistance leading to a small permeation flux [1–3]. Very recently, one-dimensional nanomaterials (e.g. nanofibers, nanowires and nanotubes) have attracted increasing interest and contributed significantly to fabrication of nanofibrous composite membranes [4–7]. Due to their peculiar properties, they impart unique structural characteristics to the membranes, such as high permeability, high porosity, high surface area and interconnected pores [4]. Currently many one-dimensional inorganic materials are used to produce high efficient nanofibrous composite membranes, including carbon nanotubes [7–9], inorganic nanowires [10], carbonaceous nanofibers [6], metal oxide nanofibers [11], and metal hydroxide nanofibers [7,12]. The resulting membranes show a great potential in ultrafiltration. However, most ultrafiltration membranes are prepared from polymers because of their low cost and high processability. Thus, it is highly imperative to develop a facile approach for the fabrication of high efficient ultrafiltration membranes from polymer nanofibers for various separation processes.

Various techniques have been applied to prepare polymer nanofibrous membranes. The electrospinning technique is the most versatile one and has been used to produce nanofibrous membranes with pore sizes usually on the sub-micrometer scale [4,13–15]. The diameters of electrospun nanofibers are generally in the range of micrometer or sub-micrometer. However, ultrafiltration membranes fabricated from ultrafine electrospun nanofibers are now a great challenge [16]. The drawback of electrospun nanofibers lies in their poor diameter control and the difficulty in fabricating ultrathin membrane with a controlled thickness [5]. Alternatives have been explored to produce polymer nanofibers, such as molecular self-assembly, lithography, template synthesis, and interfacial polymerization [17–23]. However, it is difficult to fabricate ultrafiltration membranes by these methods due to their intricate operations and specific outcome of nanofiber. Therefore, the development of facile and versatile pathways of synthesis of polymer nanofibers to fabricate nanofibrous composite membranes for ultrafiltration is an important and interesting task.

In this work, we demonstrate a facile and green approach to fabricate CA nanofibrous composite membranes for ultrafiltration. Briefly, CA nanofiber dispersions were first prepared via the freeze-extraction method and then filtered on a CA microfiltration membrane to form a free-standing nanofibrous layer. Fig. 1a depicts the as-prepared nanofibrous composite membranes with an ultrathin CA nanoporous layer (separation layer) covered on a

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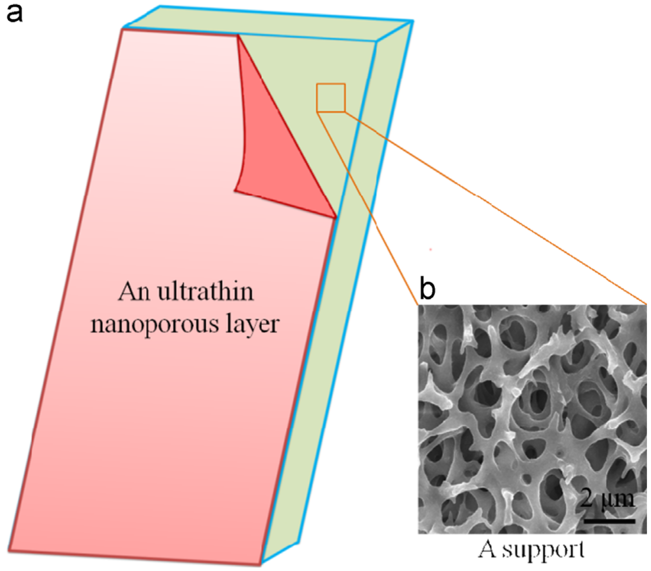

Fig. 1. (a) Schematic structure of CA nanofibrous composite membranes. (b) Top-view SEM image of the CA microfiltration filter with a cut-off of 0.2 μm.

CA macroporous membrane (support, Fig. 1b) with a cut-off of 0.20 μm. CA, the acetate ester of cellulose, is one of the earliest materials used and still finds utility in membrane separation processes due to its outstanding formability, reasonable resistance to degradation by chlorine and low fouling. Membranes made from CA are nowadays used in seawater desalination, water purification, wastewater treatment, concentration of fruit juices, and life science [24]. The as-fabricated nanoporous membranes with a tiny membrane resistance show ultrahigh water flux and good ferritin rejection during ultrafiltration.

2. Experimental

2.1. Materials

CA, with average molecular weight of 30,000 g mol^{-1} and approximately 54.5–56.0% acetic acid bonded, was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). CA membranes, with a cut-off of 0.2 μm and 25 mm in diameter, were purchased from Toyo Roshi Kaisha Ltd. (Japan). Dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), N, N-dimethylacetamide (DMAc), and glacial acetic acid (GAA), of analytical grade, were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 5 nm gold nanoparticle solution and ferritin (from equine spleen) were obtained from British Biocell International and Sigma-Aldrich, respectively.

2.2. Preparation of CA nanofiber dispersions

CA solutions were initially prepared by dissolving CA in each of the solvents (DMAc, DMSO, NMP and GAA) with vigorous stirring at 60 °C for 6 h to obtain homogenous transparent solutions of 0.1 mg ml^{-1} CA. 10 ml of the CA solutions was then directly frozen in liquid nitrogen contained in a 250 ml beaker to form a thick white solid. 90 ml of ethanol (at −40 °C) was then added in the beaker and the contents were then transferred to a refrigerator maintained at about −40 °C for 24 h. The resulting freeze-extracted solution containing 0.01 mg ml^{-1} CA was the expected CA nanofiber dispersion.

2.3. Fabrication of CA nanofibrous composite membranes

A given volume of the as-prepared CA nanofiber dispersions was filtered through a CA microfiltration membrane placed on a glass filter holder (Millipore Co., USA) at a suction vacuum pressure of 80 kPa. The filtration area was 2.27 cm^2. During filtration, the CA nanofibers were freely deposited on the CA membrane to form a free-standing nanoporous layer, resulting in the formation of the CA nanofibrous composite membrane. The thickness of the nanofibrous layer could be easily controlled by regulating the volume of the dispersion filtered.

2.4. Filtration experiments

Filtration was performed using the glass filter holder mentioned above at the suction vacuum pressure of 80 kPa. Pure water flux (J, l m^{-2} h^{-1} bar^{-1}) of the CA nanofibrous composite membranes is measured by filtering 100 ml of water across the membrane, and calculated by

$$J = V/(Atp) \tag{1}$$

where V is the volume of the water filtered (l), A is the effective membrane filtration area (m^2), t is the filtration time (h), and p is the suction pressure across the membrane (bar).

Ferritin and 5 nm gold nanoparticle solutions were used to evaluate the separation performance of the CA nanofibrous composite membranes. 20 ml of 20 μg ml^{-1} ferritin solution was filtered on the fabricated membranes using the glass filter holder at the suction vacuum pressure of 80 kPa. Filtration of 5 nm gold nanoparticles was also conducted in a similar way using an aqueous solution (20 ml) that had been diluted 20 times from the original solution. The feed and the permeate solutions were characterized using an ultraviolet and visible (UV–vis) spectrophotometer (Model UV-1800 series, Shimadzu, Japan). The rejection (R, %) is calculated by

$$R = (1 - C_p/C_f) \times 100\% \tag{2}$$

where C_f and C_p are the concentration of the ferritin or 5 gold nanoparticles in the feed and the permeate, respectively.

2.5. Characterization

Transmission electron microscopy (TEM) (JEM-2100F, 200 kV, JEOL, Japan) was used to observe the CA nanofiber dispersions. A dispersion was initially diluted 10 times using deionized water and then dropped on a copper grid coated with a carbon film and dried in the air to obtain the sample for TEM observation. Morphology of the CA nanofibrous composite membranes was characterized using scanning electron microscopy (SEM, LEO1530, Germany). Before the observation, all the samples were gold plated to prevent charging and improve the membranes' electro conductivity, and the samples for cross-sectional observation were prepared by freeze-fracturing in liquid nitrogen.

3. Results and discussion

3.1. Preparation and characterization of CA nanofiber dispersions

Freeze-extraction used to prepare CA nanofiber dispersions is a feasible technique that has also been used to prepare microporous membranes and highly porous polymer scaffolds. In this method, a high concentration (usually above 5 wt%) polymer solution is frozen, and then immersed in a non-solvent bath at a temperature lower than the freezing point of the polymer solvent, resulting in the formation of porous structures with porosity of up to 80% [25–27].