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Fabrication of TiO_2 nanofiber membranes by a simple dip-coating technique for water treatment

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ABSTRACT

A TiO_2 nanofiber membrane was fabricated by coating TiO_2 nanofibers on a ceramic hollow fiber membrane support using a simple dip-coating technique. Scanning electron microscopy reveals that the TiO_2 nanofibers uniformly cover the entire surface of the membrane, and the anatase crystal phase of TiO_2 is present based on X-ray diffraction spectroscopy data. The TiO_2 nanofiber membrane has a porosity of about 80% and a pure water flux of 1700 L/(m^2·h). Meanwhile, the performance of this TiO_2 nanofiber membrane was evaluated using humic acid (HA) as a test substance, and a high HA removal of 90% is achieved. This approach provides a simple technique for fabricating photocatalytic membranes for water treatment.

1. Introduction

Ceramic membranes have many outstanding properties including high mechanical strength, superior chemical resistance, long service life, low energy consumption, and excellent thermostability, allowing for their use in various applications such as water purification, petrochemical materials separation, and radioactive materials enrichment [1–4]. Since conventional ceramic membranes are only capable of separation, they generally suffer from membrane fouling. Considering that the texture of the functional layer controls the performance of the resultant membrane in terms of flux, coating of a functional layer on the surface of the ceramic membrane has been proposed to reduce membrane fouling [5,6].

TiO_2 is regarded as one of the most promising candidate materials for environmental applications due to its high photocatalytic ability [7–10], relatively low cost [11], remarkable photostability [12], and non-toxicity [13,14]. In particular, TiO_2 has unique self-cleaning behavior which prevents contaminants from adhering to the TiO_2 surface. Because of this attractive self-cleaning behavior, combining TiO_2 on ceramic membrane surfaces to fabricate TiO_2 functional membrane has been demonstrated to alleviate membrane fouling [15–18]. However, conventional TiO_2 functional membrane structures (plate-like, flake-like etc.) currently suffer from low permeability because most of the volume of the TiO_2 layers is occupied by particles rather than by the voids that function as passageways. Consequently, the flux decreases dramatically when the pore sizes are reduced.

Compared with plate-like or flake-like membrane structures, a recent mesh structure formed with nanofibers represents a very effective structure for pressure-driven membrane filtration processes. Such mesh structures have a high membrane flux, as the porosity can exceed 70% of its volume without forming dead-end pores [19]. Therefore, using TiO_2 nanofibers to construct a mesh structure layer on a ceramic membrane is an effective approach for developing anti-fouling membranes. Here, a TiO_2 nanofiber membrane with high flux and excellent photocatalytic performance is fabricated using a simple dip-coating process by coating TiO_2 nanofibers onto ceramic hollow fiber membranes. The influence of the dip-coating duration is investigated, and the photocatalytic activity of the TiO_2 nanofibers membrane is evaluated using humic acid (HA) as a test material. This work provides a new approach for the development of TiO_2 functional membranes and their potential applications in water treatment.

2. Materials and methods

2.1. Chemicals and materials

Ceramic powder ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and polyethersulfone (PESf) were provided by Shanghai Kaidu Industrial Development Co., Ltd., China. 1-methyl-2-pyrrolidinone (NMP) was obtained from Tianjin Fuyu Fine Chemical Co., Ltd., China. Humic acid (HA) was provided by

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MP Biomedicals, Inc (Eschwege, Germany). TiO_2 (P25) was purchased from Evonik-Degussa GmbH, Germany.

2.2. Preparation of TiO_2 nanofibers

The synthesis of our TiO_2 nanofibers is based on a hydrothermal method [20]. In brief, 1 g TiO_2 (P25) was mixed with 60 mL NaOH (10 M) in a polytetrafluoroethylene autoclave. The hydrothermal reaction was carried out at 180 °C for 8, 16, 24 or 36 h. The resulting products were isolated using centrifugation, washed several times with deionized water, and re-dispersed in 100 mL HCl (0.1 M) for approximately 20 min via ultrasonication. Finally, the obtained TiO_2 nanofiber products were washed with deionized water.

2.3. Preparation of ceramic hollow fiber membrane

The substrate of ceramic hollow fiber membrane was fabricated by dry-jet wet-spinning process. Briefly, the ceramic powder was added to a mixture of PESf and solvent NMP in the ratio of 6:1:10 (w/w/w) to create a spinning dope. This mixture was continuously stirred for about 2 h. The spinning solution was then extruded using a tube-in-orifice spinneret to form a hollow fiber. Either spinning dope or pure water was used as the bore fluid at a rate of 25 mL/min or 15 mL/min, respectively. To eliminate the influence of NMP, the as-prepared ceramic hollow fiber membrane was dipped in pure water for 24 h. Finally, the ceramic hollow fiber membrane was calcined at 1200 °C for 2 h.

2.4. Coating TiO_2 nanofibers on ceramic hollow fiber membrane

As shown in Fig. 1, a simple dip-coating technique was used for coating the TiO_2 nanofibers onto the ceramic hollow fiber membrane supports. Briefly, TiO_2 nanofibers (0.5 g) were dispersed in 500 mL deionized water and sonicated for 30 min. The ceramic hollow fiber membrane was dipped into this solution, with one end of the membrane was sealed and the other end connected to a pump (50 r/min). The coating process was maintained for 15 s (TNM 15), 30 s (TNM 30) and 45 s (TNM 45) depending on the desired sample. Finally, the obtained TiO_2 nanofiber membranes were calcined at 500 °C for 2 h. In order to evaluate the photocatalytic performance of the nanofiber structures, TiO_2 membranes were also prepared using TiO_2 nanoparticles instead of TiO_2 nanofibers.

2.5. Characterization

The morphology of the TiO_2 nanofiber membranes was investigated using a scanning electron microscope (SEM; Quanta 200 FEG). The specific surface area of TiO_2 nanofibers was determined by Brunauer—Emmet—Teller method using an automated surface area and pore size analyzer (Quantachrome Autosorb-1 MP). Chemical composition was determined using a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) coupled with an energy dispersive X-ray (EDX) detector. The crystal structure and phase composition were analyzed by X-ray diffraction (XRD) using a diffractometer with Cu Kα radiation (Shimadzu LabX XRD-6000). The optical absorption edge of the membrane sample was recorded by UV–Vis diffuse reflectance spectroscopy (DRS) (UV-2000, Shimadzu, Japan) from 200 to 800 nm.

The porosity of TiO_2 nanofiber membranes was determined by gravimetric method and calculated using the following formula [21]:

$$\varepsilon = \frac{4m_2 - 4m_1 - \pi l \rho d_{inner}^2}{\pi l \rho \left(d_{outer}^2 - d_{inner}^2\right)}.$$

where ε is the porosity of the TiO_2 nanofiber membrane (%); m_1 and m_2 are the mass of dry and wet membrane, respectively; l is the effective length; ρ is the water density; d_{outer} and d_{inner} are the outer and inner diameter of the membrane, respectively.

The permeation flux of the TiO_2 nanofiber membranes was also investigated at an absolute pressure of 100 kPa based on the following equation [22]:

$$J = \frac{V_\mu - V_\theta}{A \times t}$$

where J is the permeation flux; V_μ is the initial volume of the feed solution; V_θ is the volume of the feed solution at time t; A is the membrane surface area. In this work, the permeation flux of the TiO_2 nanofiber hollow membranes was also measured under UV light irradiation at an incident light intensity of 35 mw/cm^2. All measurements were carried out at room temperature.

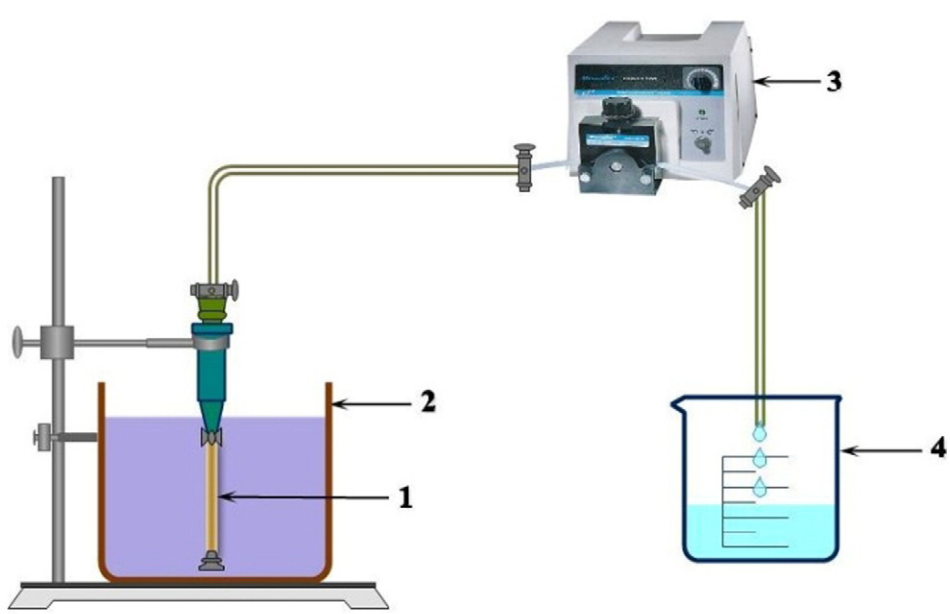

Fig. 1. Schematic diagram of the setup used for the fabrication of TiO_2 nanofiber membranes. (1) ceramic hollow fiber membrane; (2) tank; (3) pump; (4) collector.