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Facile fabrication and characterization of poly(tetrafluoroethylene)@polypyrrole/nano-silver composite membranes with conducting and antibacterial property

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ABSTRACT

Porous poly(tetrafluoroethylene) (PTFE) membranes play an important role in air purification and separation engineering. To achieve the bi-functionality of conducting and antibacterial property, two kinds of poly(tetrafluoroethylene)@ polypyrrole/nano-silver composite membranes have been prepared. One involves hydrophobic polypyrrole/nano-silver composite with hollow capsule nanostructures immobilized on the surface of the PTFE membranes. The other is a type of composite membranes with polypyrrole/nano-silver composite wholly packed on the fibrils of the expand PTFE membrane to form core/shell coaxial cable structures. The structure and morphology of the two kinds of composite membranes have been characterized by FTIR, UV–vis, XRD, TGA and SEM measurements. Possible formation mechanisms of the hollow capsules and the core/shell nanocable structures have been discussed in detail. The antibacterial effects of composite membranes are also briefly investigated.

1. Introduction

As one of the most important dielectric polymers, the expand poly(tetrafluoroethylene) (PTFE) membrane with a microstructure of interconnected continuous fibrils has many unique properties such as good chemical stability, superior thermal resistance, excellent hydrophobicity and dielectric property as well as high mechanical strength [1–3], thus playing an significant role in diversified applications, for instance air filtration, gas/solid separation, cleaning by removing dust, product purification in chemical process and so on. However, such dielectric filter membrane may accumulate electric charges due to the rubbing effect aroused from the materiel contact, leading to explosions, fires or personal injury from shock [4–8]. Earlier work on rendering the PTFE surface conductive involved the coating of PTFE surfaces with thin films of electrically conductive polymers [9]. PTFE possesses low surface energy, which results in surface inertness, and makes the adhesion of any other material difficult. A variety of treatments have been practiced to activate PTFE surfaces to enhance their ability of adhesions, such as chemical etching with sodium naphthalene [10], UV lasers, electron and ion beams irradiation [11,12], plasma modification [13,14], and coating technology [15]. For example, argon plasma pretreated PTFE film was subjected to UV-induced graft polymerization of aniline and its derivatives [16]. However, using a simple strategy without additional plasma/UV irradiation to realize PTFE surface conductive and functional remains a scientific and technical challenge.

On the other hand, it is well known that silver has inherent anti-microbial property and is capable of causing a bacteriostatic (growth inhibition) or a bactericidal (antibacterial) impact [17,18]. Also, silver is very effective in purification systems for disinfecting water or air [19,20]. Recently, the hybrids of silver nanoparticles with amphiphilic hyperbranched macromolecules have been reported as an effective antimicrobial surface coating [21]. To fabricate facilely the novel functional materials combining the conductivity, environmental stability, redox feature and antibacterial property together have been attracting a great deal of interests.

In the present work, for the first time we report a simple strategy to synthesize two kinds of novel composite membranes with bi-functionality of conductivity and antibacterial property. In our case, the composite membranes are based on PTFE, polypyrrole (PPy) and nano-silver (Ag). One involves polypyrrole/nano-silver composite with hollow capsule nanostructures immobilized on the PTFE membranes. The other is a type of composite membranes with polypyrrole/nano-silver composite wholly packed on the fibrils of the expand PTFE membrane to form core/shell coaxial cable structures. The surfaces of poly(tetrafluoroethylene)@polypyrrole/nano-silver is highly hydrophobic with the character of water repellency. Interpretations to the hollow capsules polypyrrole/nano-silver of the

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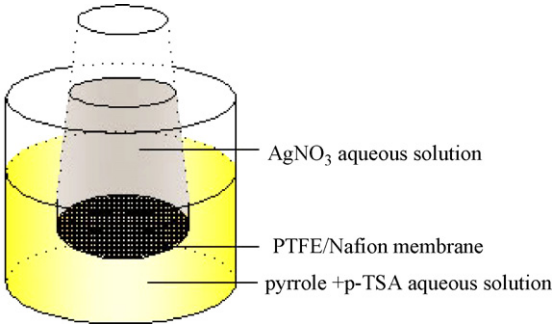

Fig. 1. Schematic illustration of reactor to prepare PTFE@PPy/Ag-I.

composite membranes and a possible formation mechanism for core/shell nanocable structures have also been discussed. The structure and morphology of the two kinds of composite membranes were characterized by FTIR, UV–vis, XRD, TGA and SEM measurements. The antibacterial effects of composite membranes are also investigated.

2. Experimental part

2.1. Materials

Pyrrole (Aldrich) was distilled twice under reduced pressure, stored in refrigerator. p-Toluenesulfonic acid (p-TSA) and silver nitrate ($AgNO_3$) were of AR grade and used without purification. Nafion-DE 520CS (DuPont Co.) was 5 wt% of Nafion diluted in a mixture solvent containing water, propanol, methanol, and unspecified ethers. The structure of Nafion is composed mainly of a PTFE backbone with side-chains containing ether groups and a sulfonic acid unit at its end [22]. PTFE membrane (5 ± 2 μm) was kindly supplied by Sinoma Science & Technology Co., Ltd. (Nanjing, China).

2.2. Preparation of PPy/Ag hollow capsule composite deposited on PTFE membranes (PTFE@PPy/Ag-I)

In a typical procedure, the pristine PTFE membranes was mounted in the plastic frame and then dipped into the Nafion solution for 30 s. These impregnated membranes were dried at 60 °C for 0.5 h and then immersed in 1 M HCl for 24 h.

The preparation was carried out in a system which was separated by the PTFE membrane pretreated with Nafion and wetted in 1 M HCl to two compartments (Fig. 1). The upper compartment comprised 50 ml of 0.05 M silver nitrate aqueous solution and the bottom one contained 50 ml of 0.06 M pyrrole and 0.02 M p-TSA aqueous solution. Pyrrole monomers together with p-TSA and oxidizer solutions (silver nitrate) were allowed to counter-diffuse simultaneously to the PTFE/Nafion membrane. The oxidation polymerization of pyrrole proceeded without agitation for 24 h at room temperature. The polypyrrole/Ag/AgCl nanoparticles deposited on the membrane were converted to hollow polymer capsules by dissolution of the AgCl in sodium hyposulfite or ammonium chloride aqueous solutions. The as-obtained composite membrane was washed with deionized water and dried in a vacuum at 60 °C.

2.3. Preparation of PPy/Ag composite packed on fibrils of the expand PTFE membranes (PTFE@PPy/Ag-II)

The pristine PTFE membranes was mounted in the plastic frame and dipped into the ethanol solution for 30 s. The preparation was carried out in a system which was separated by the PTFE membrane wetted by ethanol to two compartments (Fig. 2). In both the upper and the bottom compartments 50 ml of 0.06 M pyrrole, 0.02 M p-TSA and 0.05 M silver nitrate aqueous solution were added. The reaction was allowed to proceed without agitation for 72 h at room temperature. Finally, the composite membrane was washed with deionized water and dried in a vacuum at 60 °C.

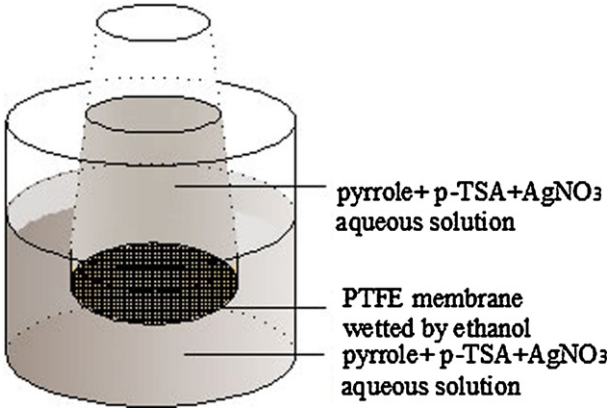

Fig. 2. Schematic illustration of reactor to prepare PTFE@PPy/Ag-II.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker IFS 66/S spectrometer. UV–vis spectra were measured on a UV–vis spectrophotometer (UV-240, Shimadzu, Japan) with air as reference. Scanning electron microscopy (SEM) images were obtained on a HITACHI S-4800. X-ray diffraction (XRD) patterns were measured on a Brucker D8 Advance instrument using Cu Kα radiation. Thermogravimetric analysis (TGA) was run on a Pyris 1 TGA instrument from room temperature to 800 °C at a heating rate of 10 °C/min under air condition. Electrical conductivity measurements were carried out by using a four-point probe method at room temperature. Contact angle (CA) were measured on optical contact angle meter (CAM200) at ambient temperature. Air permeability was detected on YG461H Fully Automatic Air Permeability Tester (Ningbo Textile Instrument Factory). The dielectric constant measurement of samples was carried out at room temperature using a 3522-50 type Hoiki Impedance Analyzer made in Japan, at frequencies ranged from 1 Hz to 10^5 Hz and with an applied voltage of 0.1 V. Ag electrodes with an area of 1 mm × 5 mm were deposited on the film surface before the measurements.

2.5. Anti-microbial test

Antibacterial activity of the synthesized membrane was test on *Escherichia coli* (*E. coli*). The bacterial pre-inoculums cultures were grown 12 h at 37 °C in 5 ml nutrient broth. An amount of 10 μl of the above bacterial suspension (approximately 1×10^8 colony forming units (CFU)/ml) was put into 5 ml lysogeny broth (LB) culture solution and placed horizontally on an orbital shaker platform with 225 rpm and agitated at 37 °C. The membrane samples were cut into 10 mm × 10 mm in size and placed in a microbial liquid suspension subjected to vigorous shaking for all test duration to assure the best contact between bacteria and membranes. A control sample containing the bacterial suspension without the membranes was also tested. The LB culture solution was choosing as blank sample. Growth or killing rates and bacterial concentrations were determined by measuring optical density (OD) at 600 nm for each 2 h. The OD measurement was carried out in triplicate and the values obtained were averaged to give final data.