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Improving protein resistance of α-Al_2O_3 membranes by modification with POEGMA brushes

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ABSTRACT

A kind of protein-resistant ceramic membrane is prepared by grafting poly(oligo (ethylene glycol) methyl ether methacrylate) (POEGMA) brushes onto the surfaces and pore walls of α-Al_2O_3 membrane (AM) by surface-initiated atom-transfer radical polymerization (SI-ATRP). Contact-angle, Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and field-emission scanning electron microscopy (FESEM) were measured to confirm that the surfaces and pore walls of the ceramic porous membranes have been modified by the brushes with this method successfully. The protein interaction behavior with the POEGMA modified membranes (AM-POEGMA) was studied by the model protein of bovine serum albumin (BSA). A protein-resistant mechanism of AM-POEGMA was proposed to describe an interesting phenomenon discovered in the filtration experiment, in which the initial flux filtrating BSA solution is higher than the pure water flux. The fouling of AM-POEGMA was easier to remove than AM for the action of POEGMA brushes, indicated that the ceramic porous membranes modified with POEGMA brushes exhibit excellent protein resistance.

1. Introduction

Membrane technology for the separation and purification of proteins plays a significant role in the dairy, food and beverage industries, and potentially in the biotechnology industry. The increased application of membranes is ascribed to the unique benefits of membrane processes, such as selective transportation, efficient separation, lower energy consumption, no-phase transformation, and no additives [1–4]. However, the adsorption and deposition of proteins on the surfaces and pore walls decreases the permeation flux through the membranes [5,6]. Long-term physical and chemical cleaning, which is necessary to remove the fouling of membranes during the flux recovery process, is detrimental to the performance of the membranes. Thus, reducing membrane fouling due to protein adsorption and deposition is the key to improving the utilization efficiency of membranes. For the permeation of protein, the surface properties, the solution conditions and operating parameters are the main influencing parameters for the extent of membrane fouling [3,7–11]. Especially, due to membrane surfaces and pore walls that contact protein solutions directly, a large number of research works have been carried out in modifying the membrane. Of all modified methods, grafting the surfaces and pore walls with a protein-resistant polymer is an effective method for the preparation of membranes that reduce fouling [4,12–15].

Poly(ethylene glycol) (PEG) is the most commonly used polymer in the fabrication of protein-resistant materials. PEG (molecular weight ≥ 10,000 Da) can significantly prevent protein adsorption because of its minimum interfacial free energy, hydrophilicity, high surface mobility, high steric stability, and unique molecular conformation in water [16,17]. Moreover, PEG and its derivatives have found extensive applications in the food and biochemical industries because of their outstanding properties, which include nontoxicity, nonimmunogenesis, nonantigenicity and excellent biocompatibility [18]. As a PEG derivative, poly(oligo (ethylene glycol) methyl ether methacrylate) (POEGMA) brushes perform similarly to PEG. In addition, the brush-like structure of POEGMA can increase the resistance of materials to protein adsorption. The primary advantage of this structure lies in its polymer brushes improving the density of functional groups on a material's surface by extending the two-dimensional distribution to a three-dimensional distribution [19]. Previous studies have shown that surfaces modified with POEGMA (thickness > 10 nm) can significantly reduce protein adsorption [20]. "Zero adsorption" and "femtomolar sensitivity" materials have been reported by researchers who grafted surfaces with POEGMA brushes [20,21].

In previous studies, polysulfone (PSF) and poly(vinylidene fluoride) (PVDF) membranes have been modified with POEGMA brushes [22–25]. For the brushes are hydrophilic, the surface property of the organic membranes become from hydrophobicity to

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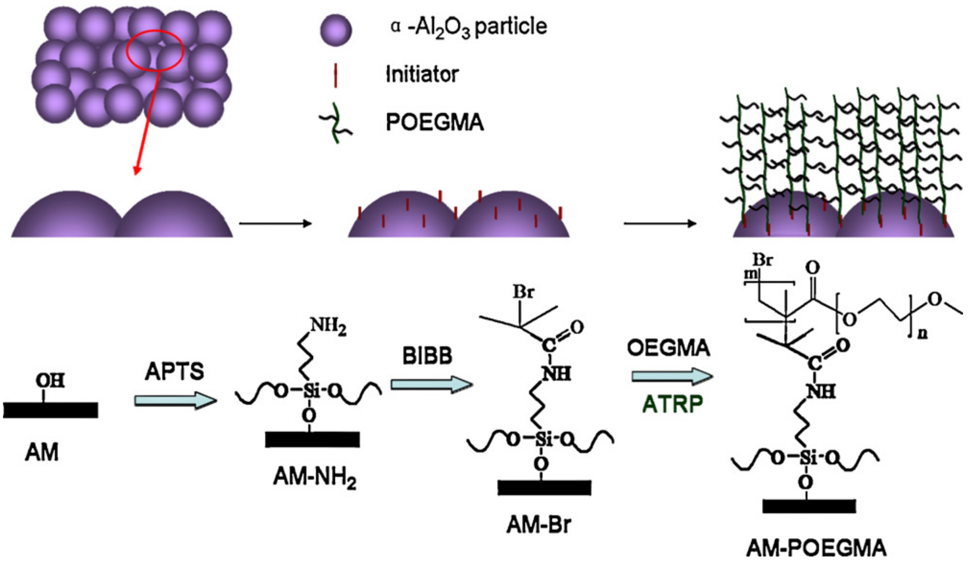

Fig. 1. Schematic representation for grafting α-Al_2O_3 membranes with POEGMA brushes via SI-ATRP.

hydrophilicity after modification. Thus, both the water flux and protein resistance of the modified membranes improved for the increase of membrane hydrophilicity. Unlike organic membrane, the surface of porous ceramic membrane which prepared by metallic oxide is hydrophilic. Therefore, the interface of POEGMA brushes which grafted onto ceramic membranes are different from similarly modified organic membranes. The following sections will successively discuss the fabrication of α-Al_2O_3 membranes modified by the grafting of POGEMA brushes onto the surfaces and pore walls by surface-initiated atom-transfer radical polymerization (SI-ATRP) [19,26,27] as shown in Fig. 1. The mechanism of protein resistance and the fouling process of the modified membranes (with an original pore size of 0.2 μm) were investigated by filtering bovine serum albumin (BSA) solution. The ability of the modified membranes to resist proteins was characterized by flux recovery measurements.

2. Experimental

2.1. Materials

The α-Al_2O_3 plate membranes (AM, 28.5-mm diameter, 2.2-mm thickness, 0.1-μm pore size) were prepared from α-Al_2O_3 powder (average size: 0.5 μm). The α-Al_2O_3 tube membranes (AM, 12-mm outer diameter, 2-mm wall thickness, 85-mm length and 0.2-μm pore size) were synthesized in our lab. (3-Aminopropyl) triethoxysilane (99%, APTS), 2-bromoisobutyryl bromide (98%, BIBB) and 2,2′-bipyridine (99%), Cu^IBr (98%) and $Cu^{II}Br_2$ (99.999%) were used as received from Sigma–Aldrich. OEGMA (average Mn ca. 475) was eluted through a neutral alumina column to remove the inhibitors before use. Solvents (analytical reagent (AR) grade), i.e., ethanol, methanol and dichloromethane, were purchased from Yasheng Chemical Co. Ltd., China. Triethylamine (AR grade, Kaidi Chemical Reagent Co. Ltd., China) and dichloromethane were distilled from calcium hydride before use. BSA (Huixing Biochemistry Reagent Co. Ltd., China) was used in the permeation experiment. Sodium hydroxide (NaOH, AR grade) was used without further purification. Deionized water with a conductivity of 11 μS/cm was obtained from a reverse osmosis system.

2.2. Modification α-Al_2O_3 membranes with POEGMA brushes

The α-Al_2O_3 plate membranes (AM) were boiled in deionized water for 1 h and then dried at 70 °C for 6 h. After drying, the cleaned membranes were immersed in APTS (0.07 mol/L) in ethanol at 35 °C for 10 h. The membranes were then rinsed with ethanol and dried at 110 °C for 4 h. Then, the APTS-functionalized membranes ($AM-NH_2$) were immersed in a solution of BIBB (0.05 mol/L) and triethylamine (0.05 mol/L) in dichloromethane under N_2 atmosphere at room temperature for 2 h, rinsed with dichloromethane and dried under N_2 atmosphere. Finally, the initiator-functionalized membranes (AM-Br) were immersed in a degassed solution of Cu^IBr (7 mmol/L), $Cu^{II}Br_2$ (0.7 mmol/L), 2,2′-bipyridine (15 mmol/L) or OEGMA (214 mmol/L) in methanol/deionized water (50/50 vol.%) under N_2 atmosphere at 30 °C for 3 h. The membranes modified with POEGMA brushes (AM-POEGMA) were rinsed with deionized water overnight and then dried at 75 °C.

The modification of the tube membranes was carried out in steps identical to those for the plate membranes. The graft polymerization time of OEGMA was 3.5 h.

2.3. Characterization of membranes

The morphology images of the unmodified and modified membranes were observed by field-emission scanning electron microscopy (FESEM, HITACHI S-4800) under standard high-vacuum conditions after the membranes were coated with gold powder by a vacuum electric sputter coater (Bal-Tec SCD005). The variation of the groups on membranes was indicated by Fourier-transform infrared spectroscopy (FTIR, Nicolet AVATAR 360). The thermal stability of the unmodified and modified membranes was investigated using thermogravimetric analysis (TGA, Netzsch STA449F3) at a heating rate of 5 °C/min up to 800 °C in atmosphere. The dynamic contact-angle of the membranes was determined using a DropMeter A-100P contact-angle system (MAIST Vision Inspection & Measurement Co. Ltd., China) in sessile drop mode by a video camera recording at 10 frames per second.

2.4. Analysis of membrane properties

A cross-flow filtration system was used to characterize the performance of the tube membranes at 20 °C under a transmembrane pressure of 0.1 MPa. Permeation flux of the membranes was calculated by the following equation:

$$J = \frac{V}{A\Delta t}, \quad (1)$$