Separation and Purification Technology 192 (2018) 230–239

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Antifouling polyimide membrane with grafted silver nanoparticles and zwitterion

Dong Yan Zhang[a,b], Qi Hao[b], Jie Liu[a], Yu Sheng Shi[a], Jun Zhu[a,*], Li Su[d], Yan Wang[b,c,*]

[a] State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, China
[b] Key Laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Wuhan 430074, China
[c] Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science & Technology, Wuhan 430074, China
[d] Key Laboratory of Molecular Biophysics of the Ministry of Education, College of Life Science and Technology, Huazhong University of Science and Technology,1037 Luoyu Road, Wuhan 430074, China

ARTICLE INFO

Keywords:
Polyimide membrane
Surface modification
Antifouling
Silver nanoparticles
Zwitterion

ABSTRACT

In order to improve the antibacterial and antifouling properties of polyimide (PI) membrane, both silver nanoparticles (AgNPs) and zwitterionic sulfobetaine methacrylate (SBMA) are grafted onto PI membrane surface via a two–step modification route. The reaction mechanism involved, as well as changes in the membrane morphology and surface properties are investigated via various characterization techniques. The antibacterial performance is assessed by the zones of inhibition and bacterial suspension immersion tests. The antifouling property of the modified membrane is evaluated via the filtration test using the bovine serum albumin (BSA) and dodecyl trimethyl ammonium bromide (DTAB) aqueous feed solutions. The results show that, the modified PI membrane exhibits significantly improved antibacterial and antifouling performances simultaneously.

1. Introduction

Water scarcity has been recognized as one of the most challenging and common concerns affecting the human survival and economic development. Membrane processes, as leading techniques for the water treatment and desalination, have been widely used for their unique advantages of high separation performance, energy efficiency, environmental friendliness, and wide pH and temperature application ranges [1]. As the key factor on the membrane performance, an ideal membrane should own the high water permeability, high selectivity, good stabilities in various harsh environments and superior antifouling properties. Among various polymeric membrane materials, polyvinylidene fluoride (PVDF), poly (ether sulfone) (PES), polypropylene (PP), polysulfone (PSF), etc. are commonly used as separation membranes for water treatment for their low cost and easy availability [2,3]. However, these materials generally suffer from poor thermal resistance and weak mechanical stability, and may not be able to withstand the harsh processing process or application environment in industries. Alternatively, polyimide (PI) with extraordinary thermal stability, excellent mechanical strength and chemical stability may be a good candidate as the membrane material, and has received more and more attention in various membrane separation fields, including gas separation [4,5], pervaporation [6,7], nanofiltration [8,9], etc.

However, for almost all water treatment membranes, the membrane fouling has always been an unavoidable obstacle in practical applications, causing a decline in the membrane performance and the service life, and increasing the maintenance and operation costs. It is generally caused by the deposition and growth of foulants such as organics, inorganic, colloids, microbial contaminants, etc. on the membrane surface. Various chemical or physical modification routes have therefore been developed to investigate and control the membrane fouling [10]. Among them, surface grafting has been extensively studied by scientists to improve the membrane antifouling performance for its wide applicability, high efficiency and good durability [11].

Various materials with superior hydrophilicity, high charge capacity, or biocidal properties have been grafted onto the membrane surface in order to improve the membrane antifouling performance [12]. In general, a hydrophilic membrane surface is preferred since a bounded water layer can form on the hydrophilic membrane surface and exhibit exclusion and size exclusion for foulants. Various

* Corresponding authors at: State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, China (J. Zhu); Key Laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Wuhan 430074, China (Y. Wang).

E-mail addresses: zhujun@hust.edu.cn (J. Zhu), wangyan@hust.edu.cn (Y. Wang).

http://dx.doi.org/10.1016/j.seppur.2017.10.018
Received 22 February 2017; Received in revised form 15 September 2017; Accepted 10 October 2017
Available online 13 October 2017
1383-5866/

Nomenclature

Abbreviations

NMP	1-methyl-2-pyrrolidone
BSA	bovine serum albumin
PBS	phosphate buffer solution
DTAB	dodecyl trimethyl ammonium bromide
LYS	lysozyme
AgNPs	silver nanoparticles
PEI	polyethyleneimine
SBMA	sulfobetaine methacrylate
BP	benzophenone
PEG	poly (ethylene glycol)
FITC	fluorescein isothiocyanate
FTIR	Fourier transform infra-red analysis
SEM	scanning electron microscopy
WCA	water contact angle
EDX	energy-dispersive X-ray
TGA	thermogravimetric analysis
MF	microfiltration
UF	ultrafiltration
NF	nanofiltration
PSF	polysulfone
PES	poly (ether sulfone)
E. coli	*Escherichia coli*
S. aureus	*Staphylococcus aureus*
LB	Luria-bertani
PI	polyimide or polyimide membrane
A	effective membrane area
m	mass of the permeated water
Δt	permeation time
J_w (initial)	initial flux of the pure water
J_w (time-x)	flux at the time x
C	BSA concentration in the membrane washing solution
C_{PI}	BSA concentration of virgin PI membrane washing solution

hydrophilic materials have been widely employed to improve the membrane hydrophilicity, including poly (ethylene glycol) (PEG), polyvinyl pyrrolidone (PVP), graphene oxide (GO), silica nanoparticles, zwitterions and so on. Among them, the zwitterionic sulfobetaine methacrylate (SBMA) with both cationic and anionic groups in the molecular structure is a promising superhydrophilic material [13–15]. Contributed by the electrostatic attraction and the hydrogen bond with water molecules, SBMA has strong hydration capacity and can form a "free water" hydration layer surrounding it, resulting in a strong exclusion and good resistance to foulants [16].

In addition, silver has also long been reported as an effective biocidal agent and extensively employed for the fabrication of antifouling membranes because of its strong inhibitory and biocidal performance against various microorganisms and low toxicity toward mammalian cells for long-term applications. It is able to interact with thiol groups (S–H) in the cysteine of bacterium cells to form S–Ag complexes, therefore killing the bacteria effectively [17,18]. Silver nanoparticles (AgNPs), as controllable sources of Ag ions, own more lasting effect than Ag ions. They can be incorporated into membranes by surface grafting, physical blending, surface coating, and so on. However, due to

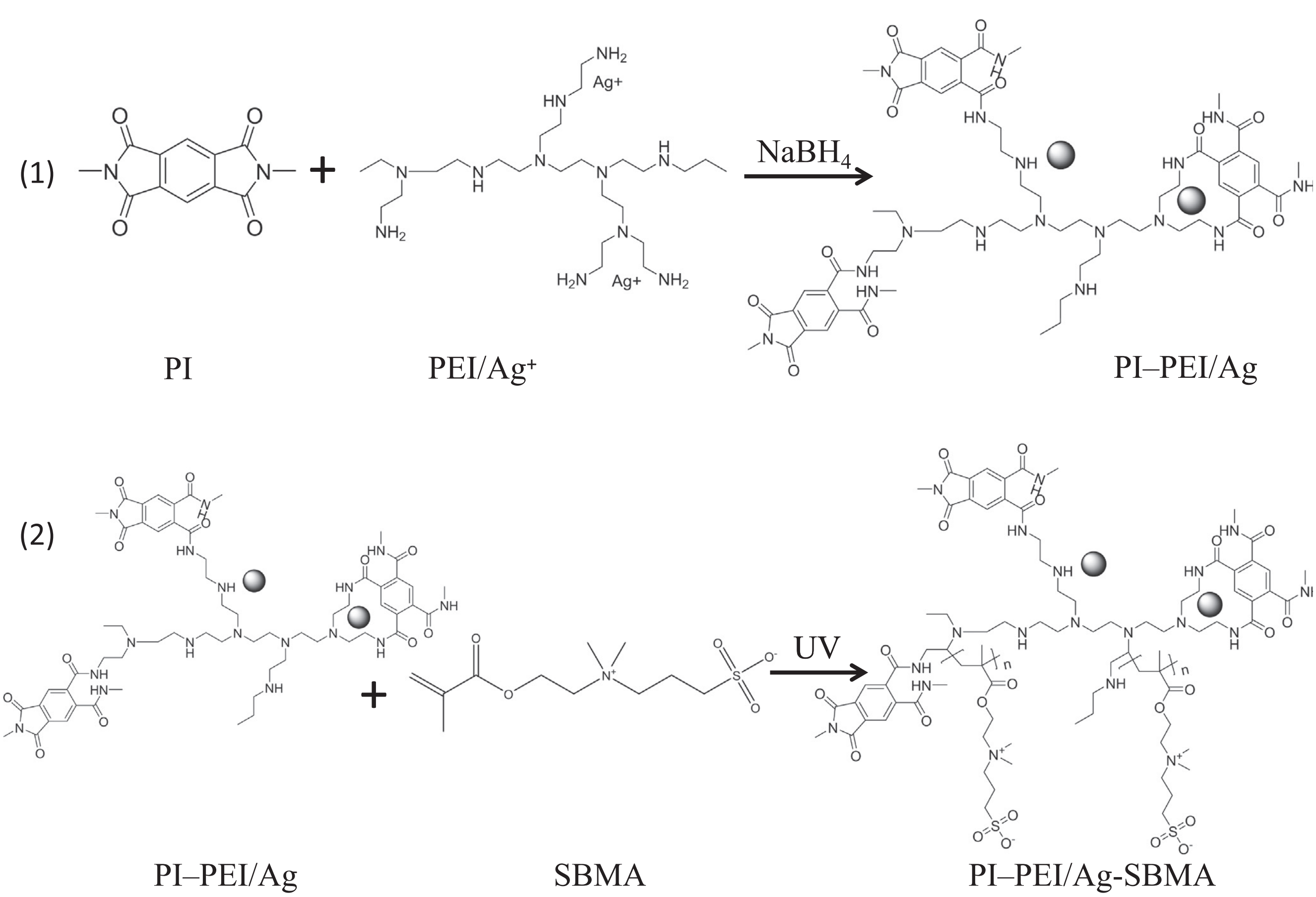

Fig. 1. Schematic diagram of modification process of PI–PEI/Ag–SBMA membrane.