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Synthesis and characterization of novel antibacterial silver nanocomposite nanofiltration and forward osmosis membranes based on layer-by-layer assembly

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ABSTRACT

Using layer-by-layer (LbL) assembly method, we fabricated novel silver nanocomposite LbL-Ag nanofiltration (NF) and forward osmosis (FO) membranes. The incorporation of silver nanoparticles (AgNPs) in the membranes did not adversely affect the membrane separation performance in NF and FO processes at low AgNPs incorporation levels (0.22–1.19 wt.% as silver). The FO performance of the xLbL-Ag membranes was better than or comparable to most NF-like FO membranes reported in the literature. In addition, the silver nanocomposite membranes exhibited excellent antibacterial properties against both Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli*. Our results showed that the performances of the silver nanocomposite membranes are highly dependent on silver incorporation in the membranes, which could be controlled by using different membrane synthesis routines and doping of AgNPs. To the best knowledge of the authors, this is the first study on fabrication and characterization of novel antibacterial silver nanocomposite NF and FO membranes through LbL assembly approach.

1. Introduction

The versatile structures fabricated by layer-by-layer (LbL) assembly are very promising for many potential applications (Jiang and Tsukruk, 2006). In LbL assembly, the membrane selective layer can be formed by depositing oppositely charged polyelectrolytes in an alternate sequence on a substrate via electrostatic interactions and van der Waals forces (Hammond, 1999). As an important membrane fabrication technology, LbL assembly method has attracted increasing attention and been successfully used in synthesizing high-performance nanofiltration (NF) (Malaisamy and Bruening, 2005; Ouyang et al., 2008) and NF-like forward osmosis (FO) membranes (Saren et al., 2011; Qi et al., 2012). LbL NF membranes are applicable to various applications (Eriksson, 1988) by offering several advantages such as high water flux, low operation pressure, less energy consumption, and low operation and maintenance costs (Hilal et al., 2004). Meanwhile, NF-like FO membranes fabricated based on LbL assembly (Saren et al., 2011; Liu et al., 2012) can also obtain higher water

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permeability and expanded applications compared with those RO-like ones (Wang et al., 2007; Tang et al., 2009; Geise et al., 2011; Setiawan et al., 2011; Wei et al., 2011a). Moreover, the NF-like LbL FO membranes have high thermal stability, good solvent resistance, and etc. (Hammond, 1999; Bertrand et al., 2000; Qiu et al., 2011). They may show great promise in wastewater treatment (such as biomass concentrating, and sludge dewatering) and food processing with a range of potential benefits (Cath et al., 2006; Zhao et al., 2012). Despite above advantages and potential applications, membrane fouling, especially biofouling, remains an obstacle in NF membrane and FO membrane operations (Ridgway et al., 1985; Flemming, 1997; Hong and Elimelech, 1997; Vrijenhoek et al., 2001; Xu et al., 2006; Herzberg et al., 2009; Gao et al., 2010; Wei et al., 2013). To reduce membrane biofouling, fabrication of membranes containing biocides or antibacterial materials has attained great attention (Diagne et al., 2012; Zhang et al., 2012).

Silver nanoparticles (AgNPs) are one of the most extensively studied biocides, which are effective against various aquatic microorganisms including bacteria, fungi, algae, and etc. (Sondi and Salopek-Sondi, 2004; Li et al., 2008; Choi et al., 2010). They may affect the cell integrity and metabolism by direct interaction with cell membranes, releasing dissolved silver species, and/or generating reactive oxygen species (ROS) (Klaine et al., 2008; Jin et al., 2010; Marambio-Jones and Hoek, 2010). AgNPs have been incorporated into nanocomposite microfiltration (MF) (Gunawan et al., 2011; Diagne et al., 2012), ultrafiltration (UF) (Taurozzi et al., 2008; Zodrow et al., 2009; Huang et al., 2012), NF (Lee et al., 2007) and reverse osmosis (RO) (Yang et al., 2009) membranes via various methods including membrane surface modification (Diagne et al., 2012), phase-inversion (Lee et al., 2007; Taurozzi et al., 2008; Zodrow et al., 2009; Huang et al., 2012) and interfacial polymerization (Yang et al., 2009). Compared to the existing method, LbL assembly is a highly versatile membrane fabrication method. The layered structure can potentially allow the incorporation of AgNPs with great flexibility in controlling the loading conditions. Nevertheless, LbL-Ag nanocomposite membranes with antibacterial properties have not been reported for NF and FO preparation.

The objectives of the current study were: 1) to synthesize novel antibacterial nanocomposite NF and FO membranes using LbL assembly method; 2) to characterize membrane surface properties and performance of the membranes under NF and FO conditions, and 3) to evaluate their antibacterial activity against Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli*. Influences of different AgNPs doping routines on membrane performances were also systematically investigated. To the best of our knowledge, this is the first study reporting the synthesis and characterization of LbL-assembly-based silver nanocomposite NF and FO membranes with antibacterial properties.

2. Materials and methods

2.1. Chemicals and solution chemistry

Polyacrylonitrile (PAN, weight-averaged molecular weight $M_w \approx 150{,}000$, Sigma–Aldrich) with additional lithium chloride (Sinopharm) as pore former were dissolved in the solvent N,N-dimethylformamide (DMF, $\geq$ 99.8%, Sigma–Aldrich) for membrane substrate fabrication. Alkali solution prepared by sodium hydroxide (Sigma–Aldrich) was used for post-treatment of PAN membrane substrate to introduce negative charges and enhance surface hydrophilicity. Polycation poly(allylamine hydrochloride) (PAH, $M_w \approx 120{,}000$–$200{,}000$, Sigma–Aldrich) and polyanion poly(sodium 4-styrene-sulfonate) (PSS, $M_w \approx 70{,}000$, 30 wt.% in H_2O, Sigma–Aldrich) were used for LbL assembly. Ionic strength of polyelectrolyte solutions was adjusted using sodium chloride (Merck). Commercial AgNPs (~100 nm, 99.5% trace metals basis, Sigma–Aldrich) were suspended in polyelectrolyte solutions or Milli-Q water (Millipore Integral 10 water purification system; Singapore) and incorporated in membrane selective layers via LbL assembly. Glutaraldehyde (GA, 25% in water, Sigma–Aldrich) was used for crosslinking of membrane selective layers. Magnesium chloride (Merck) was used to determine membrane intrinsic separation properties and FO performance. Live/Dead Baclight bacterial viability kit (Molecular Probes) was used to determine the percentage of bacteria with compromised cell membranes. Unless otherwise specified, all reagents and solutions were prepared using chemicals of analytical grade and Milli-Q water.

2.2. Synthesis of Nanocomposite NF and FO membranes via LbL assembly

The detailed procedures of PAN substrate preparation, post treatment, LbL assembly and crosslinking have been reported elsewhere (Qiu et al., 2011; Saren et al., 2011; Qi et al., 2012). Briefly, top surface of substrates was firstly soaked with 1 g/L positively charged PAH solutions and then with 1 g/L negatively charged PSS solution for 30 min. After each soaking step, the substrate surfaces were rinsed with Milli-Q for 5 min to remove excess polyelectrolytes. Specifically, for LbL process of nanocomposite membranes, controlled amount of AgNPs (0.01 wt.% unless otherwise specified, see Supporting information S1) was added in PSS solution, Milli-Q water, or PAH solution respectively after ultrasonicated (Ultrasonic Bath S450H, 50/60 Hz, 2000 W, Fisher Scientific Pte. Ltd.; Singapore) for 30 min at room temperature (23 $\pm$ 1 °C). The AgNPs suspensions were continuously stirred during LbL process. In our current study, 2.5 PAH/PSS bilayers (i.e., twice PAH/PSS coating procedures with an additional PAH coating on the outermost layer) was adopted based on previous optimization results (Qi et al., 2012). The membranes were crosslinked by immersing them in 0.1 wt.% GA solution at room temperature (23 $\pm$ 1 °C) for 2 h followed by Milli-Q water washing according to our previously published procedures (Qiu et al., 2011) to prepare crosslinked LbL (xLbL) membranes. The AgNPs-free membrane was labeled as xLbL2.5. Silver nanocomposite membranes were labeled as xLbL2.5-Ag(XXXN), where XXX indicates the solution incorporating AgNPs and N indicates the layer numbers containing them (i.e. xLbL2.5-Ag(PSS1) means Ag being incorporated into PSS solution and coated only once). The detailed designation and compositions of nanocomposite membranes can refer to Table 1.