



Full Length Article

Facile and efficient *in situ* synthesis of silver nanoparticles on diverse filtration membrane surfaces for antimicrobial performance



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ABSTRACT

Membrane biofouling remains a major limiting factor for the membrane-based water purification technology. The development of antibacterial membrane surfaces is very important for membrane biofouling mitigation. In this study, we developed a one-pot method of synthesizing silver nanoparticles (Ag NPs) and immobilizing them onto membranes via simply soaking the membranes in a mixture solution of silver nitrate, poly (ethylene glycol) methyl ether thiol (mPEG-SH) and dopamine. Results illustrate that mPEG-SH works as a ligand to slow down the reduction process of silver ions by dopamine for the synthesis of Ag NPs in a controllable manner and also the prevention of Ag NPs aggregation in solution. Moreover, the Ag NPs could be *in situ* immobilized onto polysulfone ultrafiltration membrane, glass fiber membrane and stainless steel, regardless of their surface properties, but the size of Ag NPs was affected by the substrates. In addition, the Ag NPs immobilization on the polysulfone ultrafiltration membranes increased the bovine serum albumin rejection rate of membrane by 16%, but decreased membrane permeability by 14% compared to that of the pristine membranes. The Ag NPs containing membranes exhibited outstanding antibacterial properties with more than 90% antibacterial efficiency against both Gram-negative bacteria *Escherichia coli* and Gram-positive bacteria *Staphylococcus aureus*. During the filtration test, the silver release from the Ag NPs containing polysulfone ultrafiltration membranes was very slow and the total accumulation of silver ions released from the membranes was only 7% of its initial Ag NPs loading after 24 h filtration operation. The silver ion concentration in the permeate water was 0.35 ± 0.16 ppb, far below the maximal contaminant limit of silver ions in drinking water with no risk for the application of Ag NPs incorporated membranes to treat water. Our work provides a facile and universal approach of synthesizing and simultaneously immobilizing Ag NPs onto diverse membranes for antibacterial properties.

1. Introduction

Membrane-based separation technology has become one of the most effective and efficient technologies for water purification and wastewater treatment [1,2]. However, membrane biofouling remains a major limiting factor for their widespread application [3–5]. Membrane biofouling involving the attachment of microorganisms on membrane surfaces, their growth and development into biofilm significantly decreases the separation performance of membrane and shortens the membrane life time [6]. Importantly, the biofilm and produced extracellular polymeric substances (EPS) are mainly responsible for the membrane water flux decline since it strongly binds on the membrane surfaces to block membrane pores and increase water transport

resistance [7,8]. Therefore, antibacterial surface modification of filtration membrane is urgently required to suppress biofilm formation on membrane surface.

The incorporation of biocides on membrane surfaces has been proved as an effective approach for antibacterial surface modification and membrane biofouling mitigation since biocides can inactivate bacteria, decrease EPS production and prevent biofilm formation [9]. The incorporated effective biocides on membrane surfaces include metal-based nanoparticles (e.g., silver nanoparticles (Ag NPs) and titanium dioxide), cationic polymers and other nanomaterials such as graphene oxide (GO) and carbon nanotubes (CNTs) [9–14]. Particularly, Ag NPs has been widely used as an effective broad-spectrum biocide to functionalize filtration membrane surfaces for biofouling

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mitigation [15–17]. The antibacterial mechanism of Ag NPs, as reported in literatures, is the release of silver ions that can induce cell membrane damage, promote generation of reactive oxygen species (ROS) and disrupt ATP production and DNA replication, ultimately causing the death of bacteria [18–20]. The release and diffusion of silver ions from Ag NPs is a key to prevent the development and growth of biofilm on membrane surfaces since the bacteria in the water solution is inevitably deposited on the membrane surface under the filtration conditions but silver ions can diffuse across the top surface of biofilm to kill the deposited bacteria [21]. In contrast, the biocides with no diffusion capability have a limited membrane biofouling mitigation performance since they cannot effectively kill the deposited and accumulated bacteria on the top surface of biofilm and thus could not efficiently prevent the biofilm growth [22].

Up to date, a variety of methods have been developed to immobilize Ag NPs onto membrane surfaces including blending, depositing, coating and chemical binding [14,23–30]. Liu et al. had developed a method for loading Ag NPs on the alkaline treated polyacrylonitrile membranes via *in situ* reduction of silver ions to form Ag NPs on membrane surface [27]. This approach is simple, but the incorporated Ag NPs may easily leach from the membranes over time under the cross-flow condition due to the weak interaction between membrane and Ag NPs. The incorporated Ag NPs via chemical binding exhibit excellent stability. For example, Yin et al. had developed anti-fouling thin-film composite membranes by grafting Ag NPs onto the polyamide surface using cysteamine as a bridging agent [31]. However, this approach of Ag NPs immobilization is highly dependent on the membrane surface properties, requiring complicated and time-consuming surface treatments. Recently, a mussel-inspired strategy has been developed as a universal and applicable approach for immobilizing Ag NPs onto various substrates. Polydopamine (PDA) from the oxidative self-polymerization of dopamine (DOPA) can tightly adhere to most of the substrate surfaces [32]. Furthermore, PDA coatings can serve as a versatile platform for secondary surface functionalization thanks to its catechol and amine groups [33]. The catechol groups of PDA have been demonstrated to reduce silver ions to form well-dispersed Ag NPs on the substrate surfaces. Several research groups have successfully synthesized Ag NPs *in situ* on membrane surfaces via the PDA deposition and the Ag NPs generation, achieving antibiofouling performances [16,34,35]. However, this method of immobilizing Ag NPs through the PDA coating requires two steps including the slow polymerization of dopamine on the substrate surface, and the subsequential generation of Ag NPs upon incubation with silver salt solution, which is a long time process limiting its practical applications on a large scale. Therefore, it remains a tremendous challenge to develop a facile and universal strategy for Ag NPs immobilization on various filtration membranes.

Herein, for the first time, we report a one-step facile and universal method of synthesizing Ag NPs and *in situ* immobilizing them onto filtration membranes upon simply soaking in a mixture solution of silver nitrate, poly (ethylene glycol) methyl ether thiol (mPEG-SH) and DOPA. Polysulfone ultrafiltration membrane, glass fiber membrane and stainless steel were selected as representative organic, inorganic, and metal substrates, respectively, and Ag NPs were *in situ* immobilized on their surfaces. The impact of Ag NPs immobilization on membrane filtration properties was investigated using the polysulfone ultrafiltration membrane as a model, and the silver ions leaching from the polysulfone membrane surface was measured during the filtration measurements. Importantly, the antibacterial properties of Ag NPs containing membranes were investigated using the diffusion inhibition zone (DIZ) method, the colony forming unit (CFU) method, and the live/dead assay. Gram-negative *E. coli* and Gram-positive *S. aureus* were selected as model strains.

2. Materials and methods

2.1. Materials

Dopamine (DOPA), polysulfone (PSF, M_n : 22,000 Da), poly (ethylene glycol) methyl ether thiol (mPEG-SH, M_n : 1000), bovine serum albumin (BSA, M_n : 67,000 Da) and propidium iodide (PI) stain were purchased from Sigma Aldrich (St. Louis, MO, USA). SYTO[®]9 green fluorescent nucleic acid stain was obtained from Invitrogen (Eugene, Oregon, USA). Silver nitrate ($AgNO_3$, analytical purity) was received from Sinopharm Chemical Reagent Beijing Co., Ltd, China. *Escherichia coli* (*E. coli*, DH5 α) was purchased from Beijing Dingguo Changsheng Biotechnology Co., Ltd., China. *Staphylococcus aureus* (*S. aureus*, CICC 10201) was obtained from China Center of Industrial Culture Collection.

Polysulfone ultrafiltration (UF) membrane was fabricated by non-solvent induced phase separation method following the reported protocol [36]. The glass fiber membrane with 0.7 μm average pore size and 420 μm thickness was purchased from GE Healthcare (GE, NJ, USA). The commercial stainless steel (ZR-030, 400 mesh, 30 μm wire diameter) was supplied from Zhongrui wire mesh industry Co., Ltd, China.

2.2. One-step synthesis and immobilization of Ag NPs on filtration membranes

Ag NPs were synthesized using DOPA as a reducing agent and mPEG-SH as a stabilizing agent. A typical procedure is as follows: 10 mg of mPEG-SH was dissolved in 100 mL 20 mM $AgNO_3$ aqueous solution and incubated for 10 min open to air at room temperature under 60 rpm shaking in a shaker (Jintan Science Analysis Instrument Co., Ltd., China). Then, 2 mL of 0.1 g mL⁻¹ DOPA aqueous solution was added dropwise into the $AgNO_3$ solution to reduce silver ions and the mixture solution was incubated for two hours. The formation and growth of Ag NPs was monitored using a UV-visible spectrophotometer (UV-Vis, TU-1810, Persee, China) with a scan range of 200–800 nm. Ag NPs were collected through 20 min centrifugation at 140,000 rpm, washed three times with deionized water, vacuum dried and finally stored at 4 °C. In order to determine the roles of $AgNO_3$, DOPA and mPEG-SH in the formation process of Ag NPs, three mixture solutions without $AgNO_3$, or DOPA, or mPEG-SH, were used as negative controls respectively, shown in Table S1.

Synthesis and immobilization of Ag NPs on membranes was performed via a simple dip-coating method. PSF UF membrane, glass fiber membrane and stainless steel were used as model substrates. Briefly, 10 mg of mPEG-SH was dissolved in 100 mL 20 mM $AgNO_3$ aqueous solution and then the membrane coupons were immersed in the solution and incubated for 10 min open to air at room temperature under 60 rpm shaking. After that, 2 mL of 0.1 g mL⁻¹ DOPA aqueous solution was added dropwise into the mixture solution. 2 h later, the membrane coupons were rinsed with deionized water three times, dried at ambient conditions and stored in a light-proof dark chamber for further characterization.

2.3. Characterization

The morphologies of Ag NPs and Ag NPs modified membranes were observed using a scanning electron microscope (SEM, S-4800, Hitachi, Japan) and a transmission electron microscope (TEM, H7650, Hitachi, Japan). The elemental compositions of Ag NPs were characterized using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi, Thermo Fisher Scientific, USA) with monochromatic Al-K α X-ray source ($h\nu = 1486.6$ eV). All binding energies were referenced to that of the neutral C 1s hydrocarbon peak at 284.6 eV. Survey spectra over 0–1200 eV were obtained with a step size of 1 eV. The average hydrodynamic diameter distribution of nanoparticles was measured using a Zetasizer Nano ZS dynamic light scattering (DLS) system (ZS90,

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