



Development of ultrafiltration membrane by stacking of silver nanoparticles stabilized with oppositely charged polyelectrolytes



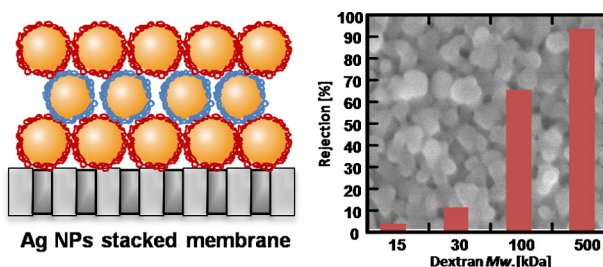
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HIGHLIGHTS

- Silver nanoparticles were prepared using polyelectrolytes as stabilizing agents.
- The nanoparticles were stacked on a support membrane by electrostatic interaction.
- A very thin nanoparticles-stacking layer was successfully formed.
- The performance of the fabricated membranes was comparable to commercial membranes.

GRAPHICAL ABSTRACT



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ABSTRACT

We have developed a nanoparticle (NP)-stacked ultrafiltration membrane with a very thin active separation layer, by using electrostatic interaction of polyelectrolyte-stabilized NPs. Oppositely charged Ag NPs were prepared by the seed-growth method using either cationic or anionic polyelectrolytes as stabilizing agents. The Ag NPs were stacked onto an inorganic supporting membrane using layer-by-layer (LbL) deposition. By controlling the ionic strength of the NP dispersion and increasing the number of LbL dipping cycles, a stacked layer of NPs was successfully formed onto the supporting membrane. The membrane fabricated with 30 cycles of LbL dipping had a water permeability of $9.5 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ and a molecular weight cutoff of 500 kDa for dextran. This value was comparable to commercial membranes, suggesting applications for water treatment and solute separation.

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1. Introduction

Membrane technology plays an important role in conserving energy and space during wastewater treatment and water purification [1–3]. Improving the performance of filtration membranes, specifically high water flux and high rejection of dispersed or dissolved materials, will expand their practical use. Ultrafiltration (UF) membranes can separate dispersed or dissolved materials 2 to 200 nm in size, and have been widely applied toward the

separation of bacteria, macromolecules, proteins [4,5]. Polymeric UF membranes, fabricated by phase separation, are commercially attractive because of their ease of fabrication, low cost, and high mechanical strength [6–8]. However, difficulties in controlling the membrane thickness and pore size limit improvement of their performance.

Metal NPs have attracted recent attention as building blocks to construct advanced materials [9,10], because of their unique properties that differ from those of bulk metal. Metal NPs are usually prepared by reducing metal ions in aqueous solution. Stabilizing agents prevent aggregation of the NPs during synthesis, and can provide the prepared NPs with surface functionality such as positive or negative charge. Although thiols are typically used as

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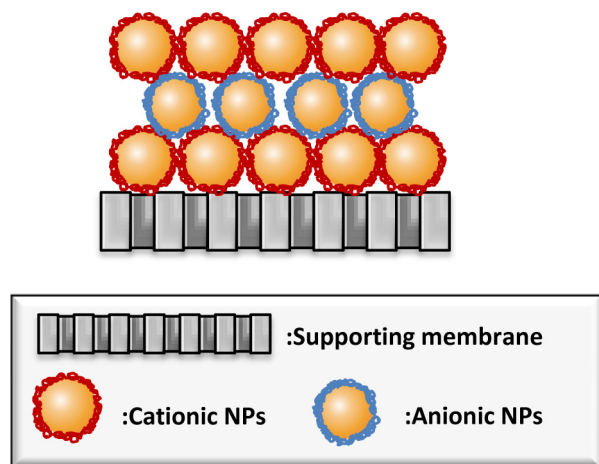


Fig. 1. Schematic of the NP-stacked membrane.

stabilizing agents [11–13], some research groups have reported the use of polyelectrolytes [14].

Layer-by-layer (LbL) deposition consists of sequentially dipping a substrate into solutions of oppositely charged polyelectrolytes [15–18]. LbL methods have also been applied to fabricate NP-stacked films [19–25]. While LbL deposition has typically been used to create functional surfaces, such as superhydrophilic films or electrochemical sensors; its application toward fabricating membranes with uniform pores has not yet been studied in detail.

Composite membranes, composed of an active separation layer and a supporting membrane, achieve high performance in water filtration. Recently, Peng et al. developed a ferritin NP-stacked membrane with a very thin (60-nm) active separation layer [26]. The flux of this membrane was much higher than that of conventional polymeric membranes. Thus, NP-stacked membranes have a great potential to improve membrane performance. However, their method has until now required many steps and expensive materials.

We describe herein an easy and economical process to fabricate NP-stacked membranes. Our NP-stacked UF membranes, with a very thin active separation layer, are fabricated by LbL deposition. Ag NPs with opposite charge were prepared by using either cationic or anionic polyelectrolytes as stabilizing agents. The prepared NPs were stacked onto an inorganic supporting membrane by LbL dipping (Fig. 1). The membrane structure and membrane performance was evaluated.

2. Methods

2.1. Preparation of Ag NPs

All aqueous solutions were prepared with Milli-Q water. Oppositely charged Ag NPs were prepared using a seed-growth method [27,28]. Polyethyleneimine (PEI; $M_w = 1800$; Wako Pure Chemical Industries, Osaka, Japan) was used as a stabilizing agent to obtain cationic Ag NPs, and poly(sodium 4-styrenesulfonate) (PSS; $M_w = 200,000$; Sigma-Aldrich, USA), was used to obtain anionic Ag NPs. The aqueous reduction mixture consisted of either, 0.4 mmol L^{-1} PEI and 2.0 mmol L^{-1} sodium borohydride, or 0.3 mmol L^{-1} PSS and 4.2 mmol L^{-1} of sodium borohydride (Wako Pure Chemical Industries). Then, 50 mL of 1 mmol L^{-1} AgNO_3 (99.8%; Wako Pure Chemical Industries) aqueous solution was added dropwise into 100 mL of each reduction mixture solution for 15 min under vigorous stirring, and reduction and stabilization were occurred. The solution was then continually stirred at room temperature for 1 h. The size of the obtained Ag NPs was evaluated

using a transmission electron microscope (TEM; JEM-2010; JEOL, Tokyo, Japan) and dynamic light scattering (DLS) apparatus (ELSZ; Otsuka Electronics, Osaka, Japan). The surface plasmon resonance (SPR) of the particles was evaluated using a UV/Vis spectrophotometer (V-650; Jasco, Tokyo, Japan).

2.2. Preparation of NPs-stacked membranes

The stacked membranes of PEI- and PSS-Ag NPs were prepared using a LbL method [24]. The ionic strength of the oppositely charged Ag NP solutions was adjusted to 3.5 mmol L^{-1} in total Na^+ concentration. A supporting membrane of anodic aluminum oxide (Anodisc 25; pore size $0.02 \mu\text{m}$, Whatman Ltd., Maidstone, England) was alternately immersed into the PEI- and PSS-Ag NP solution for 30 s. After each immersing operation, the membrane was washed with Milli-Q water and ethanol, and dried with nitrogen gas. This cycle was repeated between 10 and 40 times. The surface structure and thickness of the fabricated membrane were characterized with field emission scanning electron microscopy (FE-SEM; JSF-7500 F; JEOL). To evaluate the surface potential of the membrane, the zeta potential was measured with an electrophoretic light scattering apparatus (ELSZ, Otsuka Electronics, Osaka, Japan).

2.3. Evaluation of membrane performances

Membrane performance was evaluated using a cross-flow membrane filtration system that has been described in a previous study by our group [29]. The effective area of each sample membrane was 0.283 cm^2 . The water permeability of the prepared membranes was evaluated using Milli-Q water as a feed solution, and calculated from the weight of the permeate solution. Four kinds of dextran (15, 35, 100, and 500 kDa), in aqueous solution containing 1 g L^{-1} ethylene glycol as a reference material, were used as feed solutions to evaluate the rejection performance. 15 kDa dextran was obtained from Nakarai Tesque (Kyoto, Japan), and the other molecular weights of dextran from Sigma-Aldrich. The dextran concentration of the permeate solution was analyzed via gel permeation chromatography (GPC) using a refractive index detector (RID-10A; Shimadzu Corporation, Kyoto, Japan) and a Shodex SB-805HQ column (Showa Denko, Tokyo, Japan) at 40°C , and rejections against dextran were calculated [30]. The feed solution was pressurized to 0.25 MPa .

3. Results and discussion

TEM images show that the average diameters of the cationic PEI-Ag NPs and anionic PSS-Ag NPs are 13.1 nm and 8.8 nm , respectively (Fig. 2A). The PEI- and PSS-Ag NPs remain stably dispersed in water for over 10 months. The PEI-Ag NP solution is vivid yellow in color; the PSS-Ag NP solution appears orange. The UV-Vis spectrum of each solution shows the characteristic SPR of Ag NPs at nearly 400 nm (Fig. 2B) [31]. These data indicate the successful preparation of Ag NPs passivated with cationic or anionic polyelectrolytes. However, compared with the PSS-Ag NPs, the PEI-Ag NPs exhibit a weaker SPR peak and stronger intensity in the higher wavelength region of the UV-Vis spectrum. This difference is likely caused by the larger diameter of the PEI-Ag NPs [32].

The effect of the ionic strength of the NP solutions on the membrane structure was investigated by adding NaCl aqueous solution to control the ionic strength of the NP solutions. It is known that the ionic strength affects the ease with which a polymer film can be stacked onto a supporting membrane via LbL deposition [17]. The SEM image of the membrane fabricated without NaCl shows a polymer-like substance on the membrane surface (Fig. S1, Supplementary data). The membrane fabricated in NaCl solution, however, exhibits granular particles uniformly stacked on the membrane

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