Preparation of carboxylated silver nanoparticles via a reverse micelle method and covalent stacking onto porous substrates via amide bond formation
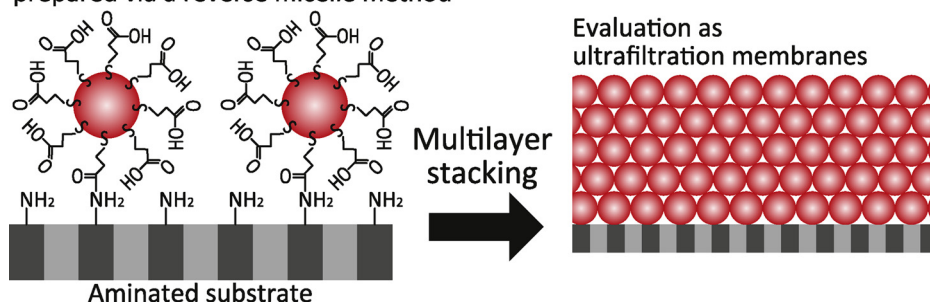
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GRAPHICAL ABSTRACT

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ABSTRACT

Covalently bound silver nanoparticle (Ag NP)-stacked ultrafiltration membranes were fabricated using carboxylated Ag NPs via amide bond formation. Carboxylated Ag NPs were prepared by a reverse micelle method using 3-mercaptopropionic acid as a NP stabilizer containing carboxyl groups. NP formation was confirmed by transmission electron microscopy and evaluation of the surface plasmon resonance. The thus-prepared spherical and monodisperse Ag NPs were stacked onto an aminated porous aluminum substrate by amide bond formation between the amino groups on the substrate surface and the carboxyl groups on the NP surface via an active ester method. The surface morphology was observed by scanning electron microscopy. To aminate the substrate surface, the substrate was treated with three kinds of aminosilanes. The type of aminosilane affected the NP-stacking behavior. The water permeability and rejection performance of the fabricated NP-stacked substrates as ultrafiltration membranes was evaluated using a cross-flow membrane filtration system. Although the substrate stacked with a single layer of NPs showed only slight rejection performance, that with a multilayer of NPs acted as an ultrafiltration membrane and had a molecular weight cutoff of 500 kDa for dextran.

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1. Introduction

Porous polymeric membranes are widely used in water purification processes owing to their energy- and space-saving potential. For high purification efficiency, high water permeability and high rejection against target solutes are desired membrane characteristics. However, conventional water purification membranes, fabricated from various polymers via phase separation methods, have a limited maximum performance [1]. Since the phase separation process is very complicated, precise control of the membrane structure is difficult, including the realization of a thin active separation layer and control of the pore size [2,3].

Recently, nanoparticle (NP)-stacked membranes have attracted attention as next-generation membranes for water purification [4,5]. NP-stacked membranes are generally composed of a highly porous substrate and an ultra-thin NP-stacked layer, which acts as an active separation layer. NPs, such as spherical NPs [6–10] or two-dimensional nanosheets [11–15], have a well-controlled structure under one nanometer. In particular, spherical metal NPs are used as advanced building blocks due to their various functions, such as electric [16], magnetic [17,18], and photonic activities [19]. Furthermore, the pore size in spherical NP-stacked membranes can be simply controlled by controlling the NP diameter; thus, they are suitable for ultrafiltration membranes [6,9]. Peng et al. fabricated ferritin NP-stacked membranes with a very thin, 60-nm active separation layer via vacuum filtration, and their membranes achieved much higher flux in comparison to conventional polymeric membranes [6]. We previously fabricated Ag NP-stacked membranes with an active separation layer that was several tens of nanometers thick via layer-by-layer (LbL) assembly, and demonstrated their performance as ultrafiltration membranes [9]. These results suggest that NP-stacked membranes have great potential for application as ultrafiltration membranes.

NPs are usually stacked on a porous substrate by coating [11,20,21], vacuum filtration [6,12,13] or LbL assembly [9,10,22–25]. Coating or vacuum filtration can be used to easily form an NP-stacked layer on a porous substrate. However, the formed layer is usually unstable because the stacked NPs are just accumulated or weakly adsorbed on the substrate. On the other hand, an LbL assembly method can be used to easily and precisely control the thickness of the NP-stacked layer because the layers are stacked one by one via intermolecular interaction (usually electrostatic interaction). The stacked NPs are electrostatically bound to each other and are difficult to detach from the substrate surface unless the NP-stacked membranes are used under very severe solvent conditions, such as ionic solution or organic solvent. The stability is further improved through the effective cross-linking of each NP-stacked layer via chemical bond formation [26]. However, surface modification of the NPs is necessary for NP cross-linking.

In this study, we developed covalently bound NP-stacked ultrafiltration membranes using carboxylated Ag NPs via amide bond formation. First, we attempted to prepare carboxylated Ag NPs via a reverse micelle method [27,28]. The reverse micelle method can be used to prepare various metal NPs while controlling the diameter uniformly and adding functional groups, though there have been few reports on its use in the preparation of Ag NPs [27]. The prepared NPs were stacked on a porous anodic aluminum oxide substrate through amide bond formation between the amino groups on the substrate surface and the carboxyl groups on the NP surface by an active ester method. To stack the NPs, the substrate was aminated using various types of aminosilanes. The performance of the NP-stacked layer as a UF membrane was evaluated in terms of its water permeability and rejection against dextran with various molecular weights.

2. Experimental

2.1. Materials

Silver nitride ($AgNO_3$; Wako Pure Chemical Industries, Osaka,

Japan) and sodium borohydride ($NaBH_4$; Wako Pure Chemical Industries) were used as sources and reducing agents of Ag, respectively. Dioctyl sulfosuccinate sodium salt (AOT; Sigma–Aldrich; St. Louis, MO, USA) was used as a surfactant to form reverse micelles. It was placed under vacuum just before use. In addition, 3-mercaptopropionic acid (MPA; Sigma–Aldrich) was used as an NP stabilizer containing carboxyl groups. Three kinds of aminosilane, 3-aminopropyltrimethoxysilane (APS; Tokyo Chemical Industry, Tokyo, Japan), *N*-(6-aminohexyl)aminomethyltriethoxysilane (AHS; Gelest, Morrisville, PA, USA), and *p*-aminophenyltrimethoxysilane (APhS; Gelest), were used to modify the substrate surfaces with amino groups. *N*-hydroxysuccinimide (NHS; Sigma–Aldrich) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC; Dojindo Laboratories, Kumamoto, Japan) were used for amine coupling reaction between the substrates and NPs. *p*-phenylenediamine (Tokyo Chemical Industry) was used to cross-link the NPs to each other. In addition, 5(6)-carboxyfluorescein (CF; Sigma–Aldrich) and fluoresceinamine (FA; Sigma–Aldrich) were used to detect amino groups and carboxyl groups on the membrane surfaces, respectively. For evaluation of the membranes' rejection performance, 15-kDa dextran (Nakarai Tesque, Kyoto, Japan) and 35-, 100-, and 500-kDa dextran (Sigma–Aldrich) were used as model solutes. Other chemicals were obtained from Wako Pure Chemical Industries. Aqueous solutions were prepared using Milli-Q water ($>18.2\,M\Omega\,cm$, Merck Millipore, Billerica, MA, USA). Isooctane and toluene were dehydrated by using molecular sieves $13 \times 1/8$ and 3 A, respectively.

2.2. Preparation of carboxylated Ag NPs

Carboxylated Ag NPs were prepared by a reverse micelle method [28]. First, 33 μL of 137.5 mmol/L $NaBH_4$ aqueous solution was added to 8.964 mL of 0.25 mol/L AOT isooctane solution and magnetically stirred at 2000 rpm. Then, 112.5 μL of 0.10 mol/L $AgNO_3$ aqueous solution was added to this solution and stirred for 15 min to reduce Ag and form Ag NPs. Subsequently, 37.1 μL of MPA was added to the reaction mixture and stirred for 1 h to stabilize the Ag NPs. The isooctane was removed by evaporation at 40 °C. The waxy residue was re-dispersed into EtOH and centrifuged at 2500*g* for 10 min, after which the supernatant was discarded. This operation was repeated at least 6 times. The sample was dried under vacuum and redispersed in water. The prepared NP suspension was centrifuged at 2500*g* for 10 min before use to eliminate aggregation. The size of the obtained Ag NPs was evaluated by transmission electron microscopy (TEM; JEM-2010; JEOL, Tokyo, Japan). The surface plasmon resonance (SPR) of the NPs was evaluated by UV/vis spectrophotometry (V-650; Jasco, Tokyo, Japan).

2.3. Fabrication of Ag NP-stacked membranes

The scheme for the fabrication of the NP-stacked membranes is shown in Fig. 1. The carboxylated NPs were covalently stacked on aminated porous substrates by an active ester method. The aminated porous substrates were prepared by a silane coupling reaction. Porous anodic aluminum oxide (Anodisc, pore size 0.02 μm, Whatman, Maidstone, England) was treated in a vacuum plasma reactor (YHS-R, Sakigake-semiconductor, Kyoto, Japan) for 1 min to increase the number of reaction sites. Then, each substrate was immersed in a toluene solution of 0.1 vol% APS, 0.1 vol% AHS or 5.73 mmol/L APhS for 2 h at 60 °C. The substrate was sequentially washed with hexane, water, and hexane in an ultrasonic cleaner for 15 min, and placed in water at 40 °C overnight. The obtained substrates were dried under vacuum before use.

Each aminosilane-treated substrate was immersed in an aqueous solution containing 0.19 mg/mL of NPs and 0.1 mmol/L of NHS and EDC. The solution was gently shaken for 2 h to form amide bonding between the amino groups of the substrate and the carboxyl groups of the NPs, and an NP stacking layer was formed on the substrate surface.