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LETTER

Facile method of preparing silver-embedded polymer beads and their antibacterial effect

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Research designed to prevent human beings from being infected by microorganisms such as bacteria, molds, yeasts, and viruses from the living environment has attracted tremendous interest. Therefore, many researchers have tried to develop novel and effective antimicrobial materials with free of resistance and low cost [1, 2]. One of the most widely used antibacterial materials is based on silver (silver ions or silver nanoparticles) which exhibits strong biocidal effects towards a broad range of microorganisms, along with advantages such as a lack of odor, taste, and color [3–6]. Until now, various routes for preparing antimicrobial silver compounds or silver nanoparticles (NPs) have been reported [7, 8]. Especially, silver NPs have more severe effects on bacterial cells than silver ions [9]. However, silver NPs are easily aggregated which causes the deterioration of their chemical properties and decreases their antimicrobial properties. Moreover, the fate of silver NPs for biological applications is still debatable [10, 11]. In addition, some synthetic methods of silver NPs as antimicrobial materials are time-consuming and require expensive instruments. In addition, silver NPs can easily become aggregated, which causes the deterioration of their chemical properties and decreases their antimicrobial properties. To solve these problems, silver has been introduced onto stable supporting materials, in which the antimicrobial mechanism is closely related to the release of silver ions. These methods have several advantages, such as sustained antibacterial effects based on the release of silver ions, good mechanical properties and inexpensive and easy manufacturing processes for industrial applications [12–17].

Recently, many different methods have been proposed to introduce silver NPs into polymers. Among the various polymers, polystyrene (PS)–divinylbenzene (DVB) porous resin is particularly useful, due to its large surface area, chemical stability, and low cost. Moreover, silver NPs can be easily embedded on it after sulfonation, and their size and the loading amount can be adjusted by changing of reaction condition [18]. The deposition of silver on polymer materials has been enhanced by the activation of the surface-functional groups. Among the various functional groups, sulfonated groups are good candidates to introduce silver NPs for the purpose of producing antibacterial materials. Recently, we introduced silver NPs into sulfonated PS–DVB resins (4–8 μm) with mild reduction using the polyol method for use as surface-enhanced Raman scattering (SERS) active materials for multiplex protein analysis [18, 19].

In this study, silver NPs embedded into ion-exchange resin (Ag-IER) (*ca.* 0.9 mm) were readily prepared by the polyol method and characterized by several instrumental analyses, such as field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy-dispersive X-ray emission (EDX), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Then, their anti-bacterial activity was tested using *Escherichia coli*, which is well known as indicator bacteria. Moreover, we investigated their antibacterial effect at a low silver loading level and silver ion release conditions.

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Preparation of Ag-IER: 10 g of ion-exchange resin (IER) was dispersed in 250 mL of ethylene glycol containing various concentrations of silver nitrate (2.5–25 mM/g resin) with or without polyvinylpyrrolidone-40 (PVP-40) (0.35 mM, MW: 40,000), and then the mixture was stirred for 6 or 12 h at 100 °C. After the reaction was finished, the resulting Ag-IER was washed with acetone and water several times to remove the excess reagents. The silver release rates were measured on separated experiments in distilled water condition.

Culture and analysis of E. coli: *Escherichia coli* (ATCC 8739), which was selected as the indicator bacteria for the antibacterial experiments, was inoculated in 50 mL of Tryptic Soy Broth (Difco Co.) medium and grown at 37 °C for 18 h. The bacteria suspension was harvested by centrifugation for 10 min at 1,000×*g* and washed twice with 50 mL of 150 mM phosphate-buffered saline (PBS, pH 7.4). The stock suspension of *E. coli* was made by resuspending the final pellets in 50 mL of 150 mM PBS solution. The number of cells was examined by the spread plate method, in which the *E. coli* cells were spread on a nutrient agar plate, incubated at 37 °C for 24 h, and then the number of colonies was checked.

Antibacterial activity evaluation: The resin samples (0.1 g) were added to 10 mL of *E. coli* cell suspensions contained in 10 mM phosphate buffer solution at pH 7.1. The suspension was thoroughly mixed and 1 mL aliquots were withdrawn at regular intervals of 0.5, 1, and 3 h after centrifuging the resin for 2 min and then the number of cells was analyzed.

To prepare the antibacterial materials, silver NPs were embedded onto bead type porous IER (830–1000 μm, average pore diameter 24 nm, porosity 0.40 mL/g) which have sulfonate groups using the well-known polyol method. After the embedding of the silver NPs, the color of the IER beads changed from dark muddy yellow to black. In the process of embedding the silver NPs, silver nitrate ($AgNO_3$) dissolved in ethylene glycol, which acts as a reducing agent and a solvent simultaneously, was added to the IER. Thus, the silver ions interacted electrostatically with the negatively charged sulfonate groups which existed inside and outside of the beads. While the resulting dispersion was subsequently stirred for 6 h at 100 °C, silver NPs were formed as shown in Fig. 1. The surface shape and EDX value of the prepared Ag-IER was stable when treated in water at 60 °C for 3 days and the antimicrobial activity of the resin was maintained. In the preparation step, PVP is normally used to stabilize the Ag NPs and prevent their aggregation. However, PVP can be released into the water under several conditions. The color of the solution containing the beads, where PVP was used, changed to black in 0.5% NaCl solution, Ag sol (PNT), and even tap water (data not shown). This can be a potential problem when used in drinking or bio applications. For this reason, we limited the use of PVP to the type D Ag-IER only in this study. The detailed synthetic conditions used to prepare the Ag-IER are summarized in Table 1.

The loading and release rate of silver ions from each of the resins were analyzed by FE-SEM and ICP, as summarized in Table 1. The loading level of silver NPs was controlled by adjusting the amount of $AgNO_3$ added or the reaction time. Regarding PVP, it did not significantly affect the silver loading level, but did affect the silver release

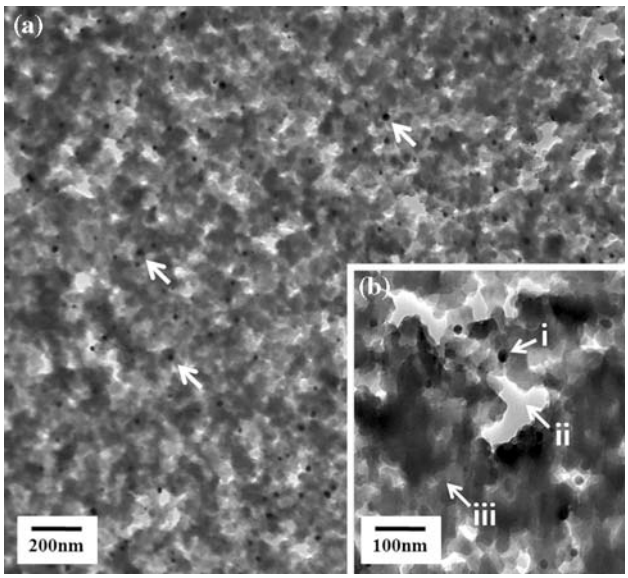

Fig. 1 TEM images of cross-sectioned Ag-IER bead (Type D). **a** The *arrows* indicate the presence of silver NPs, **b** amplified TEM image; (*i*) embedded silver NP, (*ii*) pore in IER, (*iii*) polymer chains

Table 1 Experimental details for preparation of the silver-embedded IER series

Series	$AgNO_3$ (g)	Additive	Reaction time (h)	Silver amount of Ag-IER (wt%)[a]	Amount of Ag^+ released (mg/L)[ab]
Bare bead (BB)	–	–	–	0	0
Type A	1	–	6	11.2	0.03
Type B	1	–	24	11.7	0.05
Type C	10	–	6	39.3	8.2
Type D	10	PVP	6	41.6	22

Reaction temperature 100 °C, ethylene glycol 15 mL, IER 10 g

[a] Analyzed by ICP, [b] Ag-IER in water 1 g/10 mL

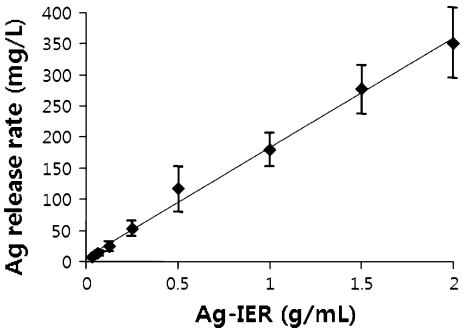

Fig. 2 Silver release rate according to the amount of Ag-IER

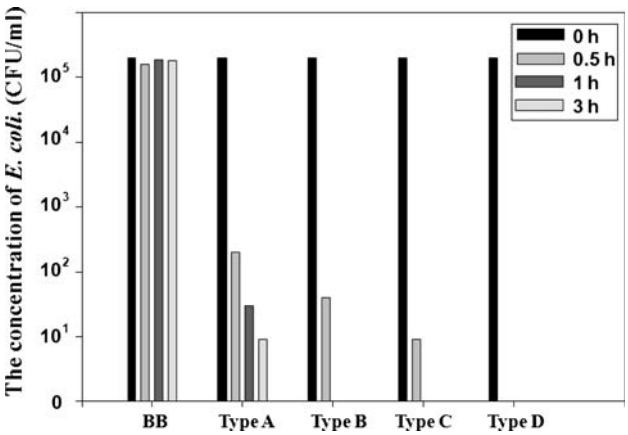

Fig. 3 Antibacterial effect of silver-embedded IERs

rate. Types C and D showed similar silver loading levels, but their silver ion release rates were different.

The silver release rate was also controlled by adjusting the amount of Ag-IER. As the amount of Ag-IER (type D) increased up to 2 g/mL, the silver ion releasing rate linearly increased, as shown in Fig. 2.

Figure 3 shows the antibacterial activity of the different Ag-IERs toward *E. coli* as a function of time. The bare IER resulted in no inactivation of *E. coli*, as expected. Type A (silver ion release rate of 0.03 mg/L) showed 3.4 log inactivation of *E. coli* and types B, C, and D achieved almost 4 log inactivation of *E. coli* after 1 h. Usually, the antibacterial effect of silver-based materials is strongly dependent on the release rate of silver ions and the direct contact of the silver NPs [20]. In this case, however, the release rate of silver ions seems to have a greater influence on the antibacterial activity, since the polymer backbone prevents the bacteria from coming into direct contact with the silver NPs. The porous and water compatible IER resin can be a useful template for embedding silver NPs and releasing silver ions, thereby producing excellent antibacterial materials.

We prepared an Ag-IER by a simple method, which exhibits excellent antibacterial activity. The results of the antibacterial tests showed that 0.03 mg/L of silver ions released from the Ag-IER inactivated most of the *E. coli*. This means that the Ag-IER in an aqueous system has great potential to be used as an antibacterial material.

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