Immobilization of Silver Nanoparticles on the Surface of Cellulose Nanofibers Using High-Pressure Wet-Type Jet Mill

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Composite material immobilized silver nanoparticles (NPs) on the surface of cellulose nanofibers (CNF) was prepared using a high-pressure wet-type jet mill. A mixture both containing an aqueous silver nitrate solution and a CNF suspension was prepared as a raw starting material. The mixture was pulverized with the high-pressure wet-type jet mill at a pressure of 100 or 200 MPa. An X-ray diffraction pattern of the obtained sample revealed the presence of not only cellulose type I crystallites but also silver metal crystallites. According to observation by field-emission scanning electron microscopy, it was found that many silver NPs were immobilized on the surface of CNF. Note that almost all the silver NPs were well dispersed on the surface of CNF. It was cleared that the silver NPs had a spherical in shape with an average particle size of about 3 nm by the transmission electron microscope observation. The average size of the silver NPs slightly increased with the number of jet milling cycles, however, the change in the discharge pressure of the high-pressure wet-type jet mill did not affect the NPs size. The silver content in the composite materials increased with increasing both the number of jet milling cycles and the discharge pressure. The silver NPs were deposited by using the thermal energy released in the jet milling process, and their grain growth was then inhibited because the suspension was cooled immediately through the cooling tube. Therefore, it was assumed that silver NPs with a narrow size distribution could be immobilized on the surface of CNF.

Keywords: silver nanoparticles, cellulose nanofiber, composite material, high-pressure wet-type jet mill, immobilization, microchemical process

1. Introduction

Metal nanoparticles (NPs) are characterized by having large specific surface area and high surface activity as compared with bulk metal. Therefore, even a small amount of metal NPs can be expected to significantly improve the properties of materials. Among the known metal NPs, silver NPs have attracted increased attention due to their excellent physical and chemical properties and relatively low cost, which render them applicable in various fields including electrochemistry and catalysis and as antibacterial materials.¹⁻⁶ Silver NPs are prepared mostly by the breakdown method (crushing method) or the build-up method (synthesis method). The latter method, in particular the liquid-phase synthesis method, is the most widely used. Other approaches including chemical methods, in which metal salts are reduced by strong reducing agents such as sodium borohydride and ethylene glycol,⁷ laser ablation methods,⁸ and emulsion methods⁹ have been also reported.

In these methods, protective materials such as polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate are often used to suppress grain growth and prevent aggregation,¹⁰ thereby improving the chemical stability of silver NPs, which is generally low for metal NPs with large specific surface area and high surface activity. However, excessive coverage of the surface of the metal NPs by the protective material may alter their properties. With the aim of maintaining high surface activity while suppressing aggregation, the immobilization of silver NPs on a substrate has been previously investigated. As an immobilizing material, cellulose nanofibers (CNF), which can be prepared by pulverizing pulp cellulose down to a nanometer size, exhibit excellent mechanical properties such as high elastic modulus and low linear thermal expansion,¹¹,¹² high chemical stability, nontoxicity, and thixotropic properties.

Composite materials containing both silver NPs and CNF can be expected to be in a nonuniform state when prepared by mixing with a magnetic stirrer because silver NPs have high self-cohesive force and CNF exhibits high viscosity. Fuji et al. reported the fabrication of silver NPs using CNF and a high-pressure wet-type jet mill.¹³ This convenient, one-step method, in which a mixture containing a CNF suspension and an aqueous metal salt solution is processed with a high-pressure wet-type jet mill, takes advantage of the slight reducing ability of CNF to avoid using reducing agents such as sodium borohydride. Furthermore, oxidation of raw CNF is not required. The as-fabricated silver NPs are immobilized on the CNF surface to form nanocomposite materials. However, despite the strong dependence of the properties of metal NPs on their shape and size,¹⁴⁻¹⁶ the effects of the treatment conditions of the high-pressure wet-type jet mill on the particle size and the amount of immobilized silver NPs have not been investigated in detail.

In this report, the effects of the treatment conditions, including the discharge pressure and the number of jet milling cycles, and the thermal energy generated in the high-pressure wet-type jet mill on the precipitation and immobilization of silver NPs are investigated.

2. Experimental Procedure

2.1 Sample preparation

A CNF suspension (0.8 mass%, 100 mL) was prepared by diluting CNF (Sugino Machine Co., Ltd., Japan, BiNFi-s: FMa-100) with ultrapure water. After stirring, the prepared
CNF suspension was processed once using a high-pressure wet-type jet mill (hereinafter abbreviated as jet mill; HJP-25001, Sugino Machine Co., Ltd., Japan), in which the suspension was discharged from a nozzle with a diameter of 100 µm to a silicon nitride ball located in a collision chamber, at a discharge pressure of 100 MPa. An aqueous silver nitrate solution (100 mL) with a concentration of 74 mM (Fuji Wako Pure Chemical Industries Co., Ltd., Japan) was prepared and mixed with the CNF suspension by stirring for one hour. The mixed suspension was processed using the jet mill at 100 MPa or 200 MPa (0–20 times). The treated mixture suspension was immediately cooled by passing through a cooling tube with a diameter of 1 mm kept at 10°C. The mixture was centrifuged at 6,800 × g for 5 min, and the resulting precipitate was recovered. After adding 50 mL of ultrapure water, the precipitate was stirred for 10 min, centrifuged at 6,800 × g for 5 min, and recovered again. This rinsing step was repeated three times to remove unreacted silver nitrate. The samples processed Y times with the jet mill at a discharge pressure of X MPa were denoted as X-Y.

2.2 Characterization

The morphology of the samples was investigated by field-emission scanning electron microscopy (FE-SEM, Hitachi High-Tech Co., Ltd., Japan, SU8220; accelerating voltage: 1 kV) and transmission electron microscopy (TEM, JEOL Co., Ltd., Japan, JEM-2100; accelerating voltage: 200 kV). For the observation, the diluted precipitate was dropped on an OkenShoji Co., Ltd., Japan, Cu mesh with a carbon film (Okeshoji Co., Ltd., Japan, UHR-C110) and air-dried. The average particle size was calculated by measuring the length of 100 particles in the TEM images.

The silver content in the obtained sample was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Fisher Scientific Co., Ltd., Japan, iCAP6500Duo). Nitric acid was added to the sample, and the mixture was heated on a sand bath at 250°C for 30 minutes and filtrated. The filtrate was used as the ICP measurement sample.

For the analysis of the crystalline phase, the obtained samples were subjected to vacuum freeze-drying and identified by X-ray diffraction (XRD, RIGAKU Co., Ltd., Japan, SmartLab; Cu-Kα, 45 kV-200 mA).

For comparison, an aqueous silver nitrate solution of the same concentration (74 mM) was processed 20 times with the jet mill at a discharge pressure of 200 MPa. The absorption spectrum of the comparative sample was measured using an ultraviolet-visible-near-infrared (UV-vis-NIR) scanning spectrophotometer (Shimadzu Co., Ltd., Japan, UV-3100PC).

3. Results

Figure 1 shows the UV-vis spectrum of an aqueous silver nitrate solution prepared by processing 20 times with the jet mill at a discharge pressure of 200 MPa and that of a pristine silver nitrate solution. Both spectra exhibited a peak at 300 nm attributable to the nitrate ion.17,18 Generally, silver NPs give rise to an absorption peak derived from their plasmon resonance at 400 nm, which shifts to high frequency as the NPs size increases.19 Such a peak was not observed in the spectra depicted in Fig. 1, which confirmed the absence of precipitated silver NPs even after processing with the jet mill.

The XRD patterns of the samples processed 5, 10, and 20 times with the jet mill at a discharge pressure of 100 MPa (samples 100-5, 100-10, and 100-20, respectively) are shown in Fig. 2. For comparison, the XRD pattern of a sample without processing (blank sample) is also shown. In the XRD patterns of all the samples, the presence of peaks derived from cellulose I type crystallites (2θ = 14.9°, 16.4°, 22.7°, and 34.5°; JCPDS 00-056-1718) was confirmed.20 More- over, additional peaks attributable to silver metal crystallite peaks (2θ = 38.1° and 44.2°; JCPDS 01-004-0783) were observed in the patterns of the samples containing silver nitrate. The intensities of the diffraction peaks derived from silver metal were found to increase with the number of jet milling cycles, indicating that the amount of precipitated silver NPs also increased. This suggests that silver ions were reduced to silver during the jet mill processing, since the diffraction pattern of the blank sample contained no silver metal crystallite peaks. Therefore, the jet mill processing is essential for the formation of silver NPs from a mixture containing both silver nitrate and CNF.
Similarly, the XRD patterns of the samples processed 5, 10, and 20 times with the jet mill at a discharge pressure of 200 MPa (samples 200-5, 200-10, and 200-20, respectively) are shown in Fig. 3. All the patterns exhibited peaks derived from cellulose I type crystallites and silver crystallites. The intensities of the diffraction peaks attributed to silver crystallites increased with the number of jet milling cycles to a greater extent than those of the samples prepared at a discharge pressure of 100 MPa, which indicates that the amount of deposited silver NPs increased upon increasing the discharge pressure.

Figure 4 shows the relationship between the silver content and the number of jet milling cycles. Regardless of the discharge pressure, the silver content increased with the number of jet milling cycles. In the case of a discharge pressure of 100 MPa, the silver content increased gradually up to the highest content of 1.4% for the 100-20 sample. For a discharge pressure of 200 MPa, the silver content rapidly increased with the number of jet milling cycles up to the highest value of 5.7% for the 200-20 sample. Regardless of the number of jet milling cycles, the silver content increased with increasing the discharge pressure.

Figure 5 shows the FE-SEM micrographs of the samples prepared using the jet mill under each condition. In all the samples, CNF exhibited a network structure without aggregation and a width of about 20 nm. Moreover, well-dispersed NPs, which were confirmed to be silver NPs by the XRD patterns shown in Figs. 2 and 3, were clearly observed on the CNF surface (indicated by the black arrows in Fig. 5). Regardless of the discharge pressure, the amount of NPs increased with the number of jet milling cycles; however, less NPs were observed in the sample processed five times with the jet mill. This result is consistent with both the peak intensity of the XRD patterns derived from silver crystallites (Figs. 2 and 3) and the silver content plotted in Fig. 4. These results demonstrate that the samples prepared using the jet mill were nanocomposite materials in which silver NPs were uniformly immobilized on the surface of CNF.

Figure 6 shows the TEM micrographs of the samples prepared using the jet mill under each condition. Well-dispersed, spherical particles without aggregation were observed, with a mean particle size of 5 nm or less and a narrow particle size distribution. During the preparation of the sample for the TEM measurement, evaporation of the solvent in the absence of a dispersant might lead to agglomeration of silver NPs; however, no aggregates were observed in any of the samples in this study. This result further suggests that the silver NPs were immobilized on CNF. It should be noted that CNF was not clearly observed in the TEM micrographs because the observation was performed without electron staining to measure the particle size accurately; as a natural polymer, CNF requires electron staining with a reagent containing heavy metals, such as phosphotungstic acid or uranium acetate, for TEM observation.

Figure 7 shows the mean particle size of silver NPs in each sample calculated by measuring the length of the particles in the TEM micrographs shown in Fig. 6. The mean particle size of the samples processed 5, 10, and 20 times at a...
discharge pressure of 100 MPa was 2.1 ± 0.7, 2.7 ± 0.9, and 3.4 ± 1.3 nm, respectively. The mean particle size gradually increased as the number of jet milling cycles increased. Meanwhile, the mean particle size of the samples processed 5, 10, and 20 times at a discharge pressure of 200 MPa was 2.6 ± 0.9, 3.1 ± 1.0, and 3.5 ± 1.5 nm, respectively. It was confirmed that the particle size distribution of the silver NPs was very narrow regardless of the number of jet milling cycles or the discharge pressure.

4. Precipitation Mechanism of Silver NPs Prepared Using the High-Pressure Wet-Type Jet Mill

The jet mill used in this paper can apply large shear force and collision force to the fluid. The flow velocity in the collision chamber was calculated according to Bernoulli’s principle to be 447 m/s at a discharge pressure of 100 MPa and 632 m/s at a discharge pressure of 200 MPa. These flow velocities are remarkably high, suggesting the occurrence of cavitation in the fluid discharged at high-pressure, which is a physical phenomenon that depends on local flow conditions such as pressure, velocity, and turbulence. Nagata et al. reported the formation of silver particles using cavitation. They used an ultrasonic generator with a frequency of 200 KHz (output 200 W) for more than 10 minutes. In the present study, silver particles did not precipitate during processing of the silver nitrate aqueous solution with the jet mill (discharge pressure of 200 MPa, 20 times), as shown in Fig. 1. Therefore, silver ions were not reduced only by cavitation in the jet mill. To examine the effect of the cooling tube connected to the collision chamber in the jet mill, the temperature change of pure water processed at each discharge pressure was evaluated with and without the cooling tube (Fig. 8). Without the cooling tube, the temperature of pure water increased rapidly from 24.8°C to 48.1°C after one jet milling cycle at a discharge pressure of 100 MPa and kept increasing with the number of jet milling cycles up to 74.3°C. At a discharge pressure of 200 MPa, the temperature of pure water increased rapidly from 24.8°C to 67.9°C after one jet milling cycle and to 80.8°C after two cycles. After three jet milling cycles, the temperature of pure water reached a saturation value of 84°C. In contrast, when the temperature of the cooling tube was kept at 10°C, the temperature of pure water was maintained at about 14°C regardless of both the discharge pressure and the number of jet milling cycles. These results indicate that the temperature of the solution temporarily raised in the collision chamber after processing with the jet mill due to the thermal energy generated in the cavitation. Specifically, the mixture containing both CNF and the aqueous silver nitrate solution was heated up to 48.1°C or 67.9°C for the discharge pressure of 100 MPa or 200 MPa, respectively. The silver ions can be then reduced to silver due to the proximity of CNF having reduction ability. In addition, the reduction ability of CNF likely increased upon processing with the jet mill because more aldehyde groups from the molecular chain ends of glucose could be exposed on the surface of CNF.

In their report, Fujii et al. confirmed that silver particles precipitated from a mixture containing both CNF and an aqueous silver nitrate solution by refluxing at 60°C for two hours. The particles had a size of 15.4 ± 9.3 nm with a wide
particle size distribution. In contrast, in the jet milling procedure, the temperature of the mixture increases momentarily in the collision chamber, and the silver NPs precipitate. Subsequently, the NPs are immediately cooled in the cooling tube, which suppresses the grain growth. Small-sized NPs with a narrow size distribution are thereby deposited on the surface of CNF. This particle precipitation mechanism is remarkably similar to that observed using a microreactor. Singh et al. reported the production of silver NPs with a narrow size distribution using a microreactor,(26) in which NPs with uniform particle size can be produced by precisely controlling both the temperature of the fluid and the reaction time to control the nucleation and particle growth. In the case of the jet milling procedure, the temperature of the mixture rises with increasing the discharge pressure, and both the extent of nucleation and the particle growth increases with the number of jet milling cycles. As a result, the size of the immobilized silver NPs increased slightly with the number of jet milling cycles. Furthermore, the silver content increased significantly as both the discharge pressure and the number of cycles increased.

In the present study, the particle size could be controlled most likely because both the ability to reduce silver ions and the amount of heat energy generated were extremely small. In addition, silver NPs were easily immobilized on the CNF surface benefiting from the reducing ability of the molecular chain ends of CNF. As a result, the agglomeration of particles was prevented without requiring a protective material such as PVP.

5. Conclusion

Silver NPs were immobilized on CNF by processing a mixture containing both CNF and a silver nitrate aqueous solution under different jet milling conditions. Well-dispersed silver NPs with a size of 2.1–3.5 nm and a narrow particle size distribution were deposited on the surface of CNF without aggregation. The size of the immobilized silver NPs increased slightly with the number of jet milling cycles. Furthermore, the silver content increased upon increasing both the discharge pressure and the number of jet milling cycles. The small and uniform particle size is attributed to the fact that the mixture containing CNF and silver nitrate was instantaneously heated and then rapidly cooled inside the jet mill.

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