Fabrication of Silver Nanoparticles Using High-Pressure Wet-Type Jet Mill

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Silver nanoparticles (NPs) were fabricated using a high-pressure wet-type jet mill. A mixture containing both aqueous silver nitrate and a cellulose nano fiber (CNF) suspension was processed with the high-pressure wet-type jet mill at a pressure of 150 MPa. An X-ray diffraction pattern of the obtained sample revealed not only cellulose type I crystallites, but also silver metal crystallites. Transmission electron microscopy revealed silver NPs in the obtained sample that were spherical in shape with an average particle size of 7.1 ± 1.6 nm. These were much smaller than those in a sample prepared by a reflux method. Note that the particle size distribution was very narrow; moreover, almost all the silver NPs were well dispersed due to their constituent CNF. It was considered that Ag(I) was reduced to Ag(0) in the mixed suspension due to the many reducing functional groups on the surface of the raw CNF. It was concluded that cellulose acted as both a reducing agent and a dispersant.

Keywords: silver nanoparticle, cellulose nano fiber, high-pressure wet-type jet mill, microchemical process

1. Introduction

Silver nanoparticles (NPs) have many attractive properties that make them suitable for application in various fields, such as electronics, optics, and catalysis.1-6 In particular, silver NPs were recently used as metal inks in printed materials. However, in general, metal NPs have poor stability in suspensions, as they easily aggregate or are oxidized due to their large surface areas and high surface activities. Two approaches are considered effective in preventing these phenomena. The first approach is to coat the metal NPs with polymers or surfactants. However, this often adversely affects their properties. The second approach involves immobilizing the metal NPs on support matrices without covering their surfaces. However, it is difficult to immobilize the NPs tightly on the support matrices without causing them to aggregate. It was reported that synthetic polymers such as polyvinyl pyrrolidone are often used to prevent aggregation and control the particle growth of metal NPs.7,8 Conventional polymer matrices are often unsuitable as support matrices, since metal NPs are easily embedded in them. In addition, particulate support materials such as carbons and inorganic materials are likely to aggregate. The ideal support matrices are chemically stable, resistant to aggregation, and have the ability to maintain highly dispersed states. Furthermore, it is desirable for them to have surface functional groups or electric charge capable of immobilizing NPs.

This study focuses on cellulose nano fiber (CNF) as a support matrix for metal NPs. Cellulose, which is a chemically stable polysaccharide, is the most abundant natural polymer and originates from plants and bacteria.9,10 It is well known that CNF is obtained by pulverizing cellulose pulp with a grinder or a high-pressure homogenizer.11,12 Native cellulose consists of nanometer-sized fibrils that are 3–20 nm in width and have extremely high crystallinity, up to 65–95%.13 Besides, cellulose has both a crystalline and a non-crystalline phase and possesses reducing aldehyde groups at its molecular chain terminals.14 The resulting CNF suspension consisted of strongly entangled and disordered networks of CNF. Thus, CNF has high dispersibility and reducibility.

In particular, Saito et al. reported an oxidative pretreatment of cellulose; this involved applying 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals before mechanical treatment in a Waring blender.15-17 They reported that TEMPO selectively catalyzes oxidation of the C6 primary hydroxyl group of cellulose to a carboxylate on the CNF surface. TEMPO-mediated oxidation is a promising method for the surface modification of native cellulosics, by which carboxylate and aldehyde functional groups can be introduced into solid native cellulosics under mild aqueous conditions. TEMPO-modified CNFs have high dispersibility, since many carboxylate and aldehyde functional groups can be introduced onto their surfaces; moreover, they can act as a scaffold for immobilizing metal ions. In previous studies, Koga et al. reported the deposition of metal NPs on the surface of TEMPO-modified CNFs using a reducing reagent such as sodium borohydride.18-20

In the present study, a high-pressure wet-type jet mill having the high shear force was investigated to check whether it gave higher dispersibility and reduction to the raw CNF. Silver NPs were prepared by pulverizing raw CNF with the high-pressure wet-type jet mill without using a reducing reagent or TEMPO-oxidized CNF.

2. Experimental Procedure

2.1 Sample preparation

CNF suspension (0.1 mass%) were prepared by diluting CNF (Sugino Machine Co., Ltd., Japan, FMa-100) with ultrapure water. Figure 1 shows a schematic drawing of the high-pressure wet-type jet mill (Masuko Sangyo Co., Ltd., MMX-L200-D10). This milling device can mix two discharged fluids through each flow channel with a diameter of 100 μm at the collision point under high pressure to pulverize them by applying a large shearing force. It can control the discharged pressure from 0 to 200 MPa; furthermore, the milled suspension can be immediately cooled by passing through a cooling tube with a diameter of 3 mm maintained at

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10°C. An aqueous solution of 80 mM silver nitrate (Wako Pure Chemical Industries, Ltd.) was prepared. Equal amounts of 0.1 mass% CNF suspension and 80 mM silver nitrate solution were mixed with a magnetic stirrer for 5 min. The mixed suspension was processed five times using the high-pressure wet-type jet mill at 150 MPa. After filtering with an ultrafilter (fractionated molecular weight: 10,000, ADVANTEC), the residue was rinsed with ultrapure water and filtered with the ultrafilter again. It was confirmed that no particles precipitated in the filtrate, because it was colorless and the light path of the laser was not visible. The obtained sample was denoted as 150-JM. Two reference samples were prepared for comparison. One was prepared by pulverizing only aqueous silver nitrate solution without CNF with the high-pressure wet-type jet mill at 150 MPa. The obtained reference sample was denoted as Ref1. Another was prepared by refluxing a mixed suspension containing both a CNF suspension and silver nitrate solution at 60°C for 2 h. After filtering with an ultrafilter, the residue was rinsed with the same method. It was confirmed that no particles precipitated in the filtrate, too. The obtained reference sample was denoted as Ref2.

2.2 Characterization
For crystalline phase analysis, the obtained samples were subjected to vacuum freeze-drying. The crystalline phases of the samples were identified by X-ray diffraction (XRD) (RIGAKU, SmartLab, Cu-Kα, 45 kV, 200 mA). The diffraction data were collected by step scanning from $2\theta = 5^\circ$ to $60^\circ$ (0.01°/step and 4°/min scanning speed). The morphology of the samples was observed by transmission electron microscopy (TEM) (JEOL, JEM-2100, accelerating voltage 200 kV). The average particle size and standard deviation were obtained from each TEM image by counting 50 particles. The absorption spectrum of sample was measured using UV-vis-NIR scanning spectrophotometer (SHIMADZU, UV-3100PC).

As an evaluation of reducing ability, the amount of reducing sugars was quantified by the 3, 5-dinitrosalicylic acid method.$^{21, 22}$ A calibration line of each glucose concentration was prepared, and the amount was converted as glucose concentration since glucose was the smallest units among the reducing sugars in the cellulose structure.

3. Results and Discussion
Figure 2 shows XRD patterns of the 150-JM and Ref2 samples. For comparison, the XRD pattern of the raw CNF is also shown. All the peaks derived from cellulose type I crystallites (JCPDS 00-056-1718) were confirmed at 14.9°, 16.4°, 22.7°, and 34.5° for the raw CNF sample.$^{23, 24}$ The raw CNF was a single-phase product of cellulose type I, as no phases other than cellulose were detected in this pattern. The diffraction patterns of the 150-JM and Ref2 samples contained not only cellulose type I crystallite peaks, but also metal silver crystallite peaks (JCPDS 01-077-6577; $2\theta = 38.4^\circ$: Ag(111)). In addition, it was confirmed that the diffraction peaks derived from cellulose type I crystallites for 150-JM were not broadened.

For comparison, Ref1 was prepared by pulverizing an aqueous silver nitrate solution without raw CNF with the high-pressure wet-type jet mill at 150 MPa to confirm the effect of the raw CNF. Figure 3 shows UV-vis spectrum for Ref1. It was confirmed that no particles precipitated since the light at some wavelength should have been absorbed if particles had formed. It was clear that Ag(I) was not reduced to Ag(0) by cavitation and heat generated in the high-pressure wet-type jet mill. Therefore, it was confirmed that the reducing CNF were essential for this reaction. The appearance of JM-150 sample contained both the aqueous silver nitrate solution and the CNF suspension did not change after pulverizing with the high-pressure wet-type jet mill. In addition, that of Ref2 did not change after refluxing either. UV-vis spectroscopy analyses were impossible since those samples were white suspension.

Figure 4 shows TEM images and size distribution histograms for the 150-JM and Ref2 samples. The CNF was invisible in the TEM images, since no staining with
heavy metals such as osmium was applied to clearly distinguish silver NPs. Even in the Ref2 sample, it was confirmed that Ag(I) was reduced to Ag(0) to precipitate particles. This suggests that CNFs have reducing ability. The silver particle size for the Ref2 sample is significantly larger \((15.4 \pm 9.3 \text{ nm})\) than for 150-JM. In the Ref2 sample, these were spherical, and large distributions were observed. Silver NPs in 150-JM were also spherical but had an average particle size of \(7.1 \pm 1.6 \text{ nm}\). Note that the particle size distribution was very narrow; moreover, almost all the silver NPs were well dispersed even though no dispersing reagent was added. It appeared that particles were aligned in the slightly visible CNF.

The reducing ability of CNF is discussed. CNF is known to possess reducing aldehyde groups at their molecular chain terminals. Therefore, it is considered that the reducing ability of the CNF suspension can be evaluated as a glucose concentration using the quantification method of the reducing sugars. Figure 5 shows the relationship between the glucose concentration in 150-JM and the number of processing cycles. The raw CNF suspension was found to contain a small amount of reducing sugars without processing with the high-pressure wet-type jet mill. This indicates that raw CNF has limited reducing ability. In the reflux method, it was considered that silver particles were deposited, since Ag(I) was reduced to Ag(0) by reducing sugars contained in the raw CNF. However, in a batch-type reaction such as the reflux method, it was impossible to control both the formation of nuclei and the growth of particles. Therefore, particles in the Ref2 sample were larger than those in the 150-JM sample, with wide size distributions. The glucose concentration increased with the number of processing cycles, as shown in Fig. 5. Two contributing factors are proposed for this trend. The first is that CNF broke down to the reducing sugars with low molecular weight, such as glucose, due to the strong shearing forces applied by the high-pressure wet-type jet mill because cellulose is a polysaccharide in which glucose units are linked by \(\beta-1,4-\) glycosidic bonds. Raveendran et al. reported that it is possible to synthesize silver nanoparticles using glucose as a reducing agent.25) The second is that CNF are finely pulverized due to the strong shearing forces applied by the high-pressure wet-type jet mill, resulting in many aldehyde groups being exposed on their new surfaces. Thus, it appears that many particles having with single nanometer size on the surface of CNF can be deposited in a short time.
Furthermore, it is possible to control the particle size by controlling both the formation of nuclei and the growth of particles with the high-pressure wet-type jet mill. In the high-pressure wet-type jet mill system, fluid is pumped instantaneously through a flow channel with a diameter of 100 μm. It is clear that the heat generated by the collision energy can be ignored, since it is removed immediately as the fluid flows through the cooling tube, as shown in Fig. 1.

The reaction system for the high-pressure wet-type jet mill is very similar to that for a microreactor in a microchemical process. In a microchemical process, it is possible to perform continuous reactions without reducing reagents, such as sodium borohydride or formic acid, or a high-pressure vessel. The fabricated silver NPs were spherical, with a narrow size distribution and an average particle size of 7.1 ± 1.6 nm. In addition, it was clear that the silver NPs were well monodispersed in the suspension without the use of dispersive reagents. Provided that the reducing ability increased with the glucose concentration, it was thought that Ag(I) was reduced to Ag(0), since the glucose concentration increased in the CNF suspension as a result of processing with the high-pressure wet-type jet mill. The increase in the glucose concentration was probably due to the increased exposure of aldehyde groups on the CNF surfaces.

4. Conclusion

Silver NPs were successfully fabricated using CNF as a reducing reagent with a high-pressure wet-type jet mill at 150 MPa. This jet milling method is very convenient for performing continuous reactions without reducing reagents, such as sodium borohydride or formic acid, or a high-pressure vessel.

REFERENCES