Preparation of Cellulose/Silver Composite Particles Having a Recyclable Catalytic Property

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ABSTRACT: We reported the preparation of porous cellulose particles by the solvent-releasing method, in which a solution of cellulose, dissolved in 1-butyl-3-methylimidazolium chloride and N,N′-dimethylformamide, was dropped into a large amount of 1-butanol using a syringe. The obtained particles had a high specific area because of their porous structure. Herein, to functionalize the cellulose particles, carboxylate groups are introduced into their porous structure by 2,2,6,6-tetramethylpiperidine-1-oxyl-mediated oxidation and ion exchange of carboxylate groups to Ag cations is conducted. Composite cellulose/Ag particles were synthesized by the reduction reaction using the carboxylate groups as a scaffold without free silver nanoparticles in the medium. The obtained composite particles exhibited a high catalytic ability, which was evaluated by examining the reduction of 4-nitrophenol. Moreover, we determined that the catalytic efficiency was maintained for at least three cycles by immobilizing Ag on cellulose particles.

INTRODUCTION

Metal nanoparticles have attracted considerable attention owing to their broad range of applications in areas such as electronics, optics, catalysis, biomedicine, and sensors. Moreover, silver nanoparticles (AgNPs) have been utilized in antibacterial, catalytic, and electronic applications. However, metal nanoparticles, including AgNPs, are generally unstable owing to their large surface area; thus, they tend to aggregate in a medium, which significantly decreases their catalytic activity. Therefore, the addition of a surfactant (stabilizer) or surface modification of metal nanoparticles is generally required to prevent self-aggregation. The immobilization and encapsulation of metal nanoparticles with polymer matrices, including polymer particles, micelles, and hydrogels, have been reported as possible methods to prevent aggregation using the polymer’s high tunability. However, because of their small diameters, which are in the nano and micrometer range, isolating these composite polymer/AgNP catalysts form the reduction-reaction system is complicated. Most composites containing AgNPs were synthesized in the presence of polymer matrices, in which a large amount of free AgNPs should be synthesized in the medium. Furthermore, catalytic-performance tests were performed only once in most of the previous studies.

Cellulose is the most abundant natural polymer on Earth and exhibits many attractive properties such as thermal and chemical stability, nontoxicity, and biocompatibility. Thus, cellulose is extensively used to produce industrial materials such as pulps, regenerated fibers, and membranes. Recently, cellulose particles have been recognized as functional materials that can be used in multiple applications such as removers for organic substances or metals, column-packing materials for biochromatography, or supports for protein immobilization owing to their interesting characteristics including a low nonspecific adsorption of proteins and the availability for surface modification in addition to the abovementioned properties. Therefore, cellulose particles have considerable potential for use as matrices of metal nanoparticles. However, because cellulose is insoluble in water and in most organic solvents because of the formation of a hydrogen bonding network, its dissolution usually requires multistep processes or drastic conditions. Xu et al. reported that AgNPs were successfully synthesized on porous cellulose particles by hydrothermal reduction, in which the cellulose microspheres played the role of a reducing agent for Ag ions, limiting the reduction site only on the cellulose microspheres. However, the dissolution of cellulose still required drastic conditions.

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dissolve cellulose under mild heating conditions.\textsuperscript{33} Since then, ILs have attracted considerable interest as solvents for cellulose.\textsuperscript{10,34,35}

We previously reported preparing porous cellulose particles by the solvent-releasing method (SRM)\textsuperscript{36,37} using a [Bmim]Cl solution of cellulose.\textsuperscript{38} The obtained particles exhibited a high specific surface area,\textsuperscript{39−41} which makes them promising for functional materials applications after modifying their surface. Furthermore, millimeter-sized cellulose particles having a high specific surface area were obtained using a similar method. Owing to their size, the millimeter-sized cellulose particles are easy to handle, and have considerable potential for recyclable scaffolds for catalysis.

In this study, we introduced carboxylate groups into the porous cellulose particles by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation,\textsuperscript{42} which enabled us to selectively convert the hydroxyl groups at the C6 position of the surface of the cellulose microfibrils into carboxylate groups.\textsuperscript{43−46} AgNPs were efficiently synthesized on the porous structures using the carboxylate groups as a scaffold without free AgNPs in the medium. Moreover, we evaluated the catalytic performance and catalyst-recycling ability of the composite cellulose/Ag particles by examining the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).

\section*{RESULTS AND DISCUSSION}

\textbf{TEMPO-Mediated Oxidation of Porous Cellulose Particles.} The cellulose particles were oxidized by a TEMPO-mediated reaction in which the hydroxyl groups at the C6 position of cellulose can be selectively converted to carboxyl groups.\textsuperscript{42} Figure 1 shows images of the wet cellulose particles and scanning electron microscopy (SEM) images of the cross sections of the freeze-dried samples before and after TEMPO oxidation. The cellulose particles had a spherical shape and a porous structure (Figure 1a,a'), which were maintained even after the oxidation (Figure 1b,b'). The specific surface area was 105.3 m\textsuperscript{2}/g, which was determined using the Brunauer–Emmett–Teller (BET) method.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Images of cellulose particles (a,b) and SEM images of the cross sections of freeze-dried cellulose particles (a',b') before (a,a') and after (b',b') TEMPO-mediated oxidation.}
\end{figure}

Fourier transform infrared (FTIR) measurements were performed to confirm the presence of carboxyl groups in the oxidized cellulose particles. Figure 2 shows the FTIR spectra of the samples before and after oxidation. The oxidized cellulose particles exhibited an absorption band at 1620 cm\textsuperscript{−1}, which can be attributed to the carboxylate ion and was not present in the spectrum of the untreated particles. This indicates that the oxidized cellulose particles contained carboxyl groups, which were quantified by electric conductivity titration. Figure 3 shows the relation between the oxidation time and carboxylate content of the oxidized cellulose particles. The carboxylate content increased from 0.1 to 0.4 mmol/g-cellulose with the oxidation time during the first 15 min and then reached a plateau level, indicating that the oxidation reaction occurred within 15 min. However, for cellulose particles having dense structures (5.7 m\textsuperscript{2}/g), which were obtained by drying porous cellulose particles after the preparation, the carboxylate content was 0.2 mmol/g-cellulose for 3 h. These results indicate that almost all hydroxyl groups on the surface and within the porous structures were converted into carboxyl groups.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{FTIR spectra of cellulose particles before (a) and after (b) TEMPO-mediated oxidation.}
\end{figure}

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure3.png}
\caption{Carboxylate contents of porous (circles) and dense (squares) cellulose particles oxidized by TEMPO-mediated oxidation at various oxidation time.}
\end{figure}

\textbf{Preparation of Composite Cellulose/Ag Particles.} To prepare the composite cellulose/Ag particles, the carboxylated cellulose particles were dipped in an aqueous AgNO\textsubscript{3} solution for 5 h, where the Ag cations were coordinated to the carboxyl groups on the cellulose particles. The reduction of Ag cations was then conducted using an aqueous NaBH\textsubscript{4} solution. The color of the cellulose particles changed from colorless to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Color change of cellulose particles before (a) and after (b) AgNP synthesis.}
\end{figure}
yellow-brown, and the transmission electron microscopy (TEM) image of the ultrathin cross section indicates that AgNPs ($D_n = 8.6 \text{ nm}$; $C_v = 33.2\%$) were successfully synthesized in them (Figure 4a,d). Furthermore, the AgNP content on the cellulose particles was determined by thermogravimetric analysis (TGA). Figure 5 shows the TGA curves for the cellulose and cellulose composite particles. The analysis was performed in a nitrogen atmosphere considering the possibility of oxidation of the AgNPs to Ag$_2$O under an oxygen atmosphere. The amount of AgNPs was determined from the remaining weight considering the weight loss of cellulose at 900 °C. The TGA results indicate that 58.5 mg of AgNPs were supported on 1 g of cellulose particles. However, in the cross section of the obtained cellulose/Ag particles, the inside of the material remained colorless, suggesting that AgNPs were produced only at the particle surface (Figure 4b). The TEM images of the ultrathin cross section show clearly that most of the AgNPs aggregated near the surface of the composite cellulose particles (Figure 4b,c). These results can be attributed to the reduction procedure: when the carboxylated cellulose particles dipped in aqueous AgNO$_3$ were immersed in the NaBH$_4$ solution, most of the NaBH$_4$ molecules were consumed to reduce the Ag cations on the surface of the particles before they could diffuse into the particles.

The alcohol reduction method was applied at 160 °C to synthesize AgNPs within the porous structures of cellulose particles. The medium filling in the porous structure of the particles can be changed from water to alcohol at room temperature before the reduction reaction, which made it possible for Ag cations to be uniformly reduced within the porous structures. After reducing Ag cations at 160 °C for 2 h, using ethanol as both the reduction agent and the surrounding medium, the color of the surface and the cross section of the obtained particles became yellow-brown, whereas there was no color change in the reaction medium. This behavior indicated that AgNPs were efficiently synthesized without free AgNPs (Figure 6a–c). Moreover, the cellulose particles maintained their spherical shape and size, indicating that the cellulose did not degrade during reduction. The TEM image of the ultrathin cross section of particles shows that AgNPs with a much higher contrast were supported on the porous structures of the obtained particles (Figure 6d). The $D_n$ and $C_v$ of the AgNPs were 9.8 nm and 25.3%, respectively, which is approximately consistent with the color of the obtained particles owing to the surface plasmon resonance effect. These results indicate that AgNPs were successfully prepared on both the surface and within the porous structure of the cellulose particles. Moreover, from the TGA measurement (Figure 5), 30.8 mg of AgNPs were supported on cellulose particles (1 g), which agrees well with the theoretical value (i.e., 39.7 mg per g of cellulose particles) calculated from the amount of carboxyl in the samples.

**Catalytic Properties of the Composite Cellulose/Ag Particles.** The catalytic performance of cellulose/Ag particles was estimated by monitoring the reduction of 4-NP to 4-AP in...
the presence of NaBH₄ by UV—visible spectroscopy. In this reaction, 4-NP was first converted to the 4-NP ion after adding NaBH₄ and then the 4-NP ion is reduced into the 4-AP ion by NaBH₄ in the presence of a catalyst. When the reduction reaction occurred after adding the obtained cellulose/Ag particles as the catalyst, the intensity of the characteristic peak for the 4-NP ion (at 400 nm) decreased, whereas that of the peak for the 4-AP ion (at 300 nm) increased (Figure 7). If the concentration of NaBH₄ is adjusted to be in large excess compared to the 4-NP concentration, the reaction should be of the first order with regard to the 4-NP concentration; therefore, the catalytic rate can be evaluated. Furthermore, the apparent kinetic rate constant, \( k_{app} \), is known to be proportional to the total surface area of the AgNPs because the catalytic reduction reaction proceeds on their surface. We calculated the rate constant \( k_1 \), normalized to \( S \), which is the total surface area of the AgNPs normalized to the unit volume of the reaction system, defined by the following equation

\[
\frac{\text{d}C_t}{\text{d}t} = k_{app} C_t = k_1 S C_t
\]

where \( C_t \) is the concentration of 4-NP at time \( t \). To calculate \( S \), the bulk density of silver (\( \rho = 10.5 \times 10^3 \) kg/m³) was used. The amount of AgNPs was estimated from the TGA results and did not change after the immobilization reaction and the reduction of 4-NP. Moreover, the diameter of the AgNPs was determined from the TEM results.

Figure 8 shows the relation between \( \ln(A_t/A_0) \) and the reaction time for the cellulose/Ag particles and cellulose-free AgNPs, where \( A_t \) is the absorbance at the determined given wavelength (at 400 nm) at different time.

\[
\ln\left(\frac{A_t}{A_0}\right) = -k_1 t
\]

where \( k_1 \) is the rate constant normalized to the total surface area of the nanoparticles in the reduction system.

Figure 8. Relation between \( \ln(A_t/A_0) \) and time for the catalytic reduction of 4-NP using composite cellulose/Ag particles (circles) and cellulose-free AgNPs (squares); the first (open circles and squares) and second (closed circles) runs are shown.

To solve this problem, the AgNPs were immobilized on the porous cellulose particles made a great contribution to the improvement of the catalytic efficiency.

Moreover, we compared the catalytic activities of our materials to those reported for other systems, as shown in Table 1. The catalytic activity of the AgNPs in the cellulose particles reported in this work (\( 1.86 \times 10^{-2} \text{ s}^{-1} \text{ m}^{-2} \text{ L} \)) is comparable to those particles immobilized in cellulose microspheres (\( 4.42 \times 10^{-2} \text{ s}^{-1} \text{ m}^{-2} \text{ L} \)) and polystyrene-poly(N-isopropylacrylamide) (PS-PNIPAm) core—shell microgels (\( 5.02 \times 10^{-2} \text{ s}^{-1} \text{ m}^{-2} \text{ L} \)) and PS-poly(acrylic acid) (PS-PAA) spherical polyelectrolyte brush particles (\( 7.81 \times 10^{-2} \text{ s}^{-1} \text{ m}^{-2} \text{ L} \)), and is higher than that of the particles encapsulated in a bulk polymer hydrogel (\( 7.80 \) or \( 7.31 \times 10^{-5} \text{ s}^{-1} \text{ m}^{-2} \text{ L} \)).

Microgel nanoparticle catalysts are generally supported on soluble, nano or microsized materials, such as dendrimers or polymeric microspheres, for recycling. In this study, millimeter-sized composite cellulose particles could be easily isolated from the reaction system. However, when the reduction was conducted using recycled cellulose/Ag composite particles recovered after the first reduction, the catalyst activity remarkably decreased (Figure 8) because the AgNPs were detached from the cellulose particles during the reaction and the washing step.

To solve this problem, the AgNPs were immobilized on the cellulose particles through Ag—sulfur (Ag—S) bonds, which were formed by bridging thiol groups to the AgNPs. A condensation reaction between the carboxyl groups of the cellulose/Ag particles and the amine groups of cysteamine was used to introduce the thiol groups on the cellulose particles and form the required Ag—S bonds. The obtained immobilized AgNPs-cellulose particles retained the yellow-brown color, and

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**Table 1. Catalytic Activity of the AgNPs for the Reduction Reaction of 4-NP**

| Samples carrier system | \( D_n (\text{nm}) \)\(^a\) | \( k_1 \) (\( \text{s}^{-1} \text{ m}^{-2} \text{ L} \))\(^b\) |
|------------------------|----------------|-----------------|
| cellulose/Ag 1st run   | cellulose particles; this work | 9.8 ± 2.4 | 1.86 × 10⁻² |
| cellulose—S—Ag 1st run | cellulose particles; this work | 8.6 ± 2.8 | 2.75 × 10⁻³ |
| cellulose—S—Ag 3rd run | cellulose particles; this work | 8.6 ± 2.8 | 3.37 × 10⁻³ |
| ref 20                | cellulose microsphere          | 8.3 ± 3.4 | 4.42 × 10⁻² |
| ref 18                | PS-PNIPAm core—shell microgel  | 8.5 ± 1.5 | 5.02 × 10⁻² |
| ref 19                | PS-PAA/Ag anionic polyelectrolyte | 3 ± 1.2 | 7.81 × 10⁻² |
| ref 22                | PVA/PS-PEGMA hydrogel          | 35 ± 5  | 7.80 × 10⁻³ |
| ref 22                | PVA hydrogel                  | 45 ± 5  | 7.31 × 10⁻³ |

\(^a\) \( D_n \) diameter of AgNPs measured by TEM images.

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**Note:**

- \( k_1 \): Rate constant normalized to the total surface area of the nanoparticles in the reduction system.
- \( D_n \): Diameter of AgNPs measured by TEM images.
AgNPs ($D_{0.3}$ 8.6 nm; $C_{v}$ 33.2%) supported on the porous structure were observed in the TEM image of the ultrathin cross section, although some AgNPs were coagulated (Figure 9). The recycling ability of the obtained particles was investigated. Figure 10 shows the relation between $\ln(A_t/A_0)$ and time for the catalytic reduction of 4-NP using immobilized AgNPs/cellulose particles; the first (circles), second (squares), and third runs (triangles) are shown.

**CONCLUSIONS**

We successfully prepared composite cellulose/Ag particles by introducing carboxylate groups into the porous structures of cellulose particles, which were used as a scaffold for synthesizing AgNPs. The catalytic ability of cellulose/Ag particles for the reduction of 4-NP to 4-AP was much higher than that of cellulose-free AgNPs. Furthermore, when AgNPs were immobilized on the cellulose/Ag particles via Ag–S bonds, the obtained immobilized particles maintained their catalytic performance during the three cycles. The knowledge obtained in this study is readily available for preparing other metal nanoparticles on the cellulose particles, and they can be handled and recycled without a complicated process. Therefore, the resultant materials have great potential for catalyst applications. Moreover, for making the preparation method easy, we have been trying to prepare cellulose composite particles immobilized metal nanoparticles via one step and will report it in the future.

**EXPERIMENT**

**Materials.** Microparticulate cellulose (powder, derived from cotton linter, $M_\text{w}$ 3.0 × 10^5, particles size; 51 μm), [Bmim]Cl, TEMPO, and cysteamine were used as-received from Aldrich Chemical Co., Ltd. N,N-Dimethylformamide (DMF), 1-butanol, ethanol, a phosphate pH standard equimolar solution (pH 6.86 at 25 °C), a sodium hypochlorite (NaClO) solution, sodium chlorite (NaClO2), hydrochloric acid, sodium hydrate (NaOH), silver nitrate (AgNO3), sodium borohydride, 4-NP, and N,N′-dicyclohexylcarbodiimide (DCC) were used as-received from Nacalai Tesque Inc. (Kyoto, Japan). N-Hydroxysuccinimide (NHS) was used as-received from Tokyo Chemical Industry Co., Ltd. The water used in the experiments was purified using an ErixUV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ cm.

**Preparation of Millimeter-Sized Cellulose Particles by SRM.** Millimeter-sized cellulose particles were prepared by SRM, according to our previous reports. Microcrystalline cellulose powder was dissolved in [Bmim]Cl at a weight ratio of 7:43 upon heating at 100 °C for 7 h. DMF was added as a cosolvent to reduce the viscosity of the solution. This cellulose–[Bmim]Cl–DMF (7/43/50, w/w/w) (8.57 g) mixture was then dropped into a large amount of 1-butanol (ca. 100 mL) under stirring (using a syringe) to remove the [Bmim]Cl and DMF from the drops. The cellulose present in the solution immediately precipitated in the form of cellulose particles, which were washed three times with 1-butanol and twice with water to remove any remaining impurities. The cellulose particles were stirred for 2 h between each washing step. The original microcrystalline cellulose had a cellulose I type crystal. However, the particles prepared by SRM changed the crystal structure to cellulose II type with very small crystals.

**TEMPO-Mediated Oxidation of Porous Cellulose Particles.** TEMPO-mediated oxidation was conducted according to the following procedure: TEMPO (3 mg) and NaClO2 (22 mg) were dissolved in a phosphate pH standard equimolar solution (10 mL, pH 6.86 at 25 °C). Then, a NaClO solution (7.5 wt %, 10 mL; diluted in a standard buffer solution) was added into the mixture, and the cellulose particles (80 mg) were immersed in this solution for 1 h upon stirring. Oxidation was performed by stirring the mixture at 60 °C in a 50 mL flask, and the obtained carboxylated cellulose particles were thoroughly washed with water.

**Preparation of Composite Cellulose/Ag Particles.** The carboxylated cellulose particles (80 mg) were immersed in aqueous AgNO3 solution (40 mL, 6.4 mM) for 5 h at room temperature upon stirring. The obtained particles were washed with water twice over 2 h to remove the free Ag cations. Reduction of the Ag cations was performed for 2 h using either aqueous NaBH4 solution at room temperature in a glass bottle.
or ethanol at 160 °C in an autoclave. The obtained cellulose/Ag particles were thoroughly washed with water to remove the free Ag cations and AgNPs.

For immobilizing the as-prepared AgNPs on the cellulose particles for improving the recyclable catalytic performance, the immobilization through covalent bonds was achieved as follows: the obtained cellulose/Ag particles (35 mg) were first dispersed in a DMF (10.0 g) medium containing dissolved DCC (26.9 mg), NHS (14.9 mg), and cysteamine (1.2 mg) and then stirred at room temperature for 2 h. The obtained cellulose/Ag particles were thoroughly washed with DMF and preserved in water.

**Estimation of the Catalytic Performance of AgNPs in the Composite Cellulose Particles.** The catalytic efficiencies of the composite cellulose particles were evaluated using the reduction of 4-NP to 4-AP in the presence of NaBH₄ as a model reaction. The AgNPs were used as catalysts. In the experiments, NaBH₄ (90.8 mg) was first added to an aqueous 4-NP solution (40 mL, 0.06 mM); furthermore, a part of the obtained mixture (4 g) was poured into a quartz cuvette, and the composite particles (3.5 mg) were dispersed in it. The reduction reaction occurred in the quartz cuvette and was monitored at fixed time intervals by UV−visible spectroscopy (UV-2500 UV−vis spectrophotometer, Shimadzu Corp., Kyoto, Japan).

**Characterization.** The cellulose particles were immersed in liquid nitrogen, freeze-dried in a freeze-dryer (FDU-1200, Tokyo Rikakikai Co., Ltd.; Tokyo, Japan), and observed using a scanning electron microscope (JSM-6510, JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV after platinum coating. To analyze their inner morphology, ultrathin (100 nm-thick) cross sections of the particles were prepared using a cryomicrotome (Leica EM UC6 equipped with EM FC7). The sliced samples were then observed using a transmission electron microscope (JEM-1230, JEOL, Tokyo, Japan). The number-average diameter (Dₐ) and the coefficient of variation (Cᵥ) were estimated from 200 AgNPs on the TEM images using image analysis (WinRoof, Mitani Co., Ltd., Japan). Nitrogen adsorption measurements were performed using a Quantachrome NOVA 3200e instrument (USA). BET specific surface area of the cellulose particles was assessed from the adsorption branch of the isotherm for a relative pressure of 0.05−0.3 at 77 K.

The products were qualitatively analyzed using a FTIR spectrometer (FT-IR, FT/IR-6200, JASCO, Tokyo, Japan) and the pressed KBr pellet technique. The electric conductivity titration method was applied to quantify the amount of carboxylate in the cellulose particles. Briefly, dried cellulose particles (80 mg) were immersed in hydrochloric acid (15 mL, 0.01 M) and disintegrated into a well-dispersed slurry by ultrasonication. Furthermore, aqueous NaOH solution (0.01 M) was added to the mixture at a rate of 0.4 mL/min while monitoring the electric conductivity of the system using a conductance meter (E-74, HORIBA Corp., Kyoto, Japan).

The amount of AgNPs supported on the cellulose particles was measured using a thermogravimetric analyzer (EXSTAR TG/DTA6200, SII Nano Technology Inc., Japan) at a heating rate of 10 °C/min from 30 to 900 °C under a nitrogen atmosphere.

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**Author Contributions**

H.M., T.S., and T.O. contributed to the design of the research and experiments. Y.F., K.I., and T.O. conducted the experiments. Y.F. wrote the first draft of the manuscript and H.M. and T.O. assisted in the writing process and data analysis.

**Notes**

The authors declare no competing financial interest.

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