Size-Controlled Preparation of Gold Nanoparticles Deposited on Surface-Fibrillated Cellulose Obtained by Citric Acid Modification

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ABSTRACT: Cellulose-based functional materials have gained immense interest due to their low density, hydrophilicity, chirality, and degradability. So far, a facile and scalable preparation of fibrillated cellulose by treating the hydroxy groups of cellulose with citric acid (F-CAC) has been developed and applied as a reinforcing filler for polypropylene composite. Herein, a size-selective preparation of Au nanoparticles (NPs) stabilized by F-CAC is described. By modifying the conditions of transdeposition method, established in our group previously, a transfer of Au NPs from poly(*N*-vinyl-2-pyrrolidone) (PVP) to F-CAC proceeded up to 96% transfer efficiency with retaining its cluster sizes in EtOH. Meanwhile, the deposition efficiency drastically decreased in the case of nonmodified cellulose, showing the significance of citric acid modification. A shift of binding energy at Au 4f core level X-ray photoelectron spectroscopy from 82.0 to 83.3 eV indicated that the NPs were stabilized on an F-CAC surface rather than by PVP matrix. The reproducible particle size growth was observed when 2-propanol was used as a solvent instead of EtOH, expanding the range of the available particle size with simple manipulation. The thus-obtained Au:F-CAC nanocatalysts exhibited a catalytic activity toward an aerobic oxidation of 1-indanol in toluene to yield 1-indanone quantitatively and were recyclable at least six times, illustrating high tolerance against organic solvents.

INTRODUCTION

In decades, bioresource-based functional materials, derived from naturally abundant materials such as woods and crustacean shells, have attracted much attention from the viewpoint of sustainable development and environment-friendly science. Among them, cellulose is a common biomacromolecule used in the world,¹ and nanocellulose,^{2,3} represented by cellulose nanofiber (CNF) and/or nanocrystal (CNC), is an important research target in the field of the materials, medicinal, and polymer chemistry because not only of the environmental issues but also its unique properties, which inorganic materials scarcely exhibit, such as flexibility, biodegradability, and so on. Thanks to the pioneering works by Isogai^{4c,e} and Yano,^{4a,d} CNF has been widely utilized in various industrial and scientific fields. Meanwhile, a surface and chemical modification of cellulose has been investigated so far to enhance their physical properties and/or to add other functionalities on it. Members of our group also developed a facile and scalable fabrication of surface-fibrillated cellulose by modifying the hydroxy groups of cellulose with citric acid (F-CAC), allowing us to obtain a bunch amount of fibrillated cellulose (~100 g/batch) through easy manipulation (Scheme 1A).^{5a,b} The electrostatic repulsion between citric acid moieties of each cellulose fibril prevents their agglomeration, retaining

their fibrillated state, whereas the CNF and cellulose microfibrils prepared by physical fibrillation method using a grinding mill suffer from an agglomeration of fibril at high concentration. Among our study on the application of the F-CAC to a reinforcing filler for polymers^{5a,b} and supramolecular hydrogels^{5c,d,e} to improve their mechanical properties, its large surface area and tolerance against organic solvents turned our attention to exploit it as a solid support for metal nanoparticles (NPs).

Metal NPs with auxiliary stabilizers, such as functionalized polymers,⁶ dendrimers,⁷ and organic ligands,⁸ have attracted significant interest in the field of the catalyst for organic reaction. Although various kinds of polymer-stabilized metal NPs have been developed so far, these catalysts often suffer from their poor reusability due to the solubility in organic solvents. Therefore, an additional elaboration on matrices is sometimes required to make the recycle process practical. In

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Scheme 1. Fabrication Scheme of Fibrillated Citric Acid-Modified Cellulose (F-CAC) (A) and Size-Selective Preparation of Au:F-CAC (B)

A) Preparation of fibrillated citric acid-modified cellulose

B) This work: size-selective preparation of Au:F-CAC through trans-deposition

the course of our study on the matrix effect of the catalytic activity at the metal surface and the interface science^{9,14b} of the polymer-stabilized metal NPs including biomacropolymers such as chitosan and starch,¹⁰ we are also interested in the inherent properties of cellulose, namely, its hydrophilicity and the high tolerance against organic solvents, which must be suitable for the matrix under the organic solvent conditions. In addition, the specific properties of F-CAC, such as the coordination ability and the Brønsted acidity of the residual dicarboxylic acid moiety, and intrinsic chirality of cellulose, were also expected to give us the opportunities to develop the unique chemical reactions. Herein, we report a preparation method of various sizes of Au NPs deposited on F-CAC by transdeposition method and their catalytic activity toward oxidation of alcohol under an organic solvent condition (Scheme 1B).

RESULTS AND DISCUSSION

Though cellulose–Au nanoparticle hybrid materials are well studied and some of the preparation methods are already established,¹¹ it is also known that the catalytic activity of metal NPs is strongly affected by their cluster sizes.¹² Therefore, development of a method for size-controlled preparation of metal NPs is a promising way to tune their catalytic activity. So far, we have established methods for size-selective preparation of AuNPs using poly(*N*-vinyl-2-pyrrolidone) (PVP) as a stabilizing matrix.¹³ The thus-prepared Au:PVP catalysts were applied for an aerobic oxidation of benzyl alcohol to reveal that the catalytic activity is influenced by the particle size.^{9a,13} In addition, the size-selectively prepared Au NPs are able to be transferred from PVP to a solid support, such as hydroxyapatite, with retaining their particle size using PVP(K-15) as a transient matrix.¹⁴ Hence, by integrating these two methods, it is possible to achieve the size-selective preparation of Au NPs deposited on a solid support. We started our investigations from the optimization of deposition conditions using Au:PVP(K-15) (2.5 μmol of Au) with a particle size of 1.7 ± 0.3 nm, and F-CAC (0.9 wt % citric acid loading) (25 mg). The transfer efficiency might be affected by the acidity of the solvent due to the surface condition and/or isoelectric point of F-CAC; therefore, the pH

value was adjusted by 0.1 mol/L aqueous hydrogen chloride solution. First, the transdeposition was attempted at 90 °C in H₂O/EtOH mixed solvent, and the pH condition was screened. Quantitative deposition was nearly achieved in a range of pH below 4, but the aggregation of Au NPs occurred and resulted in the substantial size growth (Table 1, entry 1).

Table 1. Optimization of Deposition Conditions^a

entry	pH	temperature (°C)	size (nm)	efficiency (%) ^b	wt %
1	3	90	4.4 ± 0.6	99	1.9
2	4	90	2.6 ± 0.5	93	1.7
3	5	90	2.6 ± 0.7	74	1.4
4	4	70	2.6 ± 0.5	87	1.7
5	4	50	2.5 ± 0.4	88	1.7
6	4	27	1.7 ± 0.4	87	1.7
7	4	0	1.8 ± 0.3	87	1.7
8 ^c	4	27	1.6 ± 0.3	86	1.7
9 ^{c,d}	4	27	1.8 ± 0.3	96	0.9
10 ^{c,d,e}	4	27	2.2 ± 0.6	22	0.2
11 ^f	4	27	1.7 ± 0.3	96	0.9

^aAu:PVP(K-15, 1.7 ± 0.3 nm) (2.5 μmol), F-CAC (25 mg), and H₂O/EtOH (0.5 mL/1.5 mL) were used. ^b[Au:F-CAC (mmol)]/[Au:PVP (mmol)] $\times 100$. ^cEtOH (2.0 mL) was used. ^dAu:PVP(K-15, 1.7 ± 0.3 nm) (1.25 μmol) were used. ^eUnmodified cellulose was used. ^fAu:PVP(K-15, 1.7 ± 0.3 nm) (12.5 μmol), F-CAC (250 mg), and EtOH (20 mL) were used.

At pH = 4, Au:F-CAC with a size of 2.6 ± 0.5 nm was obtained in 93% deposition efficiency (entry 2), whereas the deposition efficiency was not sufficient in the case of a pH value above 4 (entry 3). In our previous reports, the electron density at the surface of Au NPs protected by PVP was evaluated by the X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) measurements.^{9a} These experiments clarified that the Au surface was negatively charged due to the electron donation from the carbonyl group of PVP. In this case, the carboxylic acid of the F-CAC would be transformed to a carboxylate under high pH condition that may reduce the transfer efficiency because of the electrostatic repulsion between the Au surface and carboxylate. The increasing of the particle size of Au NPs at low pH condition would be

Figure 1. TEM images and their size distribution of Au:F-CAC (Table 2).

ascribed to the high Cl^- concentration, which often induces the aggregation of Au NPs. To this end, we decided to continue the optimization under $\text{pH} = 4$ condition. Significant improvement was not observed by decreasing the temperature to 70 or 50 °C (entries 4 and 5); meanwhile, the particle size was retained when the deposition was performed below 27 °C (entries 6 and 7). As the use of pure EtOH as a solvent did not affect the transfer efficiency (entry 8), the investigation was continued with using EtOH as a solvent for facile operation. The best result was obtained when a half amount of Au:PVP (1.25 μmol) was used, yielding Au:F-CAC in 96% efficiency with maintaining the same particle size and the distribution from the initial Au:PVP (entry 9, Figure 1, and Figure S2). It is noteworthy that the deposition did not work successfully when unmodified cellulose (without citric acid modification and fibrillation) was used instead of F-CAC under the same conditions (entry 10), clearly indicating the crucial role of citric acid modification and/or nanofibrillation for efficient transdeposition. The enhancement of deposition efficiency would be attributed to the fluffy surface structure of F-CAC. Additionally, it is also possible that the bidentate coordination of citric acid moieties to the Au surface occurred, immobilizing Au NPs effectively. Moreover, this condition was applicable to a 250 mg scale preparation in a batch without additional optimization (entry 11). We also conducted the transdeposition using F-CAC with higher citric acid loading (1.8 wt %) under the same conditions, but severe aggregation of Au NPs and low deposition efficiency (<20%) were observed. With the optimized deposition conditions in hand, we applied these conditions to the Au:PVP with the other particle sizes. In all cases, the Au NP transfer from PVP to F-CAC uneventfully proceeded to give four different sizes of Au:F-CAC with keeping their particle sizes within the error margin (Table 2, Figure 1, and Figure S2).

During the optimization study, we found that the particle size of Au:F-CAC was influenced by the solvent (Table 3). The size-retaining deposition was achieved in both EtOH and MeOH solutions; however, EtOH was superior to the

Table 2. Transdeposition from PVP to F-CAC with Particle Sizes of 2.3, 4.8, and 9.5 nm^a

entry	size of Au:PVP (nm)	size of Au:F-CAC (nm)	efficiency (%) ^b	wt %
1 ^c	1.7 ± 0.3	1.7 ± 0.3	96	0.9
2	2.3 ± 0.5	2.5 ± 0.4	94	0.9
3	4.8 ± 0.7	4.9 ± 0.6	95	0.9
4	9.5 ± 1.7	9.5 ± 1.9	85	0.8

^aAu:PVP(K-15) (1.25 μmol), F-CAC (25 mg), EtOH (2.0 mL), $\text{pH} = 4$, 27 °C, 90 min. ^b[Au:F-CAC (mmol)]/[Au:PVP (mmol)] × 100.

^cEntry 11 in Table 1.

Table 3. Solvent Dependency on Deposition of Au NP from PVP to F-CAC^a

entry	solvent	size (Au:PVP) (nm)	size of Au:F-CAC (nm)	efficiency (%) ^b	wt %
1	EtOH	1.8 ± 0.3	1.8 ± 0.3	96	0.9
2	MeOH	1.8 ± 0.3	1.8 ± 0.4	85	0.8
3	1-PrOH	1.8 ± 0.3	2.1 ± 0.3	97	0.9
4	1-BuOH	1.8 ± 0.3	2.4 ± 0.5	98	1.0
5	2-PrOH	1.8 ± 0.3	3.4 ± 0.7	97	0.9
6	2-PrOH	2.5 ± 0.4	4.3 ± 0.7	95	0.9
7	2-PrOH	4.9 ± 0.6	5.2 ± 0.7	94	0.9
8	2-PrOH	9.5 ± 1.9	9.9 ± 2.2	91	0.9

^aAu:PVP(K-15) (1.25 μmol), F-CAC (25 mg), $\text{pH} = 4$, 27 °C, 90 min. ^b[Au:F-CAC (mmol)]/[Au:PVP (mmol)] × 100.

efficiency of the transfer (entries 1 and 2). In the case of larger alcohol solvent, the reproducible aggregation happened to furnish the slightly larger Au NP with keeping a Gaussian function shape size distribution (entries 3–5). Hence, this result indicated the possibility to control the size distribution of Au NPs only by changing the solvent. In addition, the tendency of the size growth seemed to be correlated with their lipophilicity. This phenomenon might be ascribed to the solubility of PVP in organic solvents. Namely, the entanglement of PVP to NPs might be loosened when an appropriate

Figure 2. Au 4f core level XP spectra (A) and Au L₃-edge XANES spectra (B) of Au:F-CAC.

Figure 3. Reusability test of Au:F-CAC (1.8 ± 0.3 nm).

solvent, which has a relevant solubility parameter, such as Hildebrand¹⁵ and/or Hansen solubility parameters,^{16,17} was used. Indeed, the deposition was carried out using different sizes of Au:PVP and 2-PrOH as a solvent to afford Au:F-CAC with particle sizes of 3.4 ± 0.7 , 4.3 ± 0.7 , 5.2 ± 0.7 , and 9.9 ± 2.2 nm with good reproducibility, allowing us to reach various sizes of Au:F-CAC (entries 5–8, Figure S3).

The surface morphology of the thus-prepared Au:F-CAC and F-CAC were observed by scanning electron microscopy (SEM) (Figure S4). It was observed that the fluffy surface morphology was retained even after deposition of Au NPs, indicating that morphology of the F-CAC scarcely changed before and after the transposition. Fourier transformed infrared (FT-IR) measurement of Au:F-CAC exhibited a similar spectrum to that of F-CAC with a slight intense signal observed at 1667 cm^{-1} , assignable to the stretching vibration of a C=O bond, which indicated the existence of carbonyl group in the Au:F-CAC sample (Figure S5). Since it was difficult to determine whether the origin of the signal was the remaining PVP or the oxidative degradation of F-CAC by Au NPs, XPS measurements were carried out. As a result, a signal corresponding to N 1s core level was observed in all samples by survey scan measurement using Mg K α radiation, indicating the contamination of the residual PVP (Figures S6–S10). To clarify the surrounding environment around Au NPs, Au 4f

XPS measurement was carried out using monochromatized Al K α radiation (Figure 2A). The binding energy of Au 4f_{7/2} core level of Au:PVP was observed at 82.0 eV^{9a} due to the electron donation from the oxygen of the carbonyl group, whereas those of Au:F-CAC showed a higher value than 83.3 eV. The high energy shift indicated that Au NPs were mainly located on an F-CAC surface rather than on PVP. Au L₃-edge X-ray absorption near edge structure (XANES) spectrum of Au:F-CAC (1.8 ± 0.3 nm) resembled that of bulk Au, indicating the absence of Au(I) and/or Au(III) species (Figure 2B). In addition, a slightly smaller intense white line signal (11 925 eV) and a broadening of the peak were observed, which are typical electronic structures of Au NP.¹⁸

The catalytic activity of these Au:F-CACs was evaluated by an aerobic oxidation of 1-indanol (**1a**) (Figure 3). In the presence of Au:F-CAC (1.8 ± 0.3 nm) (1.0 atom % Au) and K₂CO₃ (300 mol %), the oxidation of **1a** took place smoothly to afford 1-indanone (**2a**) in 96% yield after stirring for 6 h under an O₂ atmosphere (1 atm, balloon). Through the screening of the solvent, the use of low-polarity solvents, such as toluene and dichloromethane, was found to be the suitable one for the catalytic oxidation reaction (Table S2). To check the durability of the catalyst, the reusability test was carried out. Au:F-CAC used in the first cycle was separated by filtration and washed with toluene, and then, the residue was

used in the next cycle without drying. As a result, it was found that the Au:F-CAC catalyst is reusable at least six times without significant loss of its catalytic activity (Figure 3). Moreover, the particle size of Au:F-CAC still remained unchanged even after the sixth cycle, proving the stability of the composite. During the course of the recyclability experiments, the aggregation of F-CAC was not observed. The amount of leached Au species was also checked by ICP-AES measurement to find that the loading amount of Au did not change (0.9 wt %) after the sixth cycle, and the Au species was not detected from the reaction mixture after filtration and concentration. A survey for the size-dependent catalytic activity was conducted. The larger sizes of Au:F-CACs were also applied for the reaction to give **2a** almost quantitative yield (Table 4, entries 1–4). To observe a size-dependent catalytic

Table 4. Oxidation of 1-Indanol (1a**) Using Au:F-CAC Nanocatalyst**

entry	Au:F-CAC (nm)	yield (%) ^a
1	1.8 ± 0.3	96
2	2.5 ± 0.4	97
3	4.9 ± 0.6	99
4	9.5 ± 1.9	98
5 ^b		0
6 ^c		0

^aDetermined by GC analysis. ^bWithout Au:F-CAC. ^cF-CAC (25 mg) was used instead of Au:F-CAC.

activity, the time course for the production of **2a** was monitored by gas chromatography to find that the reaction rate was independent from these particle sizes (Figure S12). Next, the aerobic oxidation of **1a** with different amounts of K₂CO₃ ranging from 25 to 300 mol % was carried out (Figure 4). The reaction was accelerated as the amount of K₂CO₃ increased, and this reaction followed pseudo-first-order kinetics against the amount of K₂CO₃. Considering the poor solubility of inorganic base to organic solvent, concentration of the dissolved K₂CO₃ is thought to be saturated. The fact that the positive linear correlation is still observed suggests that the reaction proceeds at the solid–solid interface between Au NPs

and K₂CO₃. After all, the rate-determining step of this reaction is dominated by the concentration of K₂CO₃, and the observation of size-dependent catalytic activity was turned out to be difficult in the case of the model system. The reaction did not occur in the absence of Au NP or catalyst (entries 5 and 6), which indicated that this reaction was not catalyzed by the F-CAC matrix. A filtration experiment was also conducted to confirm the actual catalytic species (Figure S11). After stirring for 2 h, the solid materials were removed from the reaction mixture by filtration using a membrane filter and then the reaction was continued using the filtrate. As a result, the reaction was completely terminated after filtration regardless of the presence of K₂CO₃ or not. This result strongly supported that the catalytic site is on the surface of Au NPs and not by the leached Au species. The activation energy was determined from the Arrhenius plots in a temperature range of 270–330 K, and the least-squares linear fitting yielded a value of 38.5 kJ/mol (Figures S13 and S14).

The reaction conditions were applicable to the oxidation of primary and secondary alcohols **1** to afford products **2** (Scheme 2). Oxidation of electron-neutral and -rich primary benzyl alcohol, such as **1b–1e**, smoothly proceeded to afford aldehydes **2b–2e** in high yield. Meanwhile, oxidation of benzyl alcohol bearing an electron-withdrawing trifluoromethyl group at para position (**1f**) was found less favorable for the reaction conditions to give aldehyde **2f** in 42% yield. Substrates having substituent at the ortho position (**1g** and **1h**) were also applicable for the conditions to afford **2g** and **2h**, respectively, in moderate yield. The relatively low yield of sterically hindered substrates would be ascribed to the slow adsorption process onto the Au surface. Substrate containing pyridine ring (**1i**) also participated in the reaction to give **2i** in 64% yield. Oxidation of acyclic secondary benzyl alcohol (**1j**) was examined to give **2j** in 45% yield. The oxidation of aliphatic alcohol was conducted but resulted in the observation of no reaction.

CONCLUSIONS

The transdeposition from size-selectively prepared Au NP from PVP(K-15) to F-CAC was achieved. Thanks to the high organic solvent tolerance of cellulose, the polymer-stabilized nanocatalyst is able to be used in organic solvents with easy recycling process. Although the size dependency of Au:F-CAC is still not uncovered, the exploration of suitable model reaction has been continued. In addition, since cellulose is

Figure 4. Time-course plots of aerobic oxidation of 1-indanol using varying amounts of K₂CO₃ (A) and linear fitting of the plots against the rate constant (B). Au:F-CAC (1.8 ± 0.3 nm) was used as a catalyst.

Scheme 2. Substrate Scope^a

^aYield was determined by GC analysis.

intrinsically chiral resource, Au:F-CAC may be applicable for catalytic asymmetric reactions.¹⁹ Furthermore, metal-immobilized catalysts are also expected to be prepared by utilizing the residual dicarboxylic moiety, which serves as a bidentate ligand for metal ions. The discovery of unique applications, which takes advantage of the characteristics of F-CAC, will be reported in due course.

EXPERIMENTAL SECTION

Au:PVPs(K-15)^{13b,20} and fibrillated citric acid-modified cellulose (F-CAC)^{5a,b} were prepared according to the literature.

Procedure for Preparation of F-CAC (ca. 0.9 wt % Citric Acid Loading). To a 500 mL round-bottomed flask were added cellulose (30 g), distilled water (300 mL), and 1 mol/L aqueous NaOH solution (1.4 mL). To the dispersion was added citric acid (90 g), and then the mixture was stirred for 30 min at room temperature. The mixture was transferred to a heat-resistant dish and incubated in an oven at 130 °C for 13 h. After cooling to room temperature, the residual citric acid was removed by washing with water until the pH of filtrate was approximately pH 7. After that, the modified cellulose was successively washed with methanol (300 mL), acetone (300 mL), and then dried under vacuum to give F-CAC (ca. 0.9 wt % citric acid loading) as a colorless powder. The surface morphology of cellulose before and after modification was compared by SEM observation. The surface morphology of cellulose and F-CAC is shown in Figure S1. The loading amount of citric acid was determined by titration using aqueous HCl and NaOH solutions.

Procedure for Preparation F-CAC (ca. 1.8 wt % Citric Acid Loading). To a 500 mL round-bottomed flask were added cellulose (30 g), distilled water (300 mL), and 1 mol/L aqueous NaOH solution (1.4 mL). To the dispersion was added citric acid (90 g), and then the mixture was stirred for 30 min at room temperature. The mixture was transferred to a heat-resistant dish and incubated in an oven at 130 °C for 30 h.

After cooling to room temperature, the residual citric acid was removed by washing with water until the pH of filtrate was approximately pH 7. After that, the modified cellulose was successively washed with methanol (300 mL), acetone (300 mL), and then dried under vacuum to give F-CAC (ca. 1.8 wt % citric acid loading) as a pale yellow powder. The surface morphology of cellulose before and after modification was compared by SEM observation. The loading amount of citric acid was determined by titration using aqueous HCl and NaOH solutions.

General Procedure for Preparation Au:F-CAC through Transdeposition Method. In a reaction tube ($\varphi = 10$ mm) equipped with a magnetic stir bar, Au:PVP(K-15) and F-CAC (25 mg) were mixed in solvent (2 mL), and then pH value was adjusted using an aqueous hydrochloric acid solution (0.1 mol/L). After stirring at 1300 rpm for 90 min, the solid was separated from the supernatant by centrifugation at 7500 rpm at room temperature and washed with ethanol (ca. 10 mL) three times. The remaining powder was dried under vacuum at 45 °C for 12 h to afford Au:F-CAC as a powder.

General Procedure for Aerobic Oxidation of 1-Indanol (1a). To a reaction tube ($\varphi = 10$ mm) equipped with a magnetic stir bar were added Au:F-CAC (1.0 atom%), 1-indanol (1a) (0.25 mmol), K₂CO₃ (0.75 mmol), and toluene (1 mL). The mixture was stirred at 27 °C under an O₂ atmosphere. After stirring for a specific time, the catalyst was removed by filtration and washed with toluene (ca. 3 mL $\times$ 3). To the filtrate was added *n*-hexadecane (36.8 μ L, 0.125 mmol) as an internal standard, and then the mixture was agitated. GC measurement was performed using an aliquot of the sample solution to determine the yield. The catalyst was used in the next cycle without drying.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c04894>.

Instrumentation and chemicals; sample preparation; optimization of reaction atmospheres; picture of Au:F-CAC after centrifugation; SEM and TEM images; FT-IR and XPS spectra; filtration experiment; and graphs of time-course plots for kinetic study (PDF)

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Notes

The authors declare no competing financial interest.

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