Development of Thermally-resistant Gold Nanoparticles

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Gold nanoparticles are expected as new materials for optical devices owing to their size-related properties. However, the typical gold nanoparticles surrounded by long-chain alkane thiols 1 (ligand molecules) are not tolerant of heating process because the interactions between the ligand molecules are not strong enough. In order to develop thermally-resistant gold nanoparticles, the authors focus on the functional groups which can form strong interactions between the ligand molecules such as hydrogen bonding and π-π stacking. In this study, 6 types of ligand molecules were synthesized and the thermal stability of the corresponding gold nanoparticles was evaluated by thermo gravimetry (TG) and differential scanning calorimetry (DSC). And, it was found that the thermal stability highly depended on the chemical structure of the ligand molecules. Since the amide group and the tolyl group which were introduced into the ligands had the ability to form intermolecular hydrogen bonding and π-π stacking, respectively. Therefore, the gold nanoparticle surrounded by amide-toly type ligand 3b was considered to be most thermally stable owing to the strong interactions between the functional groups.

Key words: gold nanoparticle, thermal stability, interligand interaction, hydrogen bonding, π-π stacking

1. INTRODUCTION

Gold nanoparticles have great potential as the materials for optical devices, chemical catalysts and biological sensors due to their size-related optical, electronic, and magnetic properties.1-5 Nanosized gold particles have strong affinity and it is very difficult to isolate them from each other. Therefore, in order to prevent the nanoparticles from aggregating, the gold core is generally surrounded by the organic molecules which are called ligands. Brust et al. reported that the gold nanoparticles surrounded by long-chain alkanethiols showed high dispersibility in nonpolar organic solvents and have high preservation stability in powder condition6 in comparison with the conventional ligands such as citrate7 and PPh3 (Schmid’s cluster). Accordingly, many studies concerning gold nanoparticles have been conducted using the long-chain alkanethiols as the ligands.9 However, from the viewpoint of thermal stability of the gold nanoparticles, the long-chain alkanethiols admit of improvement.

In the case of the typical long-chain alkanethiol 1, the thiol group anchors the ligand molecule to the surface of the gold core. On the other hand, the long-chain alky groups interact intermolecularly with each other by van der Waals force and stabilize the gold nanoparticle. However, since van der Waals interaction is weak, the gold nanoparticles surrounded by the typical ligand 1 are not tolerant of heating process.

Consequently, aiming for developing thermally-resistant gold nanoparticles, the authors designed the novel ligands which contained the functional groups such as an amide group and/or a tolyl group (Figure 1).

The amide group which was introduced into ligands 2 and ligand 3b can form intermolecular hydrogen bonding.

On the other hand, the tolyl group of ligands 3 is expected to form π-π stacking. Owing to the combination of these interligand interactions, the packing of the ligands becomes tight and the thermal stability of these gold nanoparticles is expected to be improved drastically. In this study, the six novel ligands (2 and 3) were synthesized and the thermal stability of the corresponding gold nanoparticles was evaluated by thermo gravimetry (TG) and differential scanning calorimetry (DSC).

Figure 1 Chemical structures of long-chain alkanethiol 1 and synthesized ligands 2, 3.

2. EXPERIMENTAL

Tetrahydrofuran (THF) was purified by distillation and stocked under N2 atmosphere. Other chemicals were used without further purification. 1H NMR spectra were measured using JEOL AL-400 and infrared absorption measurement was carried out with JEOL FT/IR-620.

2.1 Synthesis

2.1.1 Amide type ligands 2

The amide type ligands 2 were synthesized according to the Chambers’s method.10

2.1.2 Toly-ester type ligand 3a

The synthetic route for the toly-ester type ligand 3a is shown in Scheme 1.
3-(tritylthio)propanoic acid was synthesized according to the method reported by Polidoli et al.\textsuperscript{11}

\begin{align*}
\text{HO-} & \quad \text{Br} \\
& \quad \text{(a)}
\text{HO-} & \quad \text{S} \\
& \quad \text{(b)}
\text{HS-} & \quad \text{S} \\
& \quad \text{(c)}
\end{align*}

Scheme 1 Synthetic route for tolyl-ester type ligand 3a; (a) p-cresol, KOH, EtOH, reflux, overnight. (b) 3-(tritylthio)propanoic acid, 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide hydrochloride (EDC), 4-dimethylaminopyridine (DMAP), CH$_2$Cl$_2$, rt, overnight. (c) trifluoroacetic acid, triethylsilane, rt.

11-(p-tolyloxy)undecyl-1-ol 5 was obtained by the reaction of 11-bromoundecan-1-ol 4 with p-cresol in the presence of KOH. Subsequently, 11-(p-tolyloxy)-undecyl 3-(tritylthio)propanoate 6 was synthesized from the compound 5 and 3-(tritylthio)propanoic acid using EDC as the condensation agent. Finally, the trityl group (the protective group of thiol) was removed and 11-(p-tolyloxy)undecyl 3-mercaptopropanoate 3a was obtained (Total yield from the compound 4 : 66 %).

\begin{align*}
\text{HO-} & \quad \text{T} \\
& \quad \text{(a)}
\text{HS-} & \quad \text{S} \\
& \quad \text{(b)}
\end{align*}

2.1.3 Toly-amine type ligand 3b

The synthetic route for the tolyl-amine type ligand 3b is shown in Scheme 2.

\begin{align*}
\text{HO-} & \quad \text{H} \\
& \quad \text{(a)}
\text{HS-} & \quad \text{S} \\
& \quad \text{(c)}
\end{align*}

Scheme 2 Synthetic route for tolyl-amine type ligand 3b; (a) PBr$_3$, CH$_2$Cl$_2$, 0°C to rt, overnight. (b) NaN$_3$, CH$_2$CN, reflux, overnight, then LiAlH$_4$, THF, 0 °C, 1 h. (c) 3-(tritylthio)propanoic acid, EDC, DMAP, CH$_2$Cl$_2$, rt, overnight. (d) trifluoroacetic acid, triethylsilane, rt.

1-(11-bromoundecyloxy)-4-methylbenzene 7 was synthesized from the amino compound 8 according to the Chambers’ method\textsuperscript{15} (Total yield from the compound 5 : 9%). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$): δ 7.05 (d, 2H, Ph), 6.78 (d, 2H, Ph), 5.60 (br, 1H, NH), 3.92 (t, 2H, CH$_2$O), 3.27 (q, 2H, CH$_2$N), 2.82 (q, 2H, SCH$_2$), 2.47 (t, 2H, CH$_2$CO), 2.28 (s, 3H, CH$_3$), 1.76 (m, 2H, CH$_3$), 1.61 (t, 1H, SH), 1.5-1.2 (br, 16H, CH$_2$). IR (KBr): 3306, 2948, 2845, 1638, 1544, 1444, 1402, 1247, 1040 cm$^{-1}$.

2.2 Preparation and characterization of gold nanoparticles

All of the gold nanoparticles (Au-1–Au-3) were prepared according to the Brust’s method.\textsuperscript{6} Generally, gold nanoparticles have the broad absorption in range of 450-600 nm which is assigned to the surface plasmon resonance of the Au cores. In order to confirm the generation of the gold nanoparticles, UV-vis absorption spectra were measured using SHIMADZU UV-3600. Furthermore, particle size of the gold nanoparticles was estimated visually on the basis of the images of transmission electron microscopy (TEM) taken by JEOL JEM-2000EX.

2.3 Thermal analysis

Thermogravimetry (TG) measurement was carried out using SH TG/DTA 6300 at heat rate of 20 °C/min. under nitrogen environment (150 mL/min.). Differential scanning calorimetry (DSC) was measured using SHI DSC 6200 at heat rate of 10 °C/min. under nitrogen environment. As the reference, α-alumina was used.

3. RESULTS AND DISCUSSION

3.1 Surface plasmon resonance of gold nanoparticles

Figure 2 shows the absorption spectrum of the tolyl-amine type gold nanoparticle (Au-3b). The broad absorption assigned to the surface plasmon resonance was confirmed in 450-600 nm. In the cases of the other gold nanoparticles, the surface plasmon resonance was observed in the same range.

![Figure 2](https://via.placeholder.com/150)

Figure 2 UV-vis absorption spectrum of gold nanoparticle (Au-3b).

3.2 Particle size of gold nanoparticles

Figure 3 shows the TEM image of Au-3b. The average size of the particles was estimated visually at approximately 2 nm based on the image. In the cases of the other ligands, the nanoparticles were comparable in size to Au-3b. The gold nanoparticles were stabilized by the ligand molecules, resulting in the particle size being determined. Therefore, the number of the ligand molecules on the gold surface was considered to be comparable.
3.3 Thermogravimetry (TG)

Figure 4 shows the TG chart of Au-3b. Weight loss occurred drastically in one step. And, almost the same TG curves were observed in the cases of the other gold nanoparticles. The orientation of the ligand molecules became disorder by heating and the gold surface was exposed partially. After heating above the onset temperature of decomposition of the gold nanoparticles, the ligand molecules desorbed from the gold surface and the gold nanoparticles grew together to become insoluble in the organic solvents. Therefore, the onset temperature of decomposition was considered to be the indicator of the thermal stability of the gold nanoparticles.

The onset temperature of decomposition was found to strongly depend on the ligand structures.

The long-chain alkanethiol type gold nanoparticle (Au-1) had the lowest thermal stability due to the weak interligand interaction, followed by the amide types gold nanoparticles (Au-2). Among the Au-2 group, Au-2a (n = 7) showed the lowest onset temperature of decomposition. The temperature was raised as the alkyl chain increased in length, and became almost the same in the cases of Au-2c (n = 15) and Au-2d (n = 17). These results suggested that the contribution of van der Waals interaction to the thermal stability of ligands was saturated when the length of alkyl chain became long enough. Meanwhile, tolyl types gold nanoparticles (Au-3) were found to decompose at higher temperatures than Au-2. In particular, Au-3b showed the highest onset temperature of decomposition among these gold nanoparticles. Additionally, the temperature of Au-3a was higher than those of Au-2 despite a lack of amide group in the ligand structure. These results indicated that the contribution of π-π stacking to the thermal stability of the gold nanoparticles was larger than that of hydrogen bonding. On the other hand, since the ligand 3b could form both interligand hydrogen bonding and π-π stacking besides van der Waals interaction, Au-3b decomposed at the highest temperature among them.

3.4 Differential scanning calorimetry (DSC)

Figure 6 shows the DSC charts of (A) Au-3a and (B) Au-3b, respectively.

In the DSC chart of Au-3b, a characteristic endothermic peak appeared at 127 °C besides an exothermic peak at 256 °C, while only one exothermic peak was observed in

Figure 5 Correlation between ligand structure and onset temperature of decomposition.
the cases of the other gold nanoparticles including Au-3a. Since the endothermic peak is generally observed when degree of order increases by heating, both of the amide group and the tolyl group were considered to be essential for reorientation of the ligand molecules.

On the other hand, one exothermic peak was observed in the cases of all gold nanoparticles except Au-2d, which was assigned to orientational relaxation of the ligand molecules by heating. Figure 7 shows the correlation between the ligand structure and the temperature of exothermic peak.

Au-3a showed the lowest temperature of the exothermic peak, followed by Au-1. In contrast, the peaks of Au-2 and Au-3b shifted toward higher temperature. This result indicated that the interligand hydrogen bonding played an important role for stabilization of the orientation of the ligands.

4. CONCLUSION

The authors synthesized the six types of novel ligands which contained an amide group and/or a tolyl group with the goal of developing thermally-resistant gold nanoparticles. The corresponding gold nanoparticles were prepared and their thermal stability was evaluated by thermo gravimetry (TG) and differential scanning calorimetry (DSC).

The onset temperature of decomposition of each gold nanoparticles was estimated based on TG analysis. The long-chain alkanethiol type gold nanoparticles (Au-1) had the lowest thermal stability due to the weak interligand interaction, followed by the amide types gold nanoparticles (Au-2). Concerning the Au-2 group, the temperature of decomposition was raised as the alky chain increased in length, and became almost the same in the cases of Au-2c (n = 15) and Au-2d (n = 17). Furthermore, the temperatures of the tolyl type gold nanoparticles (Au-3) were higher than those of Au-2. In particular, the temperature of Au-3b drastically shifted to 310 °C owing to the combination of the interligand hydrogen bonding and π-π stacking besides van der Waals interaction.

In the DSC chart of Au-3b, the characteristic endothermic peak appeared, which was considered to be assigned to reorientation of the ligand molecules. In addition, it was found that the temperature of exothermic peak shifted to higher temperature when an amide group was introduced into the ligands.

Figure 8 shows the schematic illustration of the interligand interactions of Au-3b. The high thermal stability of Au-3b can be explained by focusing on the interactions between the ligand molecules as follows. The interligand hydrogen bonding formed near the gold surface behaves as a temporary joint, which is considered to stabilize the orientation of the alkyl chain. As a result, the tolyl group which is introduced at the end of the each ligand becomes to form interligand π-π stacking easily, and the thermal stability of Au-3b is improved drastically.

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REFERENCES


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