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Conductive Gold Thin Film Prepared by the Two-Dimensional Assembly of Gold Nanoparticles on a Plastic Surface

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ABSTRACT. Gold thin films are useful as conductive materials for electrical devices and sensors owing to their high conductivity and inertness. In the present study, we propose a novel alternative to conventional gold-coating techniques (i.e., gold-vapor deposition and gold plating) to prepare a gold thin film on a plastic surface using a gold colloidal solution. Gold nanoparticles (AuNPs) were immobilized on a plastic surface with a high density of amino groups (two-dimensional assembly of AuNPs), and subsequently grew to form a gold thin film. The growth of the AuNPs was induced using an amino acid as a reducing agent. The selection of the amino acid significantly influenced the growth of the AuNPs and the morphology of the gold thin film. Microscopic observations and absorbance measurements demonstrated the growth and connection of the AuNPs on the surface. The thickness of the gold thin film was limited to between 50 nm and 0.5 μm by varying the growth conditions. The formed film was lustrous and exhibited electrical conductivity comparable with that of a gold-vapor deposited surface. Moreover, we successfully micropatterned the gold thin film on the plastic substrate using the present method combined with a microcontact printing method. The results indicate that our approach has significant potential for use in the manufacture of electrical devices and biosensors.

1. INTRODUCTION

Gold is highly conductive, ductile, inert, and corrosion resistant. It is therefore indispensable for modern electronic devices including sensors, wearable technology, wireless systems, industrial machinery, and household appliances. Since the late 20th century, gold (Au) thin film substrates have also been used as platforms for the detection of biomolecular events (interactions between molecules), in which thiolated biomolecules and ligands are immobilized on the gold surface to capture target molecules.[1-3] The immobilization of molecules is based on the interaction between gold and sulfur, which is convenient and stable under physiological conditions. Owing to the considerations of cost and weight associated with gold, a gold thin film is a rational choice for detection devices. Gold-vapor deposition is the most reliable and widely used method for preparing gold thin films with controlled thicknesses and designed patterns.[4-6] However, gold-vapor deposition requires a high-vacuum apparatus and considerable energy consumption, and is therefore unfavorable in terms of high-throughput manufacturing and the environmental burden. Gold plating is another method of preparing gold thin films on solid materials. However, plating involves toxic chemicals and produces effluents containing environment pollutants.[7] In both methods, a second thin metal film (Cr or Ti) is often used as an adhesive layer to improve the adhesion between the gold and the substrate surface. This raises further environmental concerns, especially when recycling. Despite high demands for an alternative approach to preparing gold thin films on various solid materials, there have been few relevant studies.[8-12]

Gold nanoparticles (AuNPs) are nanomaterials and have been studied extensively. They are synthesized using a variety of approaches, some of which are energy-saving and employ "green chemicals" as reducing agents for chloroaurate ions and also as capping agents for the AuNPs.[13-17] In fact, we have also succeeded in synthesizing AuNPs using various amino acids.[18] Several research groups have reported two dimensional (2D) arrays of AuNPs formed by depositing AuNPs.[9, 19-26] Many of the studies on the preparation of the 2D arrays have featured inorganic substrates. However, to the best of our knowledge, there has been no report on the preparation of a conductive gold thin film with a designed pattern using AuNPs.

Because many modern electronic devices are wearable or portable, it is important that they are lightweight. Plastics are useful materials for the bodies and boards of devices because they are lightweight, inexpensive, insulating, and easy-to-process. A method for directly fabricating a gold thin film on a plastic would greatly benefit the electronic industry and the manufacture of sensing devices. We have previously developed a facile method for the preparation of a plastic surface displaying amino groups of controlled density,[27] and subsequently succeeded in the preparation of a dense 2D array of AuNPs on a plastic substrate.[21] Based on our previous studies, we herein propose a novel method for preparing a gold thin film with a designed micropattern on a plastic surface. Our approach is to grow and connect the AuNPs immobilized on a plastic surface using an amino acid to form a gold thin film. A gold thin film prepared using the method is lustrous and electrically conductive. By combining the novel method with microcontact printing,[28] we were also able to form a micropattern of a conductive gold thin film on a plastic surface.

2. EXPERIMENTAL SECTION

Materials

The chemicals and substrates used in the present study are described in detail in the Supporting Information.

Synthesis of 2-(*tert*-butoxycarbonylamino)ethyl methacrylate (Boc-AEMA)

Boc-AEMA was synthesized according to the procedure described in our previous report.[29] 2-Aminoethyl methacrylate hydrochloride (AEMA-HCl, 6.04 mmol) and trimethylamine (18.15 mmol) were added to chloroform (22.5 mL). After stirring for 20 min, di-*tert*-butyl dicarbonate (6.64 mmol) was added to the solution, which was then stirred at 4 °C overnight. Ethyl acetate (30 mL) was added to the solution, and the precipitate was separated by filtration. The filtrate was evaporated, and the residue was washed three times with water and freeze-dried overnight. The yield of Boc-AEMA was 69%. The synthesis was confirmed by ^{1}H-NMR spectroscopy, and the mass-to-charge ratio (m/z) was determined by direct analysis in real time–time-of-flight mass spectrometry (DART-TOF/MS). The ^{1}H-NMR analysis was performed using an Avance-500 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) and deuterated chloroform containing 0.03 wt% tetramethylsilane as a solvent. The results of the ^{1}H-NMR analysis are shown in Fig. S1. DART-TOF MS (m/z) (MS-5414, JEOL, Tokyo, Japan): $[M+H]^+$ calculated for $C_{11}H_{19}NO_4$, 230.1; found, 230.1 (positive). The results of the DART-TOF-MS analysis are shown in Fig. S2.

Synthesis of poly(MMA-*r*-(Boc)AEMA)

Poly(MMA-*r*-(Boc)AEMA), which is referred to hereafter as PMBA (Fig. 1a), was synthesized according to the procedure described in our previous report.[21] Methyl methacrylate (MMA; 24.12 mmol), Boc-AEMA (2.68 mmol), and azobisisobutyronitrile (0.094 mmol) were dissolved in ethyl acetate (14 mL) and stirred at 70 °C overnight. The reaction solution was precipitated by excess *n*-hexane, and the precipitates were washed three times with excess *n*-hexane. The purified copolymer was dried under vacuum overnight. The synthesis was confirmed by ^{1}H-NMR analysis, and the monomer composition ratio (MMA: Boc-AEMA) was 93:7. The results of the ^{1}H-NMR analysis are shown in Fig. S3. The weight-average molecular weight (Mw) and number-average molecular weight (Mn) were determined by size-exclusion chromatography (SEC) using a GPC 8020 system (Tosoh Corporation, Tokyo, Japan) equipped with a 7.5 × 300 mm SEC column (GF510, Showa Denko K.K., Tokyo, Japan) and a refractive index detector (RI-8031, JASCO, Tokyo, Japan). The analysis was conducted at 40 °C using tetrahydrofuran as an eluent. Poly(methyl methacrylate) was used for the molecular weight standards. The SEC measurements showed that the PMBA had an Mn of 7.0×10^4 and an Mw/Mn of 1.04.

Amino group presentation on acrylic substrate via dip-coating

PMBA was dissolved in ethyl acetate to prepare a 3 wt% polymer solution. An acrylic substrate (1×1 cm^2) was immersed into a PMBA solution for a few seconds. The substrate was dried at room temperature under vacuum overnight. The Boc groups protecting the amino groups were deprotected with 4 M HCl aq. at 40 °C overnight. The substrate was then washed three times with Milli-Q® water. This process exposed the amino groups on the outermost surface.[27]

Quantification of the amino group density presented on an acrylic substrate surface

The density of amino groups was quantified using the cleavable fluorescent compound fluorescein isothiocyanate (FITC)-S-S-COOH, according to the method described in our previous study.[29] The synthesis of FITC-S-S-COOH was also carried out as described in our previous study.[27] Dip-coated acrylic substrates were immersed in 4 M HCl aq. at 40 °C overnight. The substrates were then washed three times with Milli-Q® water, immersed in phosphate buffer (0.1 M, pH 8.0, 2 mL) containing 0.6 mM FITC-S-S-COOH, 5 vol% dimethyl sulfoxide, and 5 mM 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride, and shaken for 2 h at 40 °C. The FITC-S-S-COOH reacted with the amino groups on the surfaces of the substrates, forming amide bonds. The substrates were washed three times with phosphate buffer (pH 8.0). They were then washed with 5 mM HCl solution (10 mL), followed by 5 mM NaOH solution (10 mL), and 5 mM HCl solution (10 mL) at 40 °C for 1 h each. The substrates were once again washed three times with phosphate buffer (pH 8.0), and immersed in phosphate buffer (0.1 M, pH 8.0, 2 mL) containing 2 mM tris(2-carboxyethyl)phosphine at 40 °C for 1 h to cleave the disulfide bonds of the FITC-S-S-CONH- groups, thereby liberating the fluorophores into the solution. The fluorescence intensity of the phosphate buffer containing the fluorophore was determined using a fluorescence spectrophotometer (FP-8200, JASCO, Tokyo, Japan).

AuNPs synthesis

AuNPs with citric acid as a capping agent were synthesized according to a modified version of the procedure reported in the literature.[21, 30] An aqueous $HAuCl_4$ solution (10^{-2} wt%, 300 mL) was brought to a vigorous boil while stirring. After boiling, trisodium citrate (3 wt%, 3 mL) was added to the solution. The solution was boiled for another 8 min. Its color changed from pale yellow to bright red. The solution was then cooled to 25 °C while stirring. The AuNPs were estimated to be 15 nm in diameter based on the maximum absorption wavelength of the Au colloidal solution. The absorption spectra were obtained using a UV-Vis spectrophotometer (V-630, JASCO, Tokyo, Japan).

Immobilization of the AuNPs on an acrylic substrate surface

The AuNPs were immobilized according to the procedure described in our previous study.[21] The plastic substrates with amino groups on their surfaces were immersed in the Au-colloidal solution, and the solution was shaken for 30 min at 25 °C. After immersion, the substrates were withdrawn and dried overnight in vacuum at 80 °C. The absorption spectra of the substrates were obtained using a spectrophotometer.

Growth of the AuNPs on the surface of an acrylic substrate

The immobilized AuNPs were grown on the surface of an acrylic substrate using the chemical reduction process. $HAuCl_4$ and a reducing agent were dissolved in water, which was used as a growth solution. The substrate bearing the immobilized AuNPs was then immersed in the growth solution and slowly shaken. After immersion, the substrate was dried overnight in a vacuum at room temperature. The growth reaction was carried out at 40 °C and 80 °C to evaluate the effect of temperature. These temperatures were chosen to be below the T_g of PMMA (around 100-110 °C).

Characterization of substrates bearing immobilized AuNPs before and after the growth of the AuNPs

The size and morphology of the AuNPs immobilized on the surface were evaluated by absorbance measurements and field-emission scanning electron microscopy (FE-SEM; JSF-7500F, JEOL, Tokyo). The SEM images were obtained at an acceleration voltage of 7 kV and an emission current of 10 μA. The surface topology was examined by dynamic force microscopy (DFM; SPA400, Hitachi, Tokyo). The electrical resistance of the substrate surface was determined using a multimeter (CDM-2000D, CUSTOM, Tokyo). The thickness of the gold film was calculated using the following formula based on the weight change of the substrate before and after the growth of the AuNPs. The thickness of the acrylic substrate was calculated using the following equation:

$$\mathrm{Gold\ film\ thickness\ [\mu m]} = \frac{\mathrm{Weight\ change\ [g]}}{\mathrm{Au\ density\ [g/cm^3]}} \div \mathrm{Substrate\ area\ [cm^2]} \times 10^4\ \mathrm{[\mu m/cm]} \quad (1)$$

The conductivity of the substrates surface was determined using the following equation, which utilized the measured resistance value and the calculated gold film thickness:

$$\sigma\ \mathrm{[S/m]} = \frac{\mathrm{L\ [m]}}{\mathrm{R\ [\Omega] \times S\ [m^2]},} \quad (2)$$

where σ is the conductivity, R is the resistance of the substrate, L is the length, and S is the area of a cross section of the gold thin film.

Patterning of gold thin films using the microcontact printing (μCP) method

A polydimethylsiloxane (PDMS) stamp with 1 mm-wide parallel lines at 1 mm intervals was prepared and hydrophilized by plasma treatment. A poly(sodium-*p*-styrenesulfonate) (PSS) aqueous solution (2 mg/mL) was dropped onto the PDMS stamp, which was then dried under vacuum. An acrylic substrate with amino groups on its surface was placed on the PDMS stamp, and the PSS layer was transferred from the stamp to the substrate. Subsequently, the substrate with the PSS micropattern was immersed in an Au-colloidal solution and dried under vacuum. The AuNPs were capped with negatively charged citrate acid. Therefore, the AuNPs were selectively immobilized only on the areas where positively charged amino groups were exposed, i.e., except for the areas covered with PSS. The substrate with the AuNP-micropattern was immersed in a growth solution, and shaken gently at 80 °C for 30 min. The growth operation was repeated thrice and the substrate was dried overnight under vacuum.

3. Results and discussion

Immobilization of the AuNPs on a plastic surface

The diameter of the synthesized AuNPs was estimated to be approximately 15 nm based on the maximum absorption wavelength of the Au-colloidal solution (520 nm).[31] A methacrylate-based random copolymer (i.e., PMBA, Fig. 1a) with Boc group-protected amino groups in its side chains was synthesized via free radical polymerization.[27]

We immobilized the synthesized AuNPs on the surface of an acrylic substrate, as described in our previous study.[21] Briefly, a PMMA substrate was dip-coated with a PMBA solution (3 wt% in ethyl acetate; Fig. 1b-1). The Boc groups of the PMBA were deprotected with a HCl aqueous solution, and the amino groups on the outermost surface of the substrate were exposed. The surface is hereafter referred to as an NH_2-displaying surface (Fig. 1b-2). The quantification using the cleavable fluorescent compounds revealed 10 pmol/cm^2 amino groups on the NH_2-displaying surface, which resulted from the surface segregation of Boc-protected amino groups during drying.[27] The substrate was immersed in an Au-colloid solution to immobilize the AuNPs on its surface via electrostatic interaction (Fig. 1b-3), and then dried overnight in vacuum at 80 °C. This enabled the formation of amide bonds between the carboxylic groups on the AuNPs and the amino groups on the surface, resulting in stably immobilized AuNPs on the NH_2-displaying surface (Fig. 1b-4).[21]

The substrate was reddish in color (Fig. 2a), indicating that the AuNPs had been immobilized. FE-SEM revealed that the AuNPs were uniformly and densely immobilized on the surface (Fig. 2b). The absorption spectrum of the substrate featured strong absorbance at approximately 530 nm, which is typical of the surface plasmon resonance of AuNPs (Fig. 2c), suggesting that the AuNPs had been immobilized without aggregation.[21]

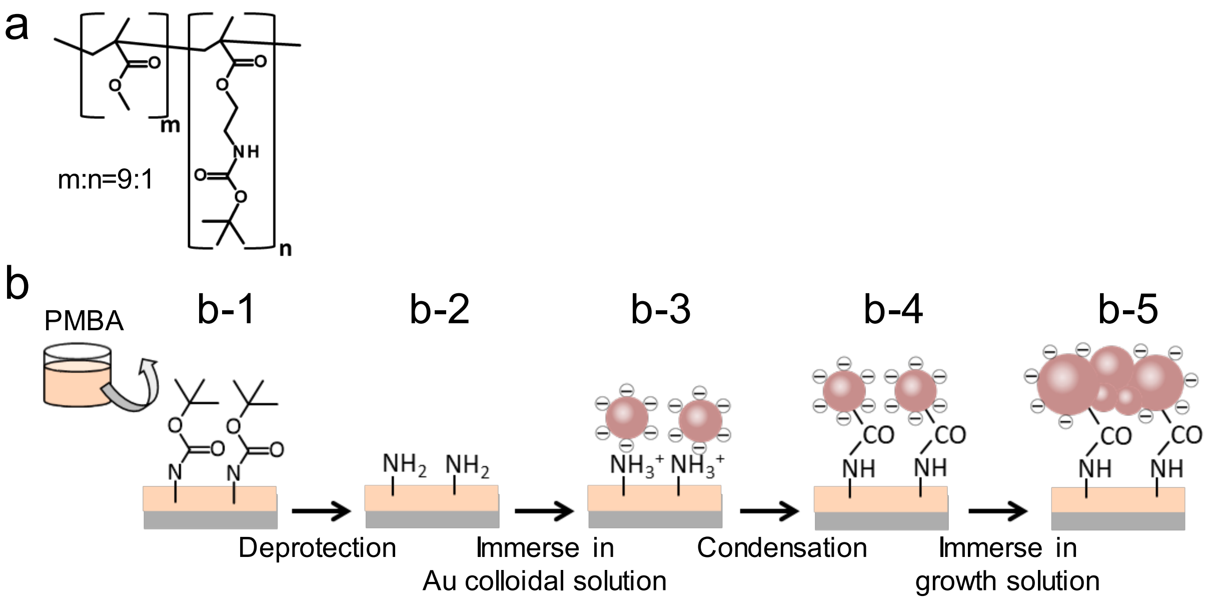

Figure 1. (a) Molecular structure of poly(MMA-*r*-(Boc)AEMA) (PMBA). (b) Schematic illustration of the immobilization and growth of AuNPs on a plastic substrate. (b-1) Surface display of Boc-protected amino groups via coating with PMBA. (b-2) Deprotection of the Boc groups to display amino groups on the surface. (b-3) Immobilization of the AuNPs via electrostatic interaction. (b-4) Formation of covalent bonds between the AuNPs and the amino groups on the

surface. (b-5) Growth and connection of the immobilized AuNPs on the surface to form a conductive gold thin film.

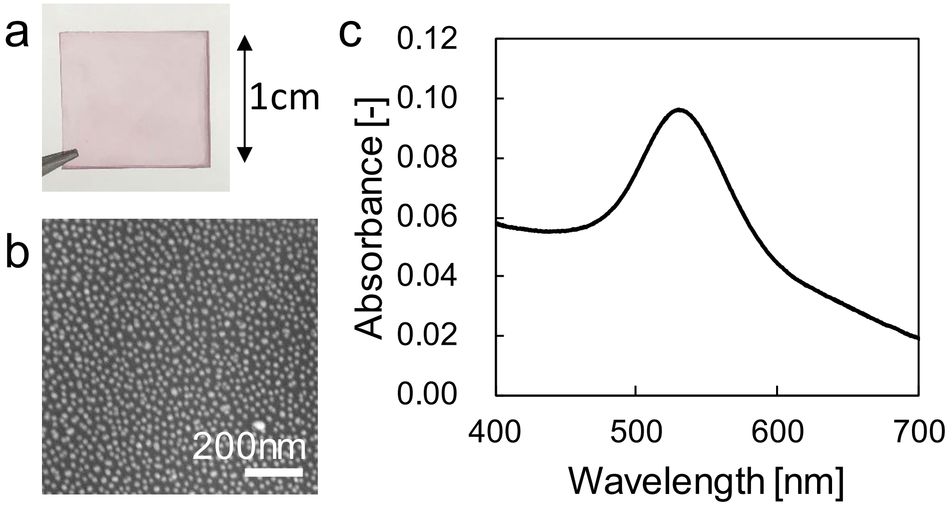

Figure 2. Characterization of an acrylic substrate bearing immobilized AuNPs. (a) Photograph. (b) FE-SEM image. (c) Absorbance spectrum of the substrate. The spectrum of the bare substrate was subtracted from that of the substrate bearing immobilized AuNPs.

Growth of the AuNPs on a plastic substrate using reducing agents

We attempted to grow AuNPs immobilized on a plastic substrate (Fig. 1b-5). First, we investigated the influence of various reducing agents on the growth of the AuNPs on a surface. Amino acids have attracted attention in recent decades as environmentally friendly and biocompatible reducing and capping agents for synthesizing AuNPs. Previous studies have demonstrated that various types of amino acids work as reducing agents for AuNP synthesis, and that the selection of the amino acid influences the diameters of the synthesized AuNPs.[13-16] We investigated AuNP growth using 20 different L-amino acids as reducing agents. A growth solution containing $HAuCl_4$ and the reducing agent was prepared so that the final concentrations of $HAuCl_4$

and the reducing agent were 1 and 10 mM, respectively, except in the case of Tyr. The concentration of Tyr was set to 1 mM in the growth solution owing to its low solubility. The substrate bearing the immobilized AuNPs was immersed in a growth solution and shaken gently at 80 °C for 1 h. After immersion, each substrate was dried overnight in vacuum at room temperature.

The growth of AuNPs on a surface was evaluated by FE-SEM. FE-SEM revealed significant differences in the growth of AuNPs depending on the amino acid used (Fig. 3). The FE-SEM images reveal that the AuNPs remained immobilized and grew on the surface in the presence of Ala, Ile, Leu, Met, Val, Pro, and Gly. The AuNPs were connected together most effectively in the presence of hydrophobic amino acids containing aliphatic side chains (Ile, Met, Val, and Leu). However, aromatic amino acids (Phe, Trp, and Tyr), which are also hydrophobic, did not significantly promote the growth of AuNPs. Asp and Glu, which are acidic amino acids, induced moderate growth of the AuNPs, whereas Arg, His, and Lys, which are basic amino acids, resulted in little growth. Amino acids with neutral or polar side chains (Asn, Gln, Ser, and Thr) induced moderate growth of the AuNPs, with the exception of Cys.

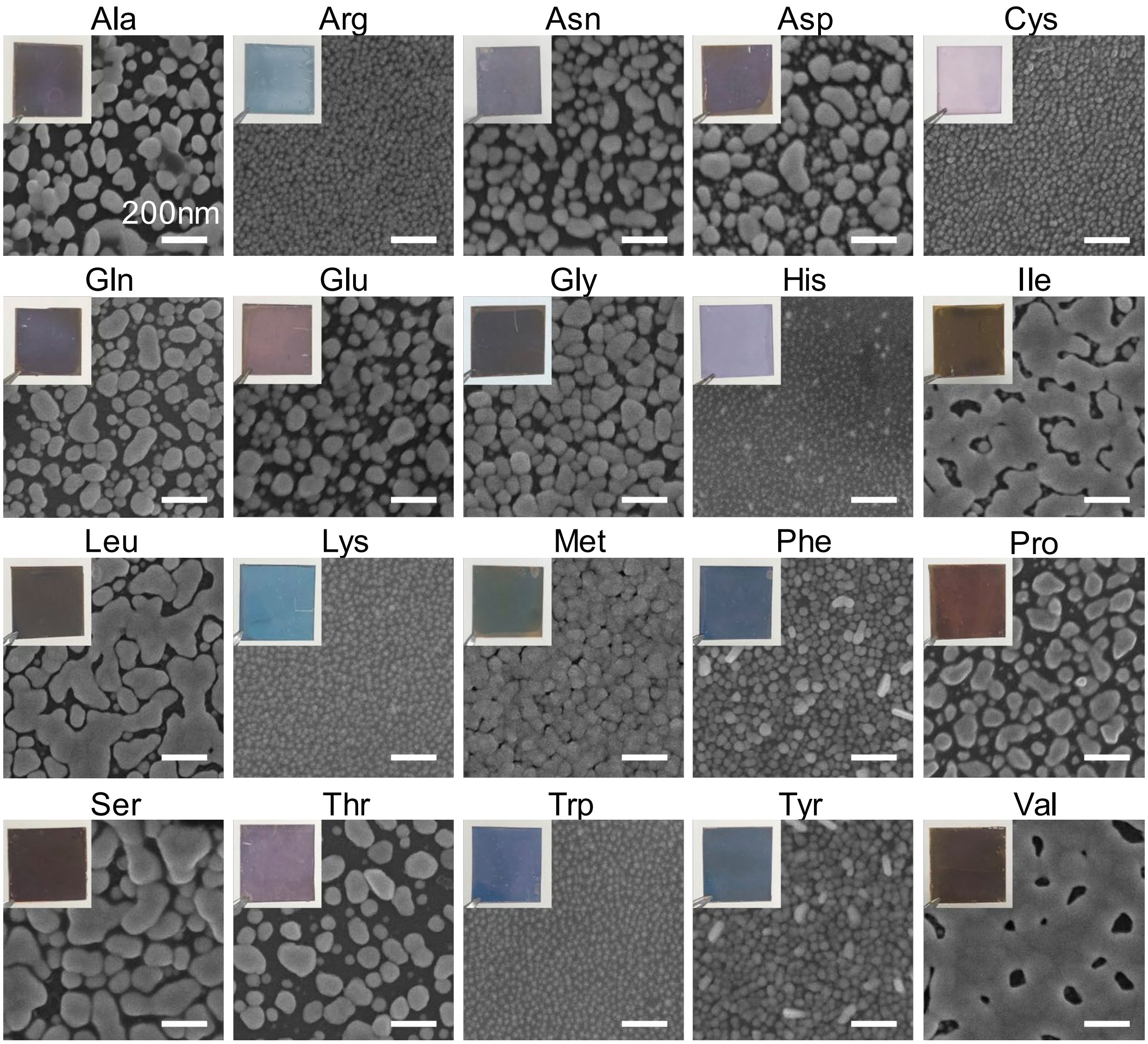

Figure 3. FE-SEM images of the substrate surfaces after the growth of the AuNPs using amino acids as reducing agents. The insets are photographs of the substrates.

Based on the results described above, we successfully grew AuNPs on the plastic substrates using certain amino acids as reducing agents while keeping the AuNPs immobilized. Intriguingly, the reducing agents suitable for the growth of AuNPs immobilized on the substrate differed from those used for synthesizing large AuNPs in bulk, as reported in previous studies. Figat *et al.*

reported the synthesis of AuNPs using all the α-amino acids except for Pro, Cys, Gln, and Arg.[17] They found that when used as both reducing and stabilizing agents, Thr, Gly, Leu, and Ala produced larger AuNPs.

It has been reported that certain amino acids are adsorbed selectively on the crystal faces of AuNPs. This might also affect the growth and connection of AuNPs on a substrate.[17, 32-34] These factors account for the differences in the amino acids that are appropriate for the growth of AuNPs on a substrate, and for the synthesis of AuNPs in bulk.

Investigation of the conditions for AuNP growth

We chose Glu as the reducing agent in our investigation of the growth of AuNPs because it enables moderate growth. We studied the effects of temperature and time on AuNP growth. A substrate bearing immobilized AuNPs was immersed in a growth solution containing 3 mM $HAuCl_4$ and 3 mM Glu, and shaken gently at 40 °C or 80 °C. The growth of the AuNPs was observed over a range of shaking times from 15 min to 4 h.

FE-SEM revealed that an increase in the reaction time promoted the growth and connection of AuNPs at both reaction temperatures (Fig. 4a). At 40 °C, the AuNPs started to connect with each other at 1 h and the spherical structures disappeared at 2 h. At 80 °C, connection began at 15 min and the AuNPs had lost their original shape at 30 min. The growth of the AuNPs was also evaluated by measuring the absorbance of substrates bearing the immobilized AuNPs (Fig. 4b and Fig. S4). The absorbance increased over a wide range of wavelengths at 40 °C over time. The absorbance also increased with time over a wide range of wavelengths at 80 °C, but seemed to reach a maximum at 1 h. In fact, there was little change in the absorbance spectrum after 2 h at 80 °C. It was obvious that the strong absorbance typical of AuNPs (at approximately 530 nm) disappeared gradually at 80 °C, indicating the connection and fusion of the AuNPs on the surface. These results suggest that the growth of AuNPs was also affected by temperature. This would be consistent with the synthesis of AuNPs.

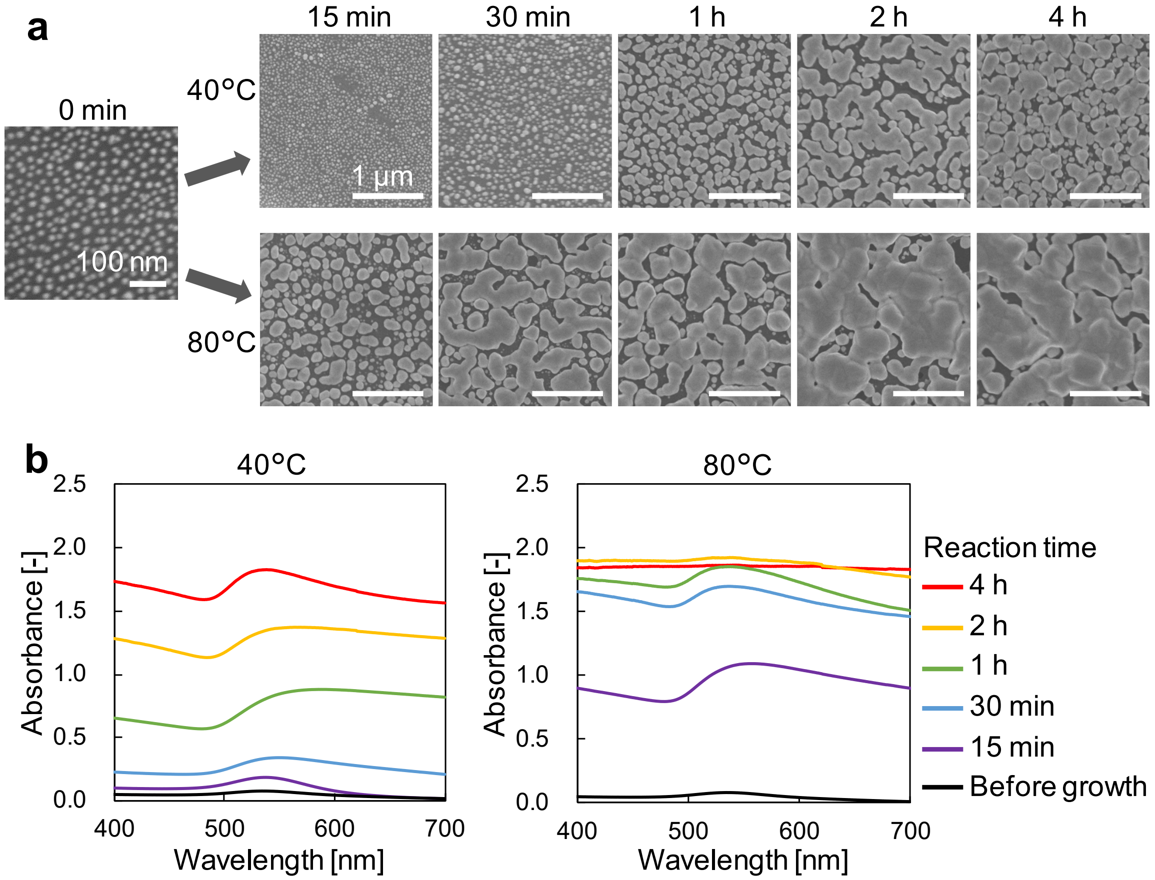

Figure 4. Effects of the growth conditions (temperature and time) on the surface morphology and absorbance of an acrylic substrate bearing immobilized AuNPs using L-Glu as a reducing agent. (a) FE-SEM images. (b) Absorbance spectra of substrates after growth under various conditions.

The substrate surfaces became lustrous after the growth of the AuNPs, and the reflectance of the substrates was measured (Fig. 5). As the AuNPs grew and were connected with each other, the reflectance increased at wavelengths longer than 600 nm, which is typical of the reflectance of a metallic surface.[35] The reflectance of the substrate increased with the reaction time at both reaction temperatures. When the AuNPs grew on the surface at 40 °C for 4 h, the reflectance (> 700 nm) reached 60% or higher.

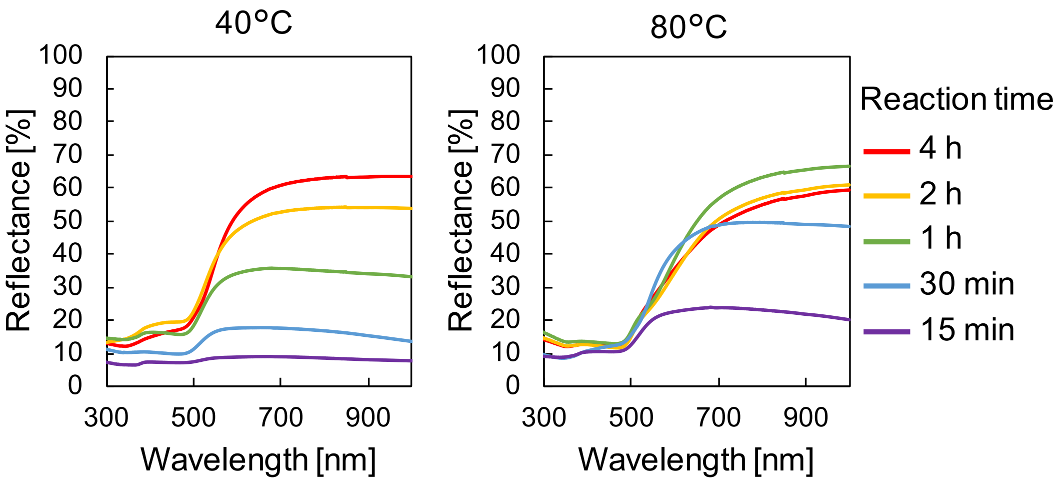

Figure 5. Reflectance measurements of substrates after growth under various conditions. L-Glu was used as a reducing agent.

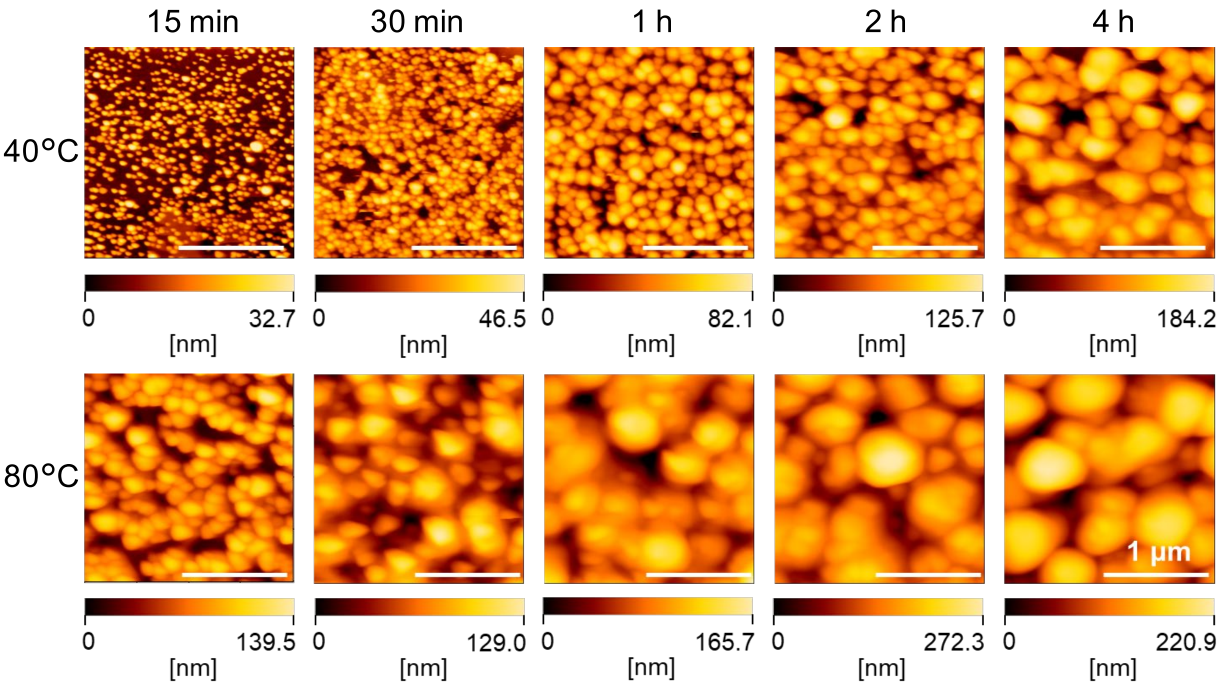

Figure 6. Dynamic force microscope (DFM) images of the substrates bearing immobilized AuNPs after growth under various conditions. L-Glu was used as a reducing agent.

We investigated the surface morphologies of the substrates bearing the immobilized AuNPs by dynamic force microscopy during the growth process (Fig. 6). The results showed that the AuNPs grew isotropically and were connected with each other at 40 °C and 80 °C.

The formation of a dense 2D assembly of metal nanoparticles is a rational approach to the creation of a patterned circuit. In fact, Szuwarzynski *et al*. prepared a conductive Ag-nanoparticle micropattern on a solid surface.[36] We measured the resistance of the substrates to evaluate their conductivity (Fig. 7a). After AuNP growth for 4 h at 40 °C, the resistance of the substrates was 16 **Ω**, whereas after growth for less than 2 h, it was too high to measure ($> 3 \times 10^7$ **Ω**). We also allowed the AuNPs to grow for more than 30 min at 80 °C and determined the resistance of the substrates. The resistance decreased with time, indicating the progressive connection of the AuNPs. The resistance following growth for at least 1 h at 80 °C was less than 10 **Ω**, which was lower than that of a commercially available gold-vapor deposited glass. Other amino acids (Ile, Met, Val, and Leu) were also used as reducing agents. Fig. S5 shows that the substrates prepared using these amino acids also had electrical resistance values ranging from 10 to 80 **Ω**.

The mean thickness of the gold thin films formed on the substrates was calculated from the weight changes of the substrates before and after the immobilization and growth of the AuNPs (Table 1). The gold thin film prepared at 40 °C for 4 h was approximately 50 nm thick. The thickness of the gold thin film prepared at 80 °C increased with the growth time. The thickness ranged from 40 to 200 nm, which was comparable with that determined by DFM.

The calculated thicknesses of the gold films and the measured resistance values were used to determine the conductivity of the substrate surfaces (Fig. 7b). The conductivity of the substrate surfaces was the highest when the AuNPs were grown at 40 °C for 4 h, and was comparable with that of a commercially available gold-vapor deposited glass. At 80 °C, the conductivity increased for the samples grown for 30 min to 1 h and decreased from 1 h to 4 h. This might be attributed to the increase in the amount of gold on the substrate. Although the amount of gold increased with the growth procedure, the connection between the AuNPs did not improve. In fact, there was no significant change in the resistance values, even after the growth reaction had exceeded 1 h (Fig. 7a). Among all the samples tested, the gold thin film was the most conductive (0.73 µS/m) when the AuNPs were grown at 40 °C for 1 h. This can be attributed to the relatively uniform growth of the AuNPs at moderate temperatures.

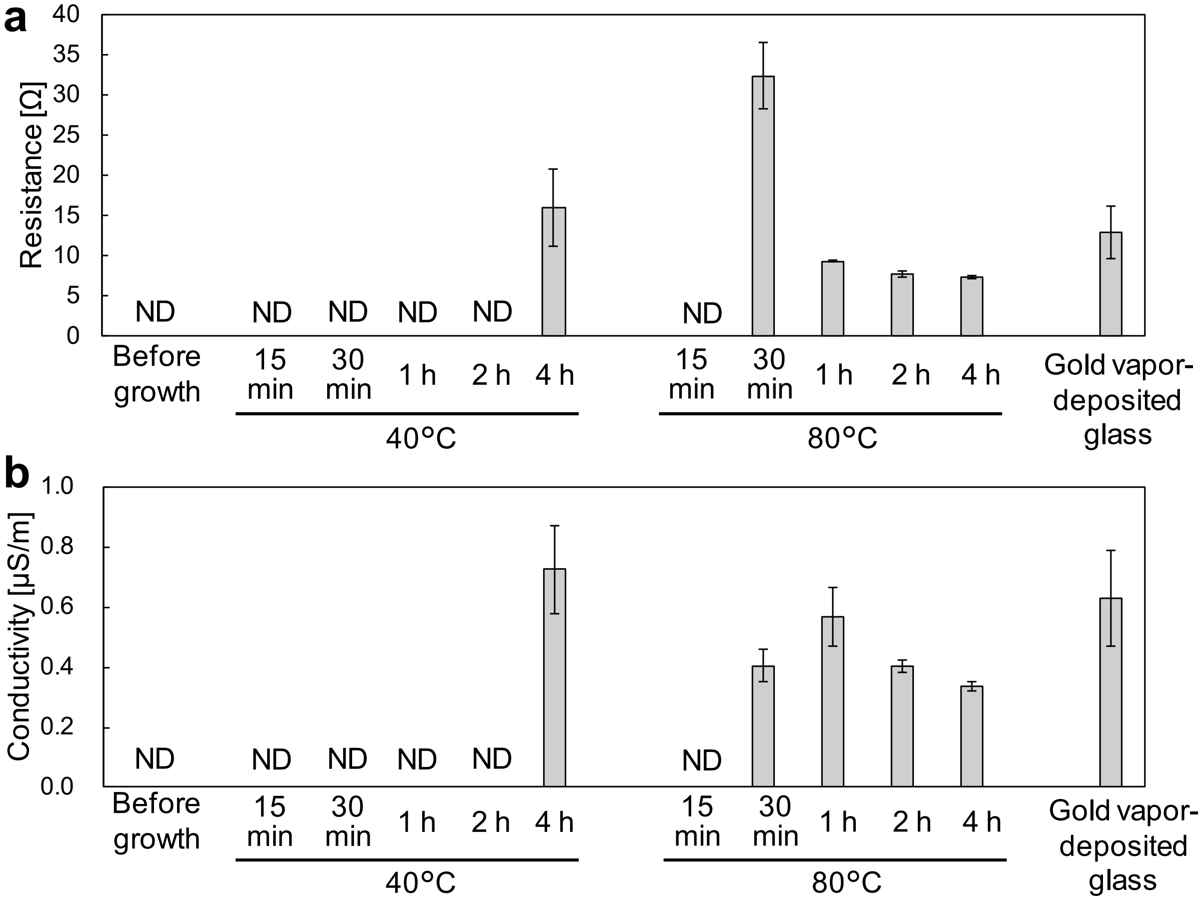

Figure 7. (a) Resistance values of the substrates after growth under various conditions. (b) Conductivity of the substrates. L-Glu was used as a reducing agent. The distance between the electrodes was 5 mm.

Table 1. Thicknesses of the gold thin films calculated from the weight changes of the substrates before and after the immobilization and growth of AuNPs.

Sample	Gold film thickness [nm]
40°C, 4 h	50 ± 3
80°C, 30 min	40 ± 2
80°C, 1 h	99 ± 14
80°C, 2 h	161 ± 3
80°C, 4 h	202 ± 8

Control of gold film thickness through repeated growth operations

The results described above suggest that the gold film thickness and the substrate conductivity can be controlled by varying the growth conditions. Thickness control was attempted by repeating the growth operation. The growth operation was repeated four times.

The FE-SEM observations revealed that the growth and connection of the AuNPs proceeded with each growth operation (Fig. 8a). The UV-vis absorption measurements indicated that the absorbance increased from the first to the second growth operation, and reached a transmittance of less than 2% (Fig. 8b). The absorbance at approximately 530 nm, which is typical of AuNPs, completely disappeared. There was little increase in absorbance after the second and third operations. These results suggest that the AuNPs were almost connected and transformed to a gold thin film by the second growth operation.

The resistance of the substrates decreased until the third growth operation (Fig. 9a), indicating an improvement in conductivity. These results also suggest that the connection of the AuNPs was promoted through the repeated growth operations, producing conductive paths. It should be noted that the fourth growth operation did not improve the conductivity. We found that the film thickness increased linearly as the growth operation was repeated (Fig. 9b). The thickness reached 0.5 μm after the fourth growth operation. These results indicate that the gold film thickness can be controlled through the repetition of the growth operation.

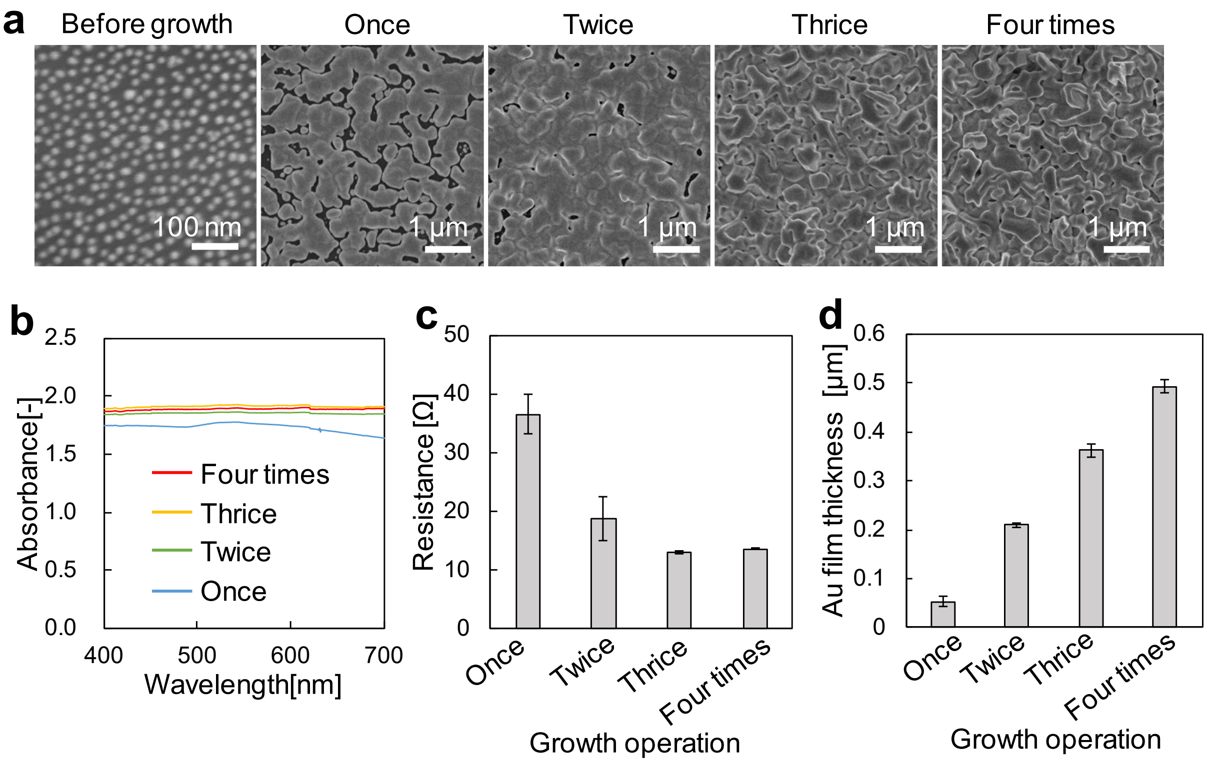

Figure 8. Growth operation repetition using L-Glu as a reducing agent for the preparation of a gold thin film on a substrate. (a) FE-SEM images. (b) Absorbance spectra of substrates after the growth operation repetition. (c) Resistance measurements after the growth operation repetition. (d) Gold

film thickness calculated from the weight change of the substrate before and after the immobilization and growth of AuNPs. The growth solution contained 3 mM $HAuCl_4$ and 3 mM Glu.

Micropatterning of gold thin films using the microcontact printing (μCP) method

The μCP method[28] was used to micropattern a gold thin film on a plastic substrate. We formed a pattern of PSS on an NH_2-displaying substrate via μCP with PSS aqueous solution (Fig. 9a). Because PSS is negatively charged, we expected the electrostatic interaction between PSS and the amino groups on the surface to inhibit the immobilization of AuNPs on the substrate. The optical microscopy observation revealed that 1 mm-wide gold thin films had been formed at 1 mm intervals (Fig. 9b), indicating successful micropatterning. FE-SEM investigations at the boundary of the gold thin film revealed that it was formed on the confined area, where PSS would not be stamped (Fig. 9c).

Finally, we applied current to the gold micropattern formed on the plastic substrate using a light bulb and a battery. When the wires were attached to both ends of the single gold film, the light bulb lit up (Fig. 9d-1). When the wires were connected to different gold films, the light bulb did not light up (Fig. 9d-2). These results demonstrated that the present strategy for gold micropatterning can be implemented in circuits and electrical devices.

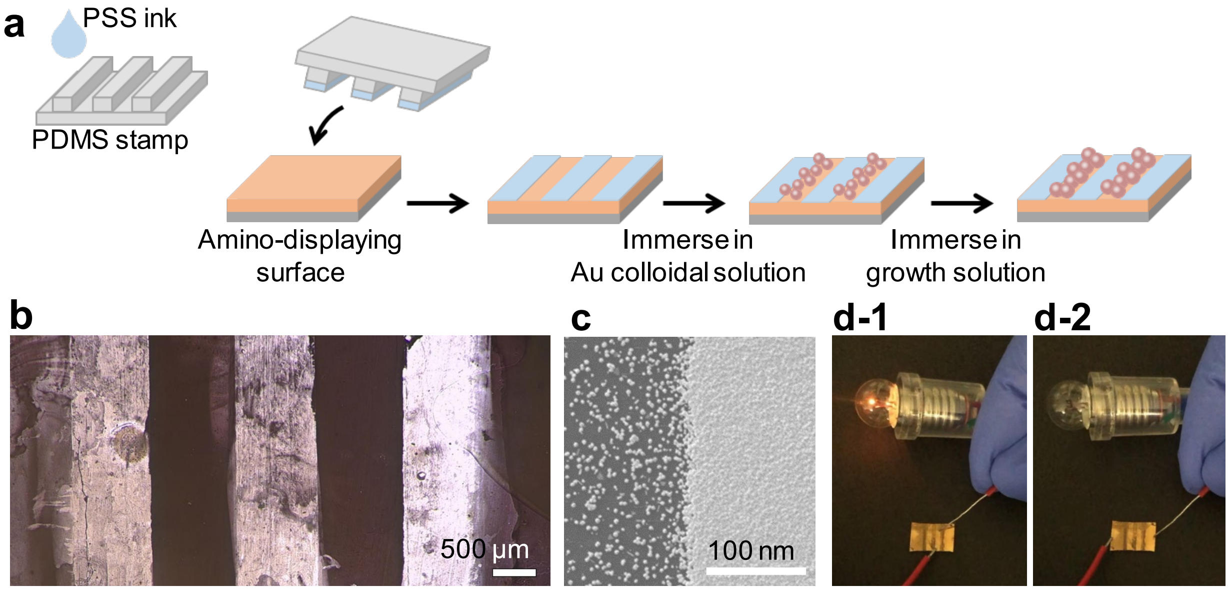

Figure 9. (a) Scheme illustrating the micropatterning of gold films by PSS µCP. (b) Optical microscope image of the gold micropattern on a substrate after the growth of the AuNPs. (c) FE-SEM image of the boundary of the micropatterned gold thin film. (d) Photographs showing the conductivity experiments using a light bulb. (d-1) Conductivity experiment on a single gold film. (d-2) Conductivity experiment between different gold films.

4. CONCLUSIONS

To date, gold-vapor deposition and gold plating have been the gold standards for the preparation of gold thin films. In the present study, we developed a novel method for preparing a gold thin film on a plastic surface using a gold colloidal solution, as an alternative to the conventional techniques. Our method also allows the micropatterning of a conductive gold thin film. We previously reported the dense 2D assembly of AuNPs on a plastic surface. The present method employed the immobilized AuNPs as seeds and grew them to connect with each other. The dense 2D assembly allowed the effective connection of the AuNPs on a surface to form a conductive gold thin film. The NH_2-displaying plastic surface used in the present study was simply prepared by dip-coating the substrate in a polymer containing amino groups. Therefore, our present strategy can be applied to other kinds of plastics and also to substrates of various shapes. The direct fabrication of a gold thin film on a plastic using AuNPs is a practical and useful strategy for preparing conductive circuits and sensing devices.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at

https://pubs.acs.org/doi/.

^{1}H-NMR spectra, a DART-TOF/MS chart, absorbance of substrates after AuNP growth at different temperatures and the results for resistance measurements of substrates prepared with 4 other kinds of amino acids (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

μCP = microcontact printing

AuNPs = gold nanoparticles

Boc-AEMA = 2-(*tert*-butoxycarbonylamino)ethyl methacrylate

DFM = dynamic force microscope

FE-SEM = field-emission scanning electron microscopy

FITC = fluorescein isothiocyanate

MMA = methyl methacrylate

PDMS = polydimethylsiloxane

PSS = poly(sodium-*p*-styrenesulfonate)

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