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End-to-End Assembly of CTAB-Stabilized Gold Nanorods by Citrate Anions

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We report studies on the end-to-end assembly of CTAB-stabilized gold nanorods (GNRs) dispersing in an aqueous solution. The addition of sodium citrate to the solution of GNRs with an aspect ratio (AR) of 3 causes the end-to-end assembly accompanied with a red-shift of longitudinal surface plasmon resonance (LSPR) band of the GNRs in the optical extinction spectrum. The red-shift in the LSPR band continues until the solution becomes colorless and transparent, whereas adding CTAB brings the color change to a stop, resulting in the long term-stable LSPR of the end-to-end connected GNRs. Added citrate anions are found to be adsorbed on only the end faces of GNRs so that they are considered to neutralize the surface charge of the GNR ends, resulting in the end-to-end assembly of the GNRs. On the other hand, GNRs with an AR of 16 are end-to-end assembled by decreasing CTAB concentration in the solution. The assembled GNRs are welded at their connecting points by the further decrease of CTAB concentration in the solution. Such end-to-end aggregated GNRs presumably have an advantage of electron conduction, whereas the end-to-end connected GNRs with a slight space between two GNRs could be ideal substrate for surface enhanced Raman spectroscopy.

Introduction

Research on metal nanostructures is driven by their shape-dependent surface plasmon resonance (SPR) effects affecting optoelectronic properties such as fluorescence,^{1,2} and surface enhanced Raman scattering (SERS).^{3–5} Among the various materials and nanostructures, the gold nanorods (GNRs) are strong candidates for the various applications because their length and aspect ratio (AR) can be easily controlled through a chemical reduction process.^{6–8} In this solution process, GNRs are frequently self-assembled in a smectic-like fashion during evaporation of the solvent,⁹ resulting in the decreased SPR effect. One technique for preventing the self-assembly in a smectic-like fashion is to connect the GNRs with an end-to-end fashion. Current methods for GNR assembly in an end-to-end fashion were developed by using particular molecules such as biotin and streptavidin,¹⁰ 3-mercaptopropionic or 11-mercaptopundecanoic acids,¹¹ dithiols,¹² or phosphatidylcholine.¹³ These techniques using extraneous molecules, however, bring unwanted effects into the optical and electronic properties of GNRs.

We recently reported the preparation method of three-dimensionally assembled GNRs with an AR of 16.¹⁴ The GNRs well dispersed in a solution were self-assembled in an end-to-end fashion by substituting Milli-Q water for the solvent without using any additive agents. After the deposition of the GNR solution on a substrate, followed by the evaporation of the whole solvent, three-dimensionally assembled GNRs were obtained, which exhibited strong longitudinal SPR signals inducing large SERS activity in near-infrared wavelength region. However, the effect of the end-to-end assembling on the SPR properties and the mechanism of the assembly of GNRs are yet to be investigated.

In this work, we studied the end-to-end assembling phenomenon of gold nanorods using transmission electron microscopy (TEM) associated with selected area electron diffraction (SAED).

The GNRs with ARs of 3 and 16 were synthesized by chemical reduction methods, followed by connecting them at their end positions. The SPR properties of the connected GNRs were also investigated with optical extinction measurement.

Experimental Section

Preparation of GNRs with Different Aspect Ratios. GNRs were synthesized by chemical reduction process to have different ARs of 3 and 16. GNRs with an AR of 3 were prepared using a one-step-seeding method described by Nikoobakht et al.⁶ First, 0.368 g of CTAB was dissolved in 10 mL of 0.25 mM HAuCl₄ solution, followed by adding 1 mL of 0.01 M ice-cold NaBH₄ solution, which was used as a seed solution. Separately, 1.841 g of CTAB was dissolved in a mixture of 50 mL of 0.5 mM HAuCl₄ solution and 450 μ L of 5 mM AgNO₃ solution. After vigorous stirring for 5 min, 400 μ L of 0.1 M ascorbic acid solution was added, which was used as a growth solution. Then 250 μ L of the seed solution was added to the growth solution. The solution was aged for 1 day in order to complete the growth process. The obtained solution was centrifuged at 4500 rpm for 15 min, and the precipitated particles having unwanted shapes such as cube, decahedron, and dodecahedron were removed.

GNRs with an AR of 16 were prepared using a three-step-seeding method developed by Jana et al.¹⁵ 0.020 g of NaBH₄ was dissolved in 50 mL of 0.025 M ice-cold sodium citrate solution, 0.6 mL of which was added to a mixture of 0.2 mL of 0.025 M sodium citrate solution and 19.8 mL of 0.25 mM HAuCl₄ solution. This solution was used as a seed solution. Separately, a growth solution was prepared by adding 350 μ L of 0.1 M ascorbic acid solution to a mixture of 2.319 g of CTAB and 63 mL of 0.25 mM HAuCl₄ solution. 9, 9, and 45 mL of the growth solution were transferred into three beakers named A, B, and C, respectively. 800 μ L of the seed-solution was added to beaker A while stirring for 5 s. 800 μ L of the solution in beaker A was added to beaker B while stirring for 10 s. Then, 4 mL of the solution in beaker B was added to beaker C and stirred for 10 s, followed by aging for 1 day to finalize the

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growth reaction of GNRs. After discarding whole solution in beaker C, the residual precipitated on the bottom of the beaker was dispersed with 10 mL of Milli-Q water by sonication.

Citrate-stabilized gold nanospheres (GNSs) were prepared by boiling a mixture of 333 μL of 24 mM HAuCl_4 solution, 750 μL of 38.8 mM sodium citrate solution, and 30 mL of milli-Q water for 5 min. The solution changed the color to bright red during the boiling. The solution was then rapidly cooled to room temperature and centrifuged at 16000 rpm for 15 min. The supernatant was replaced with Milli-Q water in order to remove excess citrate anions from the solution. CTAB-stabilized GNSs were also prepared by adding 200 μL of 0.1 M CTAB solution to 2 mL of the citrate-stabilized GNS solution.

End-to-End Connection of GNRs. A 26 mL aliquot of the GNR-containing solution was centrifuged twice at 15000 rpm for 15 min, and then 25.3 mL of the transparent supernatant was removed, followed by adding 25.3 mL of Milli-Q water. After the substitution, various amounts of 1 mM sodium citrate solution was added to 5 mL of the solution of GNRs with an AR of 3. During this treatment, the solution gradually changed the color from reddish to bluish violet. Then 0.5 mL of 40 mM CTAB solution was added in order to suspend the color change. On the other hand, the solution of GNRs with an AR of 16 was aged for 2 weeks to spontaneously precipitate the particles, followed by additional substitution of Milli-Q water for the solvent.

Sample Characterization. The optical extinction spectra were measured to detect the SPR frequency variation using a Jasco V-570. The morphologies of the samples were observed with a JEOL JEM-2000EXII TEM. The SAED was conducted on the same microscope. The electrokinetic potentials were measured with an Otsuka ELS-6000KS system.

Results and Discussion

Assembly of GNRs with Various Aspect Ratios. Figure 1 shows the TEM images of the prepared gold nanoparticles. It is evident that nanoparticles with the diameter of 10 nm and ARs of 1, 3, and 16 are prepared by using a variety of seeds and surfactants. In this work, seed-mediated growth method was used to form rod-shaped nanoparticles. For the preparation of longer nanorods, the growth process was separated into three parts to accelerate the direction-fixed growth.¹⁵

In Figure 1a, the GNSs, which are prepared by using sodium citrate alone as a surface stabilizer, are well dispersed without any coagulation. On the other hand, the GNRs tend to be parallel aligned to each other with slight intervals (Figure 1, parts b and c). This smectic-like structure of the GNRs is generally observed as the result of the self-assembly of anisotropic colloidal particles.^{16–18} With the formation of this structure, SPR effects of GNRs, however, diminish in intensity due to plasmon coupling among adjoining GNRs.

Formation of End-to-End Assembled GNRs. During the end-to-end connection process of the solution containing GNRs with an AR of 3, the solution changed the color to bluish violet, suggesting the change in the SPR properties. The typical optical extinction spectra for the GNRs before and after adding sodium citrate are demonstrated in Figure 2a. In the spectrum of the GNRs-containing solution before adding sodium citrate, two SPR bands are observed at 519 and 690 nm wavelengths. It is known that an Au nanorod gives two SPR signals due to the transverse and the longitudinal plasmon modes of the rod. Among two modes, the transverse plasmon mode gives the absorption band at around 520 nm corresponding to that from gold nanosphere. On the other hand, the peak position of the

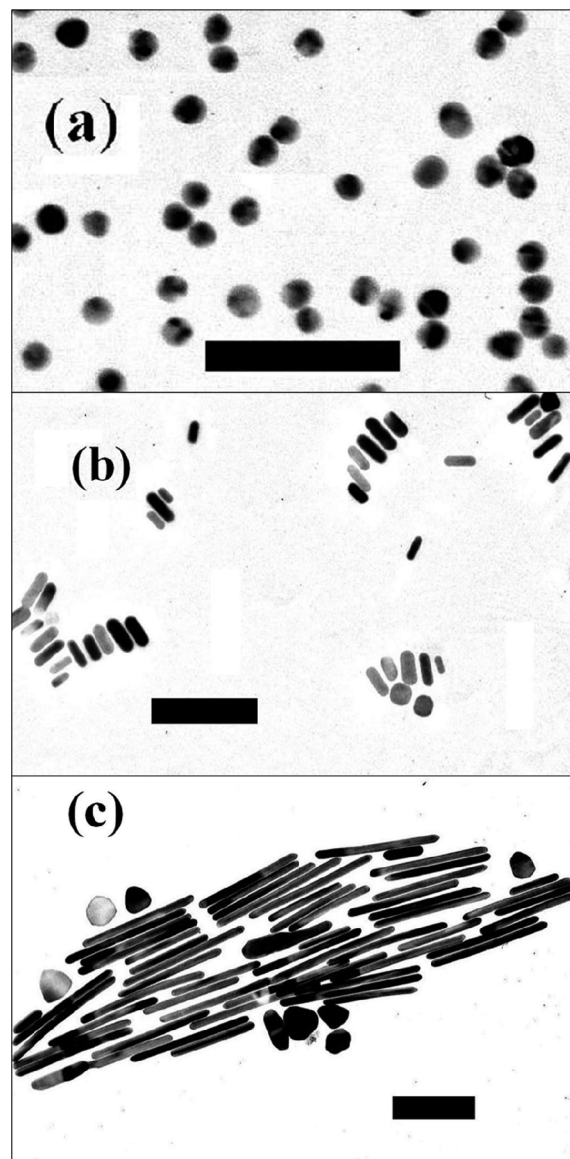


Figure 1. TEM images of the prepared gold nanoparticles with a diameter of ~ 10 nm and ARs of 1 (a), 3 (b), and 16 (c). Scale bars in parts a and c are 200 nm. The scale bar in part b is 100 nm.

longitudinal plasmon mode is dependent on the aspect ratio of the rod, the wavelength (λ_{LSPR}) of which can be easily calculated using the discrete dipole approximation (DDA) formula; $\lambda_{\text{LSPR}} = 96\text{AR} + 418$.¹⁹ The peaks at 519 and 690 nm observed in Figure 2a are well assigned to the transverse and longitudinal plasmon modes of GNRs with an AR of 3. After the addition of sodium citrate to the solution, the longitudinal SPR (LSPR) signal decreases in intensity, followed by an appearance of new peak at longer wavelength region. This observed-red shift of the LSPR signal suggests the end-to-end connections of GNRs^{11,20} or the formation of GNRs with a larger AR value. According to the DDA equation,¹⁹ the peak positions of the LSPR of GNRs with ARs of 6 and 9, where two and three GNRs are linearly combined to generate one longer rod, should be calculated as 994 and 1282 nm, respectively. The wavelengths of the LSPR signals for the GNRs prepared in this experiment are much shorter than the theoretically calculated values, suggesting that the formed GNRs are not linearly combined but connected each other at their end positions.²⁰ However, in contrast to the similar observations in the optical extinction spectra of end-to-end connected GNRs,¹¹ the gradual change

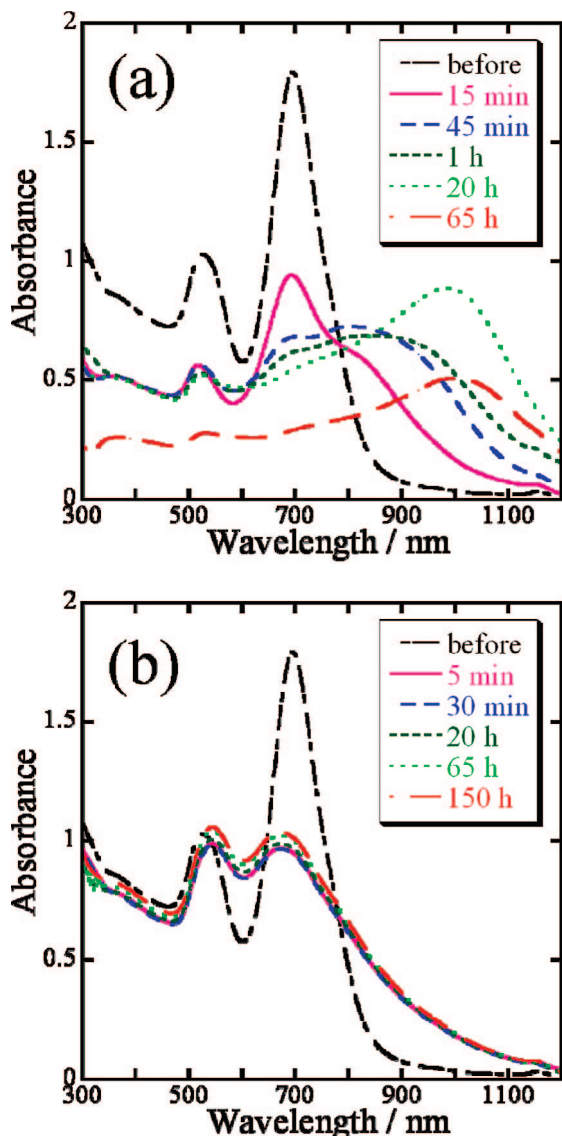


Figure 2. Optical extinction spectra of the solution of GNRs with an AR of 3 prepared by adding 40 μL of 1 mM sodium citrate (a), and adding 0.5 mL of 40 mM CTAB 5 min after the addition of 60 μL of 1 mM sodium citrate (b). The described times in parts a and b are the time intervals after the addition of sodium citrate and CTAB, respectively.

in the spectrum can be suspended by adding 0.5 mL of 40 mM CTAB to the solution, and then the solution can keep more than a month with a slight blue shift of the LSPR peak (Figure 2b). Also, the addition of the CTAB solution is effective at any stages of the change in the spectrum (Supporting Information). This finding suggests that the addition of CTAB to the GNR solution stop the progress of the end-to-end assembly and keeps the then assembly state. The tunable and stable LSPR of the end-to-end connected GNRs seems favorable for the practical uses.

The TEM images of the GNRs obtained after the end-to-end connection process described in experimental section are shown in Figures 3a and 3b. It is evident that GNRs are connected each other in an end-to-end fashion, and a fraction of GNRs are connected in an end-to-side or a side-to-side fashion (Supporting Information). As GNRs with an AR of 16 were not able to be observed with the optical extinction measurement due to the overlapping LSPR peak with strong absorption bands of water, we had to confirm whether the nanorods were assembled in the solution or during the drying step in air. For

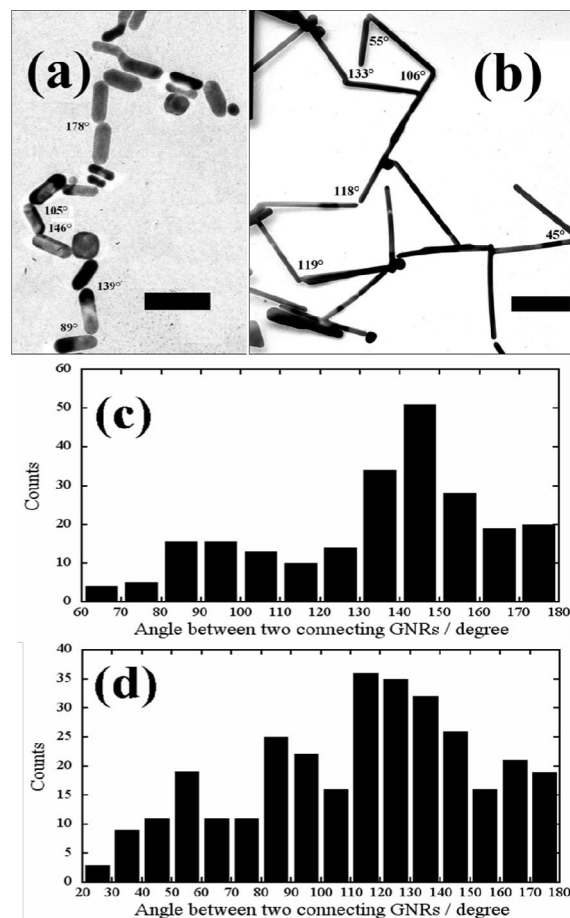


Figure 3. TEM images of the end-to-end connected GNRs with ARs of 3 (a) and 16 (b). Scale bars in parts a and b are 50 and 200 nm, respectively. Parts c and d are the corresponding distributions of the angles between two connecting GNRs shown in parts a and b, respectively.

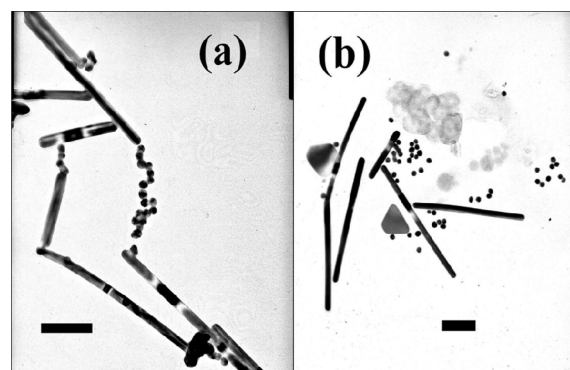


Figure 4. TEM images of the CTAB-covered GNRs reacted with the citrate-stabilized GNRs (a) and the CTAB-stabilized GNRs (b). Scale bar is 100 nm.

that reason, the end-to-end connected GNR solution was spin-coated onto poly(styrene sulfonate) modified slide glass. The nanorods on the glass were observed with a scanning electron microscope and found to be the end-to-end connected state, indicating the GNRs were assembled in the solution (Supporting Information). As shown in Figures 3c and 3d, the connection angle between two GNRs is widely distributed with the mean values of $\sim 140^\circ$ and $\sim 130^\circ$ for the GNRs with ARs of 3 and 16, respectively. The tendency for the connection with obtuse angles could be related to the difference in the surface energy

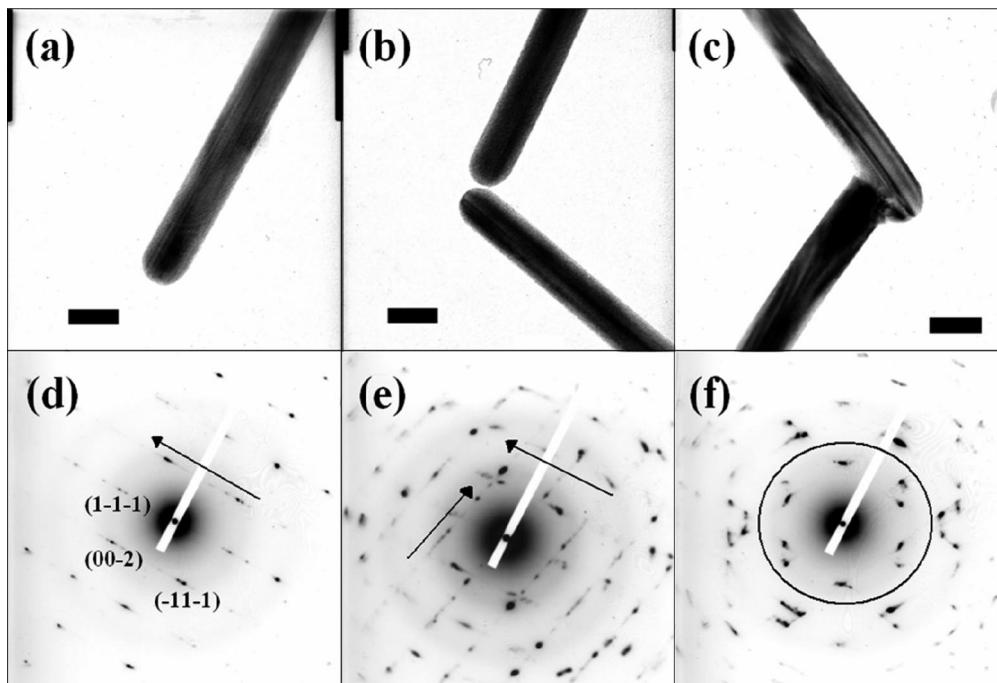


Figure 5. TEM images of the isolated (a), loosely (b), and tightly connected GNRs (c). (d–f) Corresponding SAED patterns of parts a–c, respectively. Scale bar is 20 nm.

between the ends and the sides of GNRs.^{21,22} It is known that the ends of GNRs consist of {111} facets of face-centered-cubic structure of gold, and their sides consist of {100} and/or {110} facets.^{23–25} Since the {111} facets are the closest packed structure of gold atoms, the surface energy of the end is low compared to that of side of GNRs.²⁶ Due to this higher surface energy on the side faces of GNRs, CTAB strongly binds to the surface of GNRs, resulting in difficulty in removing CTAB from the sides of GNRs. Moreover, The estimated CTAB concentration in the end-to-end connected GNR solution is about the exact quantity to have all molecules spent by covering the whole surface of the GNRs (e.g., In the case of GNRs with AR of 3, the concentrations of CTAB and Au are 0.07 and 0.5 mM). Therefore, the observed obtuse angles between the connected GNRs presumably rely on the fact that the well CTAB-covered sides of GNRs repel each other even after substituting Milli-Q water for the solvent involving the drastic decrease of CTAB concentration in the solution.

In order to investigate an effect of sodium citrate on the end-to-end assembly in the solution, two kinds of GNSs were prepared to be modified with citrate anions or CTAB bilayers on their surfaces. Their electrokinetic potentials were measured as -27.8 and $+13.4$ mV for citrate- and CTAB-modified GNSs, respectively. Figure 4 shows the TEM images of the end-to-end connected GNRs reacted with these citrate- or CTAB-modified GNSs. It is apparent that the citrate-modified GNSs preferentially bind with the ends of GNRs (a), while the CTAB-modified GNSs are isolated in the solution irrespective of the existence of GNRs (b). This result is the direct evidence that the ends of GNRs preferentially attract citrate anions in the solution. The mechanism of the attraction is probably explained by considering the CTAB-covering rate on the surface of GNRs. As mentioned above, the ends of GNRs have weak affinity for CTAB, therefore, a part of the end faces could be exposed in the solution after the substitution of Milli-Q water for the solvent. The exposed ends of GNRs can be covered with citrate anions, since citrate anions play the role as surface stabilizer for gold nanoparticles.

With above-mentioned experimental results, four hypothesizes behind the mechanism of the end-to-end assembly of GNRs are considered: (i) the adsorption of citrate anions (negatively charged) to the ends of CTAB-modified GNRs (positively charged) neutralizes the electric charge on the surface, resulting in the aggregation of the GNRs at the end positions; (ii) the low covering rate of CTAB on the GNR ends causes interdigitations of carboxyl groups of CTAB at the gap of GNRs to assemble them;^{27,28} (iii) the cationic head groups of CTAB and citrate anions adsorbed on the GNR ends attract each other electrostatically; (iv) the carboxyl groups of sodium citrate form intermolecular hydrogen bonds at the GNR ends in nonpolar hydrophobic environment provided by the long alkyl chains of CTAB adsorbed on the GNR surface.¹¹ Among these conceivable mechanisms, we observe that (i) and (ii) are the consistent mechanisms for GNRs with ARs of 3 and 16, respectively, because of the following reasons: if (iii) is the driving force behind the assembly, citrate adsorbed ends and CTAB adsorbed sides of GNRs should attract each other, resulting in an end-to-side assembly; if (iv) is the driving force, GNRs with an AR of 3 should be separated by adding enough CTAB (e.g., 0.5 mL of 40 mM CTAB) to cover whole surface of the GNRs because the citrate anions are easily replaced by CTAB due to the strong affinity of CTAB to gold surface. Also in the case of GNRs with an AR of 16, the concentration of citrate anions is simply too low to connect so many GNRs (The estimated concentration of citrate anions in the solution is <10 nM.); the addition of 0.5 mL of 40 mM CTAB to the end-to-end connected GNR solution (AR = 16) results in the singly dispersed GNRs in the solution, therefore, the GNRs are not aggregated (i), but connected by the interdigitated CTAB at the gap where the CTAB-covering rate is comparatively low (ii). In contrast, the GNRs with an AR of 3 are aggregated at the end positions so that the GNRs are not separated by adding CTAB to the solution.

Welding of End-to-End Connected GNRs. Since the GNRs with an AR of 3 are aggregated at the end positions, we thought that the end-to-end aggregated GNRs with an AR of 16 could be produced, too. Figure 5 shows the TEM images of an isolated

(a), loosely (b), and tightly connected GNRs (c). The tightly connected GNRs are found as the welded form (Figure 5c), indicating the end-to-end aggregation in the solution has occurred. Because the yield of the aggregated GNRs increases by decreasing CTAB concentration in the solution, it is suggested that the fairly low CTAB-covering rate cause the end-to-end aggregation of the GNRs. The corresponding SAED patterns of Figure 5a–c are shown in Figure 5d–f, respectively. Since extra reflections along the longitudinal axis of the GNRs are observed in Figure 5d (indicated by an arrow), it is confirmed that the GNRs have a “twin defect structure”.²⁵ In the loosely connected GNRs, the extra reflections from two GNRs are simply superimposed (indicating by arrows in Figure 5e). On the other hand, the aggregated GNRs show Debye–Scherrer rings (indicating by circle in Figure 5f). The observation of Debye–Scherrer rings indicates that the crystal structure changes around the end positions of GNRs from single crystal to polycrystalline state by the aggregation. We believe that such welded GNRs can be applied to conducting materials, in contrast to the loosely connected GNRs which have the potential to be used as SERS substrate that takes advantage of strongly enhanced electromagnetic field generated at the interparticle region.

Conclusions

We have shown that GNRs with an AR of 3 are assembled in an end-to-end fashion by adding sodium citrate to the GNR solution with decreased CTAB concentration. The SPR properties of GNRs changes by the end-to-end assembly, where the LSPR band is shifted to longer wavelength region as the GNRs interact with each other at their end positions. The red-shift in LSPR band gradually progresses after the addition of sodium citrate. However, it can be suspended by adding CTAB, and furthermore, the solution can store for at least a month with an initial slight blue-shift in LSPR band. As citrate-modified GNSs are preferentially adsorbed on the GNR ends, citrate anions are considered to neutralize the surface charge of the GNRs at their end positions so that the end-to-end connection is promoted. GNRs with an AR of 16 are assembled in an end-to-end fashion by only decreasing CTAB concentration in the solution. The further decrease of the CTAB concentration leads to the formation of end-to-end aggregated GNRs in the solution.

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Supporting Information Available: Figures showing TEM and SEM images, and optical extinction spectra of the end-to-end assembled GNRs. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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