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Large-Scale Synthesis of Gold Nanorods through Continuous Secondary Growth

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Abstract

Gold nanorods (GNRs) exhibit a tunable longitudinal surface plasmon resonance (LSPR) that depends on the GNR aspect ratio (AR). Independently controlling the AR and size of GNRs remains challenging but is important because the scattering intensity strongly depends on the GNR size. Here, we report a secondary (seeded) growth procedure, wherein continuous addition of ascorbic acid (AA) to a stirring solution of GNRs, stabilized by cetyltrimethylammonium bromide (CTAB) and synthesized by a common GNR growth procedure, deposits the remaining (~70%) of the Au precursor onto the GNRs. The growth phase of GNR synthesis is often performed without stirring, since stirring has been believed to reduce the yield of rod-shaped nanoparticles, but we report that stirring coupled with continuous addition of AA during secondary growth allows improved control over the AR and size of GNRs. After a common primary GNR growth procedure, the LSPR of GNRs is ~820 nm, which can be tuned between ~700–880 nm during secondary growth by adjusting the rate of AA addition or adding benzyltrimethylhexadecylammonium chloride hydrate (BDAC). This approach for secondary growth can also be used with primary GNRs of different ARs to achieve different LSPRs and can likely be extended to nanoparticles of different shapes and other metals.

Keywords

gold; silver; nanorods; seeded growth; surface plasmon resonance

Introduction

Gold nanorods (GNRs) exhibit intense longitudinal surface plasmon resonances (LSPRs), whose wavelength is controlled by the ratio of the length to the width of the GNR (aspect ratio, AR), as well as a weaker transverse surface plasmon resonance that is fixed at ~510 nm. As the AR increases above unity, the LSPR is tuned toward longer wavelengths and into the near-infrared spectrum. Light absorbed by GNRs is converted into heat, which is useful for photothermal therapy, and scattered light is useful for biomedical imaging and surface-enhanced Raman spectroscopy. For biomedical applications, there is particular interest in adjusting the LSPR to 800–1000 nm, where blood and tissue are minimally absorbing.^{1,2}

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Supporting Information Available: Detailed description of adjustments performed to the absorbance scale for the optical spectra and plots of GNR AR versus width measured from TEM for all samples presented in Figures 1, 3, 4 and 5. Description of calculations of the AA:Au molar ratios used in Figures 1 and 2. Plots of the peak absorbance versus injection rate and BDAC:CTAB ratio for the samples in Figures 3 and 5, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Chemical synthesis of GNRs utilizing cetyltrimethylammonium bromide (CTAB) and AgNO_3 to direct the nanoparticle shape into nanorods was pioneered by Murphy and coworkers,^{3,4} with improvements to the seeding process and a commensurate increase in the yield of rod-shaped particles by El-Sayed and coworkers.⁵ CTAB forms a cationic bilayer that encapsulates the GNRs and facilitates their dispersion in aqueous solutions.⁶ Several modifications of these methods have allowed for further tailoring of the GNR shape, size, and purity.^{7–10} Related methods have been developed for the synthesis of gold nanoparticles with shapes other than nanorods.^{11–22}

When synthesizing GNRs, the solution containing the GNRs usually is not stirred²³ during growth. Early in the development of methods for synthesizing GNRs, rodlike micelles formed by CTAB in water²⁴ were thought to be critical for directing the structure into nanorods.³ Stirring during GNR growth would perturb the rodlike micelles, which could reduce the yield of rod shapes. Here, we show that during continuous secondary (seeded) growth of GNRs, once the seeds have evolved into rod-shapes, stirring does not decrease the GNR yield but rather gives improved control over the GNR size and shape while also accelerating the reaction. More recent experiments have also shown that the rodlike micelles may be less important than initially believed and that bromide ion,^{6,25–27} selective adsorption of cetyltrimethylammonium to certain faces of the nanoparticles,^{6,28,29} and introduction of aromatics^{5,30} may be more important for directing the growth of nanorods.

In many of the methods known for synthesizing GNRs, the Au(III) is reduced to Au(I), but much of the Au(I) remains in solution and is not deposited onto GNRs.^{29,31–34} Subsequent addition of more ascorbic acid (AA) to the solution has been shown to reduce the remaining Au(I) to Au(0), which is deposited onto the GNRs.³⁵ We refer to this additional step of adding more AA as “secondary growth.” Predominately two kinds of secondary growth have been explored: instantaneous and gradual AA addition. In the simplest case, quickly adding a large amount of AA results in nanodogbones (NDBs) when Au atoms are added disproportionately to the ends of the GNRs, where edges and corners destabilize the CTAB bilayer.^{35–38} Formation of NDBs can be avoided, and improved control over the secondary growth process has been obtained by adding AA in smaller increments but still allowing the reaction to proceed in a still (not shaken or stirred) solution.^{39,40}

Here, we report the continuous addition of AA during secondary growth with stirring, which has significant advantages. As with other methods for secondary growth of GNRs, adding more AA allows complete consumption of the Au precursor. In our experiments, only 29% of Au precursor has been reduced into GNRs at the beginning of secondary growth. Continuous addition of AA with stirring is less laborious than stepwise addition, imparts improved uniformity over the reaction, and completes the reaction more quickly due to mixing and a constant influx of reducing agent. For growth from a set of seeds whose LSPR is ~815–830 nm, the LSPR wavelength of the final GNRs can be adjusted between ~700–820 nm by varying the rate of AA addition. For the same GNR seeds obtained through primary growth, the LSPR peak of the final GNRs can be further redshifted to ~880 nm by altering the surfactants used for secondary growth. Under properly optimized conditions, different sizes of GNRs can be grown, while maintaining the same LSPR wavelength at ~820 nm, which allows control over the scattering intensity.^{40–42} A related method of secondary growth is to add more Au precursor,^{43–53} over which greater control might also be obtained by performing continuous addition with stirring. It should also be noted that continuous addition of metal ions has already been utilized for other kinds of metal nanoparticles to give control over the growth kinetics and structures.^{2,54–62}

Some very recent studies have demonstrated improved control over GNR size and shape by adding other surfactants,^{30,63} eliminating CTAB,⁶⁴ replacing AA with other reducing

agents,⁶⁵ or using a microfluidic reactor.⁶⁶ Substitutes for CTAB are desired to overcome sensitivity to iodide impurities,^{14,67–70} and alternatives for AA may overcome sensitivity to the amount and manner of AA addition.⁶⁵ Here, we exploit the sensitivity to the method of AA addition and show that it can provide precise control over the AR and size of GNRs. Under certain conditions, secondary growth processes, whether through addition of metal precursor, reducing agent, or some combination thereof, can provide improved control over the shape and size of metal nanostructures.

Experimental Section

Gold Nanorod Synthesis

The general scheme for synthesizing a 100 mL solution of GNRs utilizes a seed solution, primary growth solution (GS), and secondary GS. The seed solution and primary GS are mixed to initiate a primary growth phase, wherein the primary GS evolves into the primary GNR solution (NRS1), which is similar to the GNR product that was obtained by El-Sayed and coworkers.⁵ We have devised a method for adding the secondary GS to NRS1, thereby initiating a continuous secondary growth phase. During this phase, NRS1 evolves into the final nanorod solution (NRSF).

A total of 100 mL deionized water (DIW, Ricca, ACS Reagent Grade, ASTM Type I, ASTM Type II) for use in the primary GS was measured at room temperature using a volumetric flask. Five separate solutions were prepared and combined in sequential order to create the primary GS. First, 3.4309 g (9.4139 mmol) cetyltrimethylammonium bromide (CTAB, Sigma Aldrich, 99%, H6269) was dissolved in 77 mL DIW. The mixture was gently heated with a heat gun to dissolve the CTAB and was kept in a water bath set to 30 °C. Even dilute iodide impurities in CTAB are known to drastically reduce the yield of rod-shaped nanoparticles, and one must exercise caution to obtain “good” CTAB and avoid “bad” CTAB for GNR synthesis.^{14,69} Unfortunately, there can be significant differences among vendors, products, and even lots of the same product.^{67,70} Our CTAB was chosen empirically by performing GNR syntheses with a few products and selecting the one that gave the best combined performance and price. For all of the experiments reported here, we used the same CTAB product number, but a few different lots were used. The differences between lots were somewhat lessened by supplementing the solutions with bromide by adding KBr, though for the best lots of CTAB, adding KBr may have slightly broadened the LSPR absorption band in comparison to omitting KBr. An amount of 0.1120 g KBr (0.9412 mmol) (Alfa Aesar, ACS, 99% min) in 1 mL DIW was added to the CTAB solution, giving 0.1 mol KBr per mol CTAB, which we refer to as 0.1× KBr. For syntheses, where NRS1 was supplemented with benzyldimethylhexadecylammonium chloride hydrate (BDAC) prior to the secondary growth phase, the KBr in the primary GS was omitted. For the set of syntheses, where the AgNO₃ concentration was varied (Figure 8), the amount of KBr in the primary GS was doubled (0.2× KBr) to compensate for a different lot of CTAB. A solution of 3.26 mg (0.0192 mmol) AgNO₃ (Alfa Aesar, 99.9995%) in 1 mL DIW was then added. A light yellow solution containing 37.9 mg (0.0962 mmol) HAuCl₄·xH₂O (Alfa Aesar, 99.999%), where *x* was estimated as 3, dissolved in 20 mL DIW was then added to the CTAB solution, which became a deep orange color. Finally, 18.6 mg (0.105 mmol) ascorbic acid (AA, J.T. Baker, 99.5%) dissolved in 1 mL DIW was added to this mixture, causing it to become colorless. After adding all of the reagents, the molar concentrations (adjusted for a volume change to 103.4 mL due to the dissolved CTAB) of the precursors in the primary GS were: $9.104 \times 10^{-2} M$ CTAB, $9.305 \times 10^{-4} M$ HAuCl₄, $1.853 \times 10^{-4} M$ AgNO₃, $9.102 \times 10^{-3} M$ KBr, and $1.019 \times 10^{-3} M$ AA.

The DIW used in all of the solutions was preheated to 30 °C before adding any reagents. Immediately after each addition step, the solution was thoroughly mixed and placed into a

temperature-controlled water bath at 30 °C. Heating at this temperature prevents solidification of CTAB, but we have also found that the GNR synthesis is highly temperature sensitive; starting with the solutions at 30 °C prior to beginning the synthesis, even for dissolving the precursors, improves the reproducibility by minimizing temperature variations. Foaming caused by CTAB is a potential impediment to reproducibility because the foam may trap precursors or reaction intermediates that are not uniformly mixed with the contents of the solution but may have deleterious effects when they are mixed into the solution at a later time. Gentle mixing during the addition of each of the precursors ensured homogeneity, but care was taken to avoid bubbles. Whenever foam formed, it was eliminated by blowing hot air from a heat gun over the surface of the solution.

Four separate solutions were prepared and combined in sequential order to give the final seed solution, which was also kept at 30 °C. Initially, 0.3640 g (0.9988 mmol) CTAB was dissolved in 8 mL DIW. Solutions of 11.9 mg (0.100 mmol) KBr in 1 mL DIW and 1.0 mg (0.002539 mmol) $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ in 1 mL DIW were added to the CTAB solution. The concentrations (without adjusting for the volume change due to the dissolved CTAB) of the precursors in the seed solution prior to adding a NaBH_4 solution to drive reduction and nanoparticle growth were: $9.988 \times 10^{-2} \text{ M}$ CTAB, $2.539 \times 10^{-4} \text{ M}$ HAuCl_4 , and $1.000 \times 10^{-2} \text{ M}$ KBr. The KBr:CTAB molar ratio in the seed solution was also 0.1, which we also refer to as $0.1 \times$ KBr. For the set of syntheses, where the AgNO_3 concentration was varied (Figure 8), no KBr was used in the seed solution. The mixture was maintained at 30 °C in a water bath with controlled and uniform vigorous stirring (~ 1150 rpm). For the fourth solution, a stock solution was prepared by dissolving 3.78 mg (0.09992 mmol) NaBH_4 (Sigma-Aldrich, 99%, 213462) in 10 mL ice-cold DIW. To obtain the highest mass accuracy when measuring this small mass, a larger amount of NaBH_4 (> 0.1 g) was first added to ice-cold DIW at a ratio of 1 mL/37.8 mg NaBH_4 . (Safety note: As aqueous NaBH_4 solutions decompose, they give off gaseous H_2 . Storing highly concentrated NaBH_4 solutions such as this one in vials with threaded caps is an explosion hazard.) A 1 mL aliquot of this solution was diluted by adding 9 mL ice-cold DIW, followed by further diluting 1 mL of this less concentrated solution with 9 mL ice-cold DIW. A 0.6 mL aliquot of this twice diluted, ice-cold NaBH_4 solution containing 0.227 mg NaBH_4 was quickly injected into the stirring seed solution precursor solution. Preparation of this NaBH_4 solution and its addition to form the final seed solution is a critical step in reproducibly preparing NRS1 and obtaining a high yield of GNRs. The seed solution was stirred for two minutes after injection and then left still for three minutes before rapid injection into the primary GS. 0.1358 mL of the seed solution was injected into the primary GS, after which the primary GS was completely inverted seven times to homogenize any seed solution caught in the foam, while taking care to avoid excessive foaming. The solution was then left still for one hour in a water bath at 30 °C, over which the seeded primary GS evolves into NRS1. The optical absorbance spectrum of NRS1 was obtained after completion of the primary growth phase, for which an LSPR near 820 nm is expected.

A secondary GS comprised of 16.7 mg (0.0948 mmol) AA in 10 mL DIW was prepared to commence and sustain the secondary growth phase. An amount of 5 mL of the secondary GS was injected by syringe pump into 100 mL of vigorously stirring NRS1 (at 500 rpm with a rod-shaped stir bar for 200 mL and smaller scales, or a $\times$ -shaped stir bar for 1 L reactions) in a water bath at 30 °C with an injection rate (IR) of 29.17 LL/min (referred to as a $10 \times$ IR), which gives a total injection time of 171.4 min. This $10 \times$ IR results in a small blueshift in the LSPR to ~ 800 nm for NRSF. For injection rates different from the default value of $10 \times$, the IR and the total injection time are proportionally adjusted. For example, secondary GS is added at 14.59 LL/min over a period of 342.8 min for $5 \times$ IR, at 7.29 LL/min over a period of 685.6 min for $2.5 \times$ IR, and at 3.65 LL/min over a period of 1371.2 min for $1.25 \times$ IR. For other reaction scales, the volumes of the secondary GS and the seed solution added to NRS1

were adjusted in proportion to the volume of NRS1. The concentration of the secondary GS can also be adjusted, provided that the moles of AA added per minute remains the same. For the 1 L synthesis with 10 $\times$ IR, for example, the volume of the secondary GS can be adjusted to 30 mL (added at a rate of 175 LL/min) rather than 50 mL, which is the amount calculated based on the 100 mL reaction scale. In one set of experiments, GNRs of different sizes were obtained by removing aliquots from the solution at different times during the secondary growth phase. Details for calculation of the AA to Au molar ratio as the reaction progresses, while removing aliquots, are provided in the Supporting Information.

Addition of BDAC to NRS1 is known to facilitate the growth of GNRs with higher ARs.⁵ For selected syntheses, BDAC (Acros, 97%) was added to NRS1 prior to starting the secondary growth phase at a ratio of 3.7288 g BDAC for every 100 mL of solution, which results in a 1:1 BDAC:CTAB molar ratio and is referred to as 1 $\times$ BDAC. Note: completely dissolving BDAC into the CTAB solution requires ultrasonication; it is recommended to make a fine powder of the BDAC before addition to NRS1. For syntheses where BDAC was added to NRS1, KBr was not added to the primary GS because mixtures of KBr and BDAC give gelatinous solutions that are difficult to stir.

For reactions conducted at scales other than 100 mL, the volumes of the solutions described above and the injection rates of the secondary GS were adjusted in proportion to the reaction scale, while maintaining the same concentrations and injection time. For all reaction scales, the seed solution was always prepared on the same 10.6 mL scale.

Optical Characterization

Optical absorbance spectra were acquired using an Ocean Optics CHEMUSB4-VIS-NIR spectrophotometer. For all measurements of the GNR solutions, aliquots of 0.5 mL were diluted to 3.0 mL with solutions of CTAB in DIW (34.3090 g CTAB per L of DIW). In order to make the absolute values of the absorbance most meaningful when comparing reactions that used different concentrations of AA in the secondary GS, minor corrections were performed to scale the absorbance spectra and to neglect the volume of the secondary GS. These corrections are presented and discussed in the Supporting Information.

Transmission Electron Microscopy

The major (length) and minor (width) axes of the nanoparticles were measured by transmission electron microscopy (TEM) using a JEOL 2000FX microscope operated at 200 kV. For determining the average length, width, and AR of the GNRs, which correlates with the LSPR peak absorbance, nanoparticles that significantly deviate from rod shapes (outliers) were omitted. The average AR was calculated as the mean of the AR values calculated from individual GNRs, which is not identical to the value of the average length divided by the average width. The outliers were determined through the following empirical procedure that works better than omitting all points that lay outside of a certain number of standard deviations from the average value; in many cases, the data do not follow a Gaussian distribution. Measurements of the nanoparticle AR and width were separately sorted. Nanoparticles with AR < 1.5 were first omitted because they had formed separately from the GNRs and would distort the measurements. Each of the remaining nanoparticles was included in the average, unless the AR or width deviated from the average values by more than 1.5 times the difference between the first and third quartiles of all of the rod-shaped nanoparticles for that sample. In every case, enough nanoparticles were measured for each sample such that at least 200 nanoparticles satisfied this criterion and were counted as nanorods after removing the outliers. Graphs of the AR plotted versus the width, excluding nanoparticles with AR < 1.5, can be found in the Supporting Information for the samples

presented in Figures 1, 3, 4, and 5, where the nanoparticles included in the average and the outliers have been labeled separately.

Results and Discussion

Secondary Growth with Fixed Aspect Ratio

Under certain reaction conditions, the GNR AR can be maintained during the secondary growth phase. Figure 1 shows results for GNRs with fixed LSPR of ~ 820 nm grown from NRS1 with average dimensions of 57×15 nm grown out to 83×23 nm over the course of 156 min using a $11\times$ injection rate (IR). Conversion of these dimensions into cylindrical volumes shows that average GNR volume in the primary growth solution (NRS1) is only 29% of that for GNRs in the final growth solution (NRSF). Thus, at the end of the primary growth phase, 71% of the Au precursor remains incompletely reduced to Au(0). The dependence of the average GNR volume and peak absorbance value on the molar ratio of AA that had been added since the beginning of the synthesis to Au is plotted in Figure 2. NRS1 contains 1.10 moles of AA per moles of Au, and after completing the secondary growth phase, the ratio grows to 1.59 in NRSF. AA is a two-electron reducing agent, though its reduction kinetics depend on pH⁷¹ (which may be explored as a lever for controlling secondary growth in future studies).⁷² Therefore, if the reduction reaction proceeds to completion, at a molar ratio of 1 AA:Au, all of the Au(III) precursor may be reduced to Au(I), and at a molar ratio of 1.5 AA:Au, all of the Au(I) may be deposited onto the GNRs. An excess of secondary GS, as seen in Figure 2, does not significantly affect the GNR shape or their optical spectra, because all of the Au precursor will have already been consumed. These results are significant because this method allows for the synthesis of a series of GNRs with well controlled sizes, while maintaining the same LSPR wavelength. The smaller sizes are only weakly scattering, but the larger sizes are known to scatter light more intensely,^{40–42} which is important for imaging applications² and SERS.⁷³

Maintaining fixed AR requires faster growth on the ends of the GNRs than on the sides. The shape of the GNRs is well preserved as rods rather than obtaining NDBs. We attribute this to the continuous addition of the secondary GS with stirring. Continuous addition keeps the AA concentration lower than stepwise addition by never adding a large amount at once. Stirring accelerates the reaction and further helps maintain a low, homogenous AA concentration. In previous studies, formation of NDBs was often triggered by instantaneously adding a large amount of AA;^{35,37,38} smaller amounts appear to favor more uniform growth. Stirring may also facilitate uniform growth on the ends of the GNRs rather than formation of NDBs by perturbing the CTAB bilayer, thus reducing the preference for growth from the corners into NDBs.

Ascorbic Acid Addition Rate and Concentration

Adding the secondary GS more slowly than $11\times$ IR allows for control over the AR, resulting in a blueshift in the LSPR (Figure 3). The dependence of the peak wavelength on the IR is plotted in the Supporting Information, Figure S1. The time needed to complete the reaction inversely scales with the IR. These results show that when AA is added more slowly, the preference for addition to the ends of the GNRs is lessened, and the deposition is more uniform. We hypothesize that in the limit of very slow addition, Au may be deposited in a shell of uniform thickness on NRS1. We could predict, if we model GNRs as cylinders, that if 29% of the Au precursor is consumed to form NRS1 with dimensions of 57×15 nm, then the remaining 71% would be consumed in growing a shell of thickness 5.3 nm, giving final dimensions of 68×26 nm and an AR of 2.64, for which an LSPR of ~ 670 nm would be predicted from the formula, $\lambda_{\text{LSPR}} = [95(\text{AR}) + 420]$ nm.⁷⁴ The $1.25\times$ IR investigated here gives an LSPR of 696 nm, with dimensions of 71×27 nm. From the trendline discussed

below and presented in Figure 6, a GNR of AR 2.64 would have an LSPR of 700 nm. Therefore, results for $1.25\times$ IR approach the long-time limit of deposition of a uniform Au shell. The reduction in AR for slower IRs must be caused by the reduced concentration of AA, because the stirring rate was the same in these experiments as for the growth at $11\times$ IR (Figure 1). The reason for the concentration dependence remains unclear, however, and needs to be further investigated. IR faster than $11\times$ gives higher concentrations of AA during the secondary growth phase, which results in non-uniform deposition of Au (approaching NDB shapes in the high concentration limit). Moreover, the smaller, longer GNRs grow more quickly than the larger GNRs, which causes a broader AR distribution and absorbance spectrum.

Large-Scale Synthesis

This method of secondary growth is scalable to larger amounts of GNRs, provided that highly uniform NRS1 can be obtained and mixing remains uniform. We did, however, observe a decrease in size monodispersity of NRS1, and therefore in NRSF, for larger reaction scales. Increasing the reaction scale from 100 mL ($10\times$ IR from Figure 3) to 1 L (Figure 4) while using otherwise identical growth parameters increased the standard deviation of the lengths from 8.5 to 12.6 nm, the width from 2.8 to 4.4 nm, and the AR from 0.39 to 0.46.

Aspect Ratio Control Using Benzyldimethylhexadecylammonium Chloride Hydrate

El-Sayed and coworkers first reported the addition of BDAC to CTAB to form GNRs with higher ARs.⁵ A plausible mechanism for obtaining high ARs through the use of BDAC is faster growth on the ends of the rods if BDAC binds preferentially to the ends due to its weaker binding caused by the substitution of a phenyl group for a methyl group or of chloride for bromide. Unfortunately, use of BDAC in the growth solution is often accompanied by a higher yield of non-rod-shaped nanoparticles.⁵ In our synthesis, we have conducted the primary growth phase without BDAC in the primary GS or in the seed solution, but BDAC was then added to NRS1 prior to the start of the secondary growth phase, which prevents BDAC from reducing the yield of nanorods, while still promoting growth of GNRs with higher ARs. For syntheses using BDAC, KBr was not added to the primary GS because addition of BDAC to solutions containing KBr results in a highly viscous mixture, which impedes uniform growth. KBr ($0.1\times$) was present in the seed solution, however. It should be noted that NRS1 for all of the experiments reported in Figures 1–5 was prepared following an identical procedure, except for the omission of KBr in the primary GS for syntheses utilizing BDAC and adjustments in the reaction scale; the differences in NRSF emerge during secondary growth. BDAC still helps direct the shape into nanorods with higher ARs, even though it has been added after completing the primary growth phase (Figure 5). In this manner, we have obtained LSPRs as high as 878 nm. To cause a redshift in the LSPR, there is a minimum amount of BDAC that needs to be added to NRS1. BDAC concentrations above $0.5\times$ give increasingly large redshifts, but the formation of NDB shapes also becomes more prominent. The dependence of the peak wavelength on the BDAC:CTAB ratio is plotted in the Supporting Information, Figure S2.

Trendline: LSPR Wavelength vs. Aspect Ratio

The LSPR wavelengths and ARs obtained from TEM for many samples are summarized in Figure 6, which exhibits a clear linear relationship, as expected.⁷⁴ A linear fit of these data points gives $\lambda_{\text{LSPR}} = [116(\text{AR}) + 393]$ nm, which agrees reasonably well with prior reports.⁷⁴ The ARs plotted in Figure 6 may differ from values calculated from the average length and width provided as insets in Figures 1, 3, 4, and 5 because the average AR was measured as the average of the ARs of individual GNRs.

Supplemental Potassium Bromide for Primary Growth

As noted earlier, bromide has a special role in the synthesis of GNRs. Since iodide impurities in CTAB are detrimental, we supplemented CTAB with KBr to ensure an excess of bromide ion. Here, we denote the molar ratio of KBr to CTAB as $\times$ KBr. A series of syntheses of NRS1 conducted with up to $0.4\times$ KBr in the primary GS showed that $0.1\times$ KBr gave results similar to no KBr, but we chose to add KBr due to the effect that it tended to have on leveling out differences (but not completely) between different lots of CTAB. Amounts of KBr exceeding $0.1\times$ were not used because they gave diminished ratios of the LSPR to transverse surface plasmon resonance absorbance and broader absorbance bands for NRS1 (Figure 7). For the standard synthesis, $0.1\times$ KBr was also added to the seed solution, which produced a slightly more redshifted LSPR for NRS1, as compared to a seed solution without KBr. Except where noted otherwise, we generally used the same proportion of KBr to CTAB in both the primary GS and the seed solution.

Silver Nitrate Concentration

AgNO_3 is well known as an additive that helps to direct and control the rod shape of GNRs. Several mechanisms for shape control using AgNO_3 have been proposed, but proving which mechanism(s) is predominant remains a topic of ongoing investigation.¹⁰ In another set of experiments, we adjusted the AR of NRS1 by varying the AgNO_3 concentration in the primary GS, which others have reported.^{5,75} Here, no KBr was used in the seed solution, and $0.2\times$ KBr was used in the primary GS to compensate for a different lot of CTAB than in the other experiments. The spectra in Figure 8 show the effects of increasing or decreasing the concentration of AgNO_3 in the primary GS by $\pm 50\%$ of the amount used in our standard synthesis ($1.853 \times 10^{-4} \text{ M AgNO}_3$). During the secondary growth phase, the AR is nearly preserved using a $10\times$ IR (Figure 8). Adjusting the AgNO_3 concentration demonstrates the potentially broad application of secondary growth procedures to enlarge metal nanoparticles of different shapes.

Conclusions

This method for secondary growth of GNRs through the continuous addition of AA with stirring to a solution containing small GNRs and unreacted Au precursor can be performed on a large scale and allows complete reduction of the Au precursor. By controlling the rate of AA addition and adjusting the mixture of surfactants present during secondary growth, the AR can be decreased, increased, or kept constant, which demonstrates unprecedented ability to tailor the optical properties of GNRs during secondary growth. With proper modifications, we anticipate that our method may be extended to secondary growth of other systems, such as the growth of gold nanoparticles of various shapes or metal nanoparticles of other compositions. The improved control available in continuous secondary growth procedures will also facilitate mechanistic studies of nanoparticle growth.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Timed aliquots during secondary growth of NRS1 with an LSPR of ~820 nm at an injection rate (IR) of 11×, which drives an increase in the AA:Au molar ratio: (a) optical absorbance spectra and (b–g) TEM images after adding different amounts of AA. Spectra and images for samples of (b) NRS1 and (c) 31, (d) 62, (e) 94, (f) 125, and (g) 156 minutes after starting the secondary growth phase.

Figure 2.

Total % of Au precursor reduced onto GNRs over 156 min at $11\times$ IR, where 100% deposition occurs when further addition of AA does not result in further growth. Two independent measurements of the % Au deposited were performed, analysis of (1) TEM images, where cylindrical shapes were assumed, and (2) the absorbance intensity at the peak LSPR for each aliquot normalized to NSRF.

Figure 3. Secondary growth of NRS1 at different injection rates (IRs), where those grown at the slowest rate experienced the greatest shift toward shorter wavelengths: (a) optical absorbance spectra and TEM images of (b) NRS1 and NRSF using (c) 1.25x, (d) 2.5x, (e) 5x, and (f) 10x IR.

Figure 4. Optical absorbance spectrum and (inset) TEM image for 1 L synthesis with 10× IR.

Figure 5.

Secondary growth of NRS1 with BDAC in addition to the standard amount of CTAB, where the number of $\times$ is the molar ratio of BDAC to CTAB: (a) optical absorbance spectra and TEM images of (b) NRS1 and NRSF using (c) 0.25 $\times$, (d) 0.5 $\times$, (e) 1.0 $\times$, and (f) 1.5 $\times$ BDAC. KBr was omitted from the primary GS, but 0.1 $\times$ KBr was used in the seed solution.

Figure 6. Analysis of the dependence of the peak absorbance wavelength on the GNR aspect ratio measured by TEM.

Figure 7.

Optical absorbance spectra showing how NRS1 is affected by adding varying amounts of KBr to the primary GS. All solutions were prepared from the same batch of the primary GS prior to addition of KBr and seed solution taken from the same stock solution. No KBr was present in the seed solution. The spectra were normalized at 510 nm.

Figure 8. Optical absorbance spectra showing how (a) NRSF and (b) NRS1 are affected by varying the concentration of AgNO_3 in the primary GS with $10\times$ IR. For these syntheses, no KBr was added to the seed solution but $0.2\times$ KBr was used in the primary GS.