Fabrication of Gold Nanorods with Tunable Longitudinal Surface Plasmon Resonance Peaks by Reductive Dopamine

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Supporting Information

ABSTRACT: Hydroxyphenol compounds are often used as reductants in controlling the growth of nanoparticles. Herein, dopamine was used as an effective reductant in seed-mediated synthesis of gold nanorods (GNRs). The as-prepared GNRs (83 × 16 nm) were monodisperse and had a high degree of purity. The conversion ratio from gold ions to GNRs was around 80%. In addition, dopamine worked as an additive. At a very low concentration of hexadecyltrimethylammonium bromide (CTAB; 0.025 M), thinner and shorter GNRs (60 × 9 nm) were successfully prepared. By regulating the concentration of silver ions, CTAB, seeds, and reductant, GNRs with longitudinal surface plasmon resonance (LSPR) peaks ranging from 680 to 1030 nm were synthesized. The growth process was tracked using UV−vis−NIR spectroscopy, and it was found that a slow growth rate was beneficial to the formation of GNRs.

INTRODUCTION

Gold nanoparticles (GNPs) have been widely used in biomedicine, catalysis, biosensing, electronic, photonics, etc.1−6 These applications depend on unique physical and chemical properties of the synthesized GNPs, which can be tuned by changing the shape, size, and crystallinity. Many efforts have been made in the synthesis of anisotropic gold nanostructures, such as nanorods, nanostars, multipods, and so on.7−10 Among them, gold nanorods (GNRs) have attracted the most attention, due to their tunable shape-dependent optical properties.6 Therefore, efficient and reliable synthesis of GNRs with a broad range of longitudinal surface plasmon resonance (LSPR) is highly desirable.

Seed-mediated growth is the most widely used method in the synthesis of GNRs, which was first developed by Murphy and El-Sayed.11,12 In their methods, hexadecyltrimethylammonium bromide (CTAB) and silver nitrate were necessary for the formation of rodlike particles; small CTAB-capped GNPs (∼4 nm) were used as seeds. GNRs with different aspect ratios were synthesized by varying the silver ion concentration or by using a binary surfactant mixture. Some other factors, such as temperature,13 pH,14 surfactant types,15−18 concentration of reactants,13,19 additives,20−22 and seed quality,23,24 also influenced the growth of GNRs. By regulating these factors, GNRs with different morphologies and LSPR peaks could be synthesized. Usually, ascorbic acid was employed as a reducing agent, and the GNR growth was very sensitive to its concentration. Low concentration of ascorbic acid led to little GNR growth, while a high concentration led to the formation of spherical particles. Therefore, it is necessary to seek effective reducing agents in the seed-mediated synthesis of GNRs.

Polyphenolic compounds are often observed to be reductants in nature. Although their reduction potentials are lower than ascorbic acid, polyphenolic compounds are able to reduce Au(III) to Au(I) at room temperature. Recently, it was reported that three different phenols were used to synthesize GNRs.25 Dopamine and other hydrophenols were found to be effective reductants in the synthesis of branched GNPs.26 Dopamine was also used in the synthesis of silver,27,28 zinc oxide,29 and iron oxide nanoparticles.30 Besides the reducing ability, dopamine and generated polydopamine can be also used as binding agents,31 which is helpful in nanoparticle stabilization and shape control. However, until now, the use of reductive dopamine in seed-mediated growth of GNRs has not been reported.

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Herein, we develop a novel route for the controlled synthesis of GNRs using dopamine as a reductant. Incubating the growth solution at 40 °C, monodispersed GNRs were successfully prepared. LSPR peaks and aspect ratios of the synthesized GNRs could be tuned by adjusting the concentration of silver ions, CTAB, seeds, and reductant.

**EXPERIMENTAL SECTION**

**Materials.** Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, ACS reagent) was purchased from Alfa Aesar. Hexadecyltrimethylammonium bromide (CTAB, >98%), silver nitrate (AgNO₃, >99%), sodium borohydride (NaBH₄, >99%), dopamine hydrochloride, and ascorbic acid were purchased from Sigma-Aldrich. All chemicals were used without further purification. Ultrapure water (18.2 MΩ·cm, Milli-Q, Millipore) was used in all experiments. All glassware was immersed into aqua regia for 1 h, then washed with ultrapure water several times, and dried before use.

**Synthesis of GNRs.** A seed-mediated method was used to prepare the GNRs. Typically, two steps were included. First, gold seeds were synthesized as reported previously. An HAuCl₄ solution (250 μL of 10 mM) was added to the CTAB solution (6.75 mL, 0.1 M). Under stirring, 50 μL of 0.1 M ascorbic acid solution was added, and next, seed solution A (3 mL) was added. After stirring for 10 min, the obtained solution was centrifuged at 13 000 rpm for 20 min. The pellet was redispersed in 10 mL of 0.1 M CTAB solution. This solution was called seed solution B.

**Synthesis of Seeds with Large Size.** Seeds with a large size were prepared according to previously reported methods with minor modification. An HAuCl₄ solution (250 μL of 10 mM) was added to the CTAB solution (6.75 mL, 0.1 M). Under stirring, 50 μL of 0.1 M ascorbic acid solution was added, and next, seed solution A (3 mL) was added. After stirring for 10 min, the obtained solution was centrifuged at 40 000 rpm for 1 h. The pellet was redispersed in 10 mL of 0.1 M CTAB solution. This solution was called seed solution B.

**LSPR Measurements.** After synthesis was finished, the growth solution was diluted for LSPR measurements. The UV−vis spectra were recorded on a Shimadzu UVmini-1240 spectrometer.

**TEM Measurements.** Before being added to the copper grids, gold seed solutions were centrifuged at 60 000 (A), 40 000 (B), or 20 000 rpm (C) for 1 h and washed once with water. GNRs were obtained by centrifuging the growth solution at 13 000 rpm for 20 min. The pellets were washed with water once and redispersed with water. The size and shape of the obtained nanoparticles were observed by transmission electron microscopy (TEM; JEM-1011, operating at 100 kV) and high resolution TEM (HRTEM; JEM-2100, operating at 200 kV).

**Gold Concentration Measurements.** Before the addition of dopamine, a small amount (0.1 mL) of the growth solution was taken, adding to 0.9 mL of aqua regia. After incubation for 1 h, the mixture was diluted for inductively coupled plasma mass spectrometry (ICP-MS) measurements (Agilent 8800). After the synthesis was finished, the growth solution was centrifuged at 13 000 rpm for 20 min. The pellets were washed with water once and redispersed in 1 mL of water as GNR stock solution. Then, 10 μL of stock solution was mixed with 990 μL of aqua regia. After incubation for 1 h, the solution was diluted with water for ICP-MS measurements. By calculating the gold contents in the GNR stock solution and growth solution, the yields of GNRs were obtained.

**Dopamine Concentration Measurements.** After the synthesis was finished, GNRs were removed by centrifugation at 13 000 rpm for 20 min. The supernatant was diluted one time and filtered with 0.45 μm pore size. A 20 μL volume of the solution was injected into a high performance liquid chromatograph (HPLC; Shimadzu LC-20AD) for analysis. A C₁₈ column (5 μm, 2.0 × 150 mm) was used for separation. UV detection (Shimadzu SPD-20A) was performed at 280 nm. The concentration of dopamine was calculated from the calibration curve.

**FTIR Spectroscopy.** The growth solution was centrifuged at 13 000 rpm for 20 min. The pellet was washed with water twice and dried in a vacuum at 50 °C for 12 h. The dried GNRs and 200 mg of KBr were ground and pressed to a pellet. Fourier transform infrared (FTIR) spectroscopy was carried out on a Nicolet i510 spectrometer (Thermo-Fisher Scientific).

**RESULTS AND DISCUSSION**

**Dopamine as a Reductant for the Synthesis of Gold Nanorods.** In the growth solution, dopamine hydrochloride was used as a reductant. At 40 °C, Au(III) could be reduced to Au(I), and the color of the growth solution changed from yellow to light yellow (Figure 1A). This process was confirmed by measuring the absorption of Au(III)−CTAB complex at 396 nm with UV−vis spectroscopy. After dopamine was added for 1 min, the absorption of the growth solution at 396 nm decreased dramatically (Figure 1B). After reaction for 20 min, almost all the Au(III) was reduced. When gold seeds (∼3.7 nm, Supporting Information, Figure S1) were added, the color of the growth solution changed from yellow to red-brown color within 3 h, indicating that the Au(I) was reduced to Au(0) as well as the formation of GNRs. As shown in the TEM images (Figure 2A,B), rodlike monodispersed particles with an aspect ratio of approximately 5 (83 × 16 nm) were obtained. The HRTEM image shows that the obtained GNRs are single crystalline (Figure 2C). The LSPR peak of the GNRs is around 910 nm as shown in Figure 2D. The concentration of the GNR

![Figure 1](image-url)
stock solution was 0.80 mg/mL measured by ICP-MS. The origin gold ion concentration in growth solution was 0.094 mg/mL. Considering their volumes, it was calculated that the conversion ratio from gold ions to GNRs was around 80%. This is a significant improvement, since the conversion ratio was only 15% when ascorbic acid was used as a reductant.33

To investigate the effect of seed size on the growth of GNRs, seeds of about 6 and 9 nm in size were synthesized (Supporting Information, Figure S1). When the 6 nm seeds were used to synthesize GNRs, a large number of non-well-defined particles mixed with some nanorods were produced (Supporting Information, Figure S2A). Furthermore, when the 9 nm seeds were used, almost no nanorods could be observed (Supporting Information, Figure S2B). Therefore, the seeds larger than 4 nm in size are not suitable for the preparation of GNRs when dopamine is used as a reductant.

In this reduction reaction, one dopamine molecule could reduce one Au(III) to Au(I). After the synthesis, the amount of dopamine was reduced from 0.105 to 0.092 mmol. Because dopamine was oxidized to a dopaminequinone, which is highly reactive to amine groups, resulting in the formation of polydopamine (Figure 1A), there is no molar equivalent between dopamine and Au(III).

**Dopamine as an Additive To Decrease the CTAB Concentration in the Growth Solution.** Recently, it has been reported that additives play an important role in the monodispersity, morphology, yield, and reproducibility of seeded growth of GNRs.20−22,32 Murray’s group reported that aromatic additives (salicylic acids or their salts) could intercalate into the CTAB bilayer and control the size and shape of the GNRs.30 Also, the CTAB concentration in the growth solution could be reduced to 0.05 M by using aromatic additives. In our experiments, dopamine with an aromatic structure acts not only as a reductant but also as an additive. Rodlike particles could be formed at lower CTAB concentration. When the CTAB concentration decreased from 0.1 to 0.075 M, the LSPR peak almost did not change (Figure 3A, Figure 2. TEM images of GNRs fabricated by the reduction of dopamine hydrochloride at 40 °C for 3 h. AgNO₃ (70 μL, 0.1 M), dopamine hydrochloride (20 mg in 0.5 mL water), and seed solution A (160 μL) were added to growth solution subsequently. [CTAB] = 0.1 M. (A) Low magnification; (B) medium magnification; (C) HRTEM image; (D) UV–vis–NIR absorption spectrum of the synthesized GNRs.

![Figure 3](https://example.com/f3.png)

Figure 3. (A) UV–vis–NIR absorption spectra of the synthesized GNRs at CTAB concentration ranging from 0.01 to 0.1 M. (B) TEM image of the synthesized GNRs at 0.01 M CTAB solution. (C) TEM image of the synthesized GNRs at 0.025 M CTAB solution. AgNO₃ (70 μL, 0.1 M), dopamine hydrochloride (20 mg in 0.5 mL water), and seed solution A (160 μL) were used in preparation.
Supporting Information, Figure S3B). The LSPR peak showed a red shift to 980 nm when the CTAB concentration decreased to 0.05 M (Figure 3A, Supporting Information, Figure S3A). Furthermore, when the CTAB concentration decreased to 0.025 M, the LSPR peak continued to red shift to 1030 nm. The TEM image shows the GNPs with an aspect ratio of 6–7 at this concentration (Figure 3C). Compared to the GNPs synthesized at the CTAB concentration of 0.1 M, the GNPs became thinner and shorter with a diameter and a length of ∼9 nm and ∼60 nm, respectively. At a lower concentration of CTAB, a higher aspect ratio of GNPs was obtained, and the yield was around 85%. Dopamine or polydopamine is likely to be involved in the interactions between the CTAB and the GNPs, which can control the size and shape of the GNPs. To prove this, the FTIR spectrum of the synthesized GNPs was obtained (Figure 4). The strong and wide band at 3445 cm⁻¹ arises from the stretching vibration of hydroxyl groups, whereas the intensity of pure CTAB at this region is weak. The strong absorptions at 2918 and 2850 cm⁻¹ are caused by the C–H stretching vibration of methyl and methylene groups of CTAB. The observed small bands at 1710 cm⁻¹ can be attributed to the carboxyl groups. The intensities of the bands at 1626 and 1402 cm⁻¹ are stronger than those of pure CTAB, which are caused by the vibrations of aromatic rings. In the spectrum of pure CTAB, the bands at the region of 1400–1500 cm⁻¹ arise from the C–H bending vibration. In the fingerprint region, the bands at 1100 and 822 cm⁻¹ are contributed from the C–O stretching and in-plane C–H bending vibration, which did not appear in the spectrum of pure CTAB. These results suggest that dopamine or polydopamine exists at the surface of the GNPs. As a result, synthesis of GNPs at a low CTAB concentration can facilitate the purification processes.

When the CTAB concentration decreased to 0.01 M, big spherical and short rodlike particles appeared (Figure 3B), which suggests that GNPs are not able to be synthesized at this concentration of CTAB.

**Tuning the LSPR Peak of the GNPs with the Concentration of Silver Ions.** Varying the concentration of silver ions in the growth solution is an often-used strategy to tune the aspect ratios and LSPR peaks of GNPs. Different amounts of 0.1 M nitrate silver solution were used in the growth of GNPs. When only 10 μL of 0.1 M nitrate silver solution was added to growth solution, GNPs with the LSPR peak at around 685 nm were synthesized (Figure 5A), corresponding to the smallest aspect ratio (≈2.5) (Figure SB,H). When the amounts of nitrate silver solution increased to 20 and 40 μL, the LSPR peaks showed a red shift to 805 and 1000 nm, respectively (Figure 5A), and the corresponding aspect ratios of GNPs increased to ∼4.0 (Figure S5H and ∼5.6 (Figure SD). By increasing the amounts of silver ions to 70, 100, and 140 μL, however, the aspect ratios of the as-prepared GNPs decreased to ∼5.1 (Figure SE), ∼4.0 (Figure SF), and ∼3.3 (Figure SG), respectively. The corresponding LSPR peaks showed a blue shift. This tendency is similar to the observation for the preparation of GNPs by using ascorbic acid as a reducing agent. Silver ions are necessary for the formation of rodlike particles; however, high silver ion concentration with high ionic strength can decrease the length of GNPs and produce more particles rather than nanorods. High silver ion concentration led to end-cap morphology changes. Figure SF, G shows the GNPs change to cylinder or trapezoid caps, instead of hemisphere caps. The structure is similar to the GNPs synthesized with hydroquinone.

**Effects of the Concentration of the Seeds and Reductant on GNP Growth.** Seed concentration is a factor that influences the LSPR peak of the GNPs. Figure 6A shows this effect on GNR growth. When the amounts of seed solution A increased from 80 to 240 μL, the LSPR peaks showed a gradual shift from 863 to 942 nm; the increase was not linear. When the seed solution increased from 80 to 120 μL, the LSPR peaks showed a 25 nm red shift; however, when it increased from 200 to 240 μL, the LSPR peaks only showed a 10 nm red shift. In this condition, the yield of the GNPs was 83%. TEM images show that GNPs synthesized with different amounts of seed solution were high quality, monodisperse, and had negligible spherical particles (Figure 6B, Supporting Information, Figure S4). Therefore, adjusting the seed concentration is a good strategy for tuning the optical properties of GNPs.

Reductant concentration is another important parameter in GNR growth. In the reported method, to obtain high quality GNPs, the molar ratio of ascorbic acid to gold ions was approximately 1:1. Figure 6C shows the effect of reductant concentration on GNR growth. When 10 mg of dopamine was used, the LSPR peak of GNPs was 937 nm. However, the TEM image shows that the quality of GNPs is poor, which has a mix of spherical particles and different sized rods as shown in Figure 6D. Some black dots can be observed in the TEM image. By amplifying the TEM images, it was found that these black dots were smaller than 5 nm, which was similar to the seed size. When 10 mg of dopamine was used, the yield was only around 46%, which was much lower than that of the synthesis when 20 mg of dopamine was used. More seeds did not grow to big particles. There is no doubt that these black dots are gold seeds. The LSPR peak showed a maximum red shift to 955 nm when the amount of dopamine increased to 15 mg (Figure 6C, Supporting Information, Figure SSA). After that, further increasing the amounts of dopamine led to the blue shift of LSPR peaks. When the amount of dopamine increased from 30 to 40 mg, the LSPR peaks showed a 55 nm blue shift (Figure 6C, Supporting Information, Figure SSB,C). When the amount of dopamine increased from 20 to 30 mg; however, the LSPR peaks of GNPs showed a negligible shift. Thus, minor variations of the reductant concentration cannot influence the growth of GNPs.

**Growth Kinetics of GNRs Synthesized by Dopamine.** The growth rate is an important parameter for the morphology of the prepared nanoparticles. The growth process was tracked by UV–vis–NIR absorption spectra (Figure 7A). In
the silver-assisted preparation of GNRs, two separate stages were identified according to the changes in the spectra. First, the LSPR peaks show a fast red shift and then a slow blue shift, which agrees with our results. In the first 1.5 h, the LSPR peak red shifted to as far as 1010 nm, and an anisotropic structure was created at this stage. When the growth was stopped after 1 h, small nanorods were formed (Figure 7B). In the next 1.5 h, the LSPR peaks blue shifted to 920 nm. At this stage, the volume of small rods increased gradually (Figure 7C), and the aspect ratios showed a slight decrease. During the reaction, the absorption intensities show a consistent increase, indicating the continuous growth of rods. When the GNRs were kept at room temperature for 12 h, the LSPR peak showed a slight blue shift. Due to atomic defects on the unstable facets, gold atoms on the nanorod surface would reconstruct and the size of the particles changed slightly, with an LSPR peak shift.

Although reductive dopamine used in the experiment was largely in excess, the whole growth process lasted for 3 h. The growth rate was much slower than the method using ascorbic acid as a reductant. A slow growth rate is beneficial to the synthesis of high quality nanorods. Increasing the growth rate by increasing the incubation temperature to 50 °C, the LSPR peak of the GNRs had almost a 100 nm blue shift (Supporting Information, Figure S6), indicating the decrease of the aspect ratios of the GNRs. At 60 °C, the growth rate was too fast to produce rods. A strong absorption at 550 nm in the UV−vis−NIR spectrum of the GNRs suggests the appearance of large amounts of spherical particles. Thus, a weak reductant decreases the growth rate, which controls the growth of GNRs to obtain high quality GNRs.

**CONCLUSIONS**

In summary, monodispersed GNRs were successfully synthesized using dopamine hydrochloride as a reductant. By replacing ascorbic acid with dopamine, and having a surfactant concentration as low as 0.025 M, high quality GNRs (60 × 9 nm) with an LSPR peak at 1030 nm were produced. This was because dopamine has an aromatic structure that can act as an additive to interact with the CTAB bilayers. The GNR yield was improved to around 80%. This method was less sensitive to reductant concentration, which was 20 or more times higher.
than the gold concentration in the growth solution. Moreover, the LSPR peaks and aspect ratios could be tuned by varying the concentration of silver ions, seeds, and reductant. The weak reducing ability of dopamine decreased the growth rate of GNRs, which was beneficial for the formation of quality GNRs.

**ASSOCIATED CONTENT**

**Supporting Information**

Additional TEM images and UV-vis-NIR absorption spectra of GNRs are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(38) Edgar, J. A.; McDonagh, A. M.; Cortie, M. B. Formation of gold nanorods by a stochastic ‘popcorn’ mechanism. ACS Nano 2012, 6, 1116−1125.