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# Seedless Synthesis of Gold Nanorods with 5—10 nm in Diameters: a Comprehensive Study

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Small gold nanorods (AuNRs), namely AuNRs with less than 10 nm in diameter, possess a high absorption-to-scattering ratio, a large surface area-to-volume ratio, as well as high cellular uptake behaviors. In this study, we systematically investigate seedless synthesis of AuNRs with diameters ranging from 5 nm to 10 nm. It has been found that several experimental conditions, including the chain length of the used cationic surfactants, and the concentrations of ascorbic acid, NaBH<sub>4</sub>, and AgNO<sub>3</sub> can profoundly affect the obtained products. Under optimal conditions, the production yields of the obtained several AuNRs with different diameters can exceed 90% and even reach almost 100%. The conversion of gold precursors to AuNRs was estimated to be 70%—77% as measured by absorption spectroscopy and inductively coupled plasma mass spectrometry.

# **1** Introduction

Gold nanorods (AuNRs) are one of the most famous anisotropic nanoparticles because of their favorable optical properties, multiple application potentials, as well as sophisticated and even artistical chemical synthesis strategies.<sup>[1–3]</sup> Due to their strong and length-diameter ratio and tunable localized surface plasmon resonance (LSPR) ranging from visible to near-infrared wavelength region, AuNRs and their homogeneous and/or hybrid selfassemblies (composites) have been widely employed in different fields, for example, bio-sensing and imaging,<sup>[4–6]</sup> disease diagnosis and treatment,<sup>[7]</sup> photoelectric devices,<sup>[8]</sup> optical active modulation,<sup>[9,10]</sup> etc.

In 1997, AuNRs have been obtained by electrochemistry.<sup>[11]</sup> Inspired by such a reaction system, in 2001, Prof. Murphy<sup>[12]</sup> developed a creative seed-mediated AuNRs synthesis system. First, gold nano seeds are fabricated by using citrate as capping ligands and NaBH<sub>4</sub> as a reducing agent; subsequently, the seeds are injected into the growing solution [containing cetyltrimethylammonium



**Keywords** Small gold nanorod; Diameter; Production yield; Conversion rate

bromide (CTAB), HAuCl<sub>4</sub>, and ascorbic acid] for rod shape products with a 4.6 respect ratio and a 42% yield [estimated from the transmission electron microscopy (TEM) images in the paper]. Further utilizing the AuNRs as "seeds" (thus, the proposed synthesis system is named "three-step" synthesis), very long AuNRs (13 and 18 respect ratios) can be obtained. However, the yields of the proposed synthesis system are still low (*ca.* 70%, estimated from the TEM images in the paper). On this basis, El-Sayed's group<sup>[13]</sup> further adopted CTAB modification for seed synthesis, which can distinctly enhance AuNRs yields to over 90%. Generally, the AuNRs obtained by the above two synthesis systems have more than 15 nm in diameter.

Smaller AuNRs, of which diameters are 2–10 nm, possess a few additional properties as compared with the large ones. First of all, they have a higher absorption-to-scattering ratio, which can therefore convert more energy to heat for photothermal applications.<sup>[14]</sup> Then, smaller-sized AuNRs have a large surface area to volume ratio, high cellular uptake, and possible renal clearance processes.<sup>[15–18]</sup> Third, for AuNRs etching-based colorimetric sensing systems, smaller size ones possess higher sensitivity to the analytes.<sup>[19,20]</sup>

The seedless-based method was first employed for smaller AuNRs synthesis. In 2005, Jana<sup>[21]</sup> employed two kinds of reducing agents (NaBH<sub>4</sub> and ascorbic acid) system for synthesizing AuNRs with *ca*. 6 nm in diameter. The

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author found that the ratio of the two reducing agents can affect the nucleation rate. The synthesis system has lots of spherical bi-products with only *ca*. 70% (estimated from the TEM images in the paper) of AuNRs yields. Then, a few experimental conditions, such as reaction temperature, pH value, NaBH<sub>4</sub> concentration, and the species of the weakening reducing agents (dopamine, resveratrol, H<sub>2</sub>O<sub>2</sub> have been used for replacing ascorbic acid) have been investigated and optimized.<sup>[22–26]</sup> AuNRs with 2–10 nm in diameter and enhanced production yields have been achieved.

In 2015, Wang and co-workers<sup>[27]</sup> developed a seedmediated synthesized system for the production of smaller AuNRs. First, the Au seeds were obtained by injecting cold sodium borohydride into a solution containing the surfactant CTAB or CTPAB (cetyltripropylammonium bromide) and HAuCl<sub>4</sub>, which were then injected into the growing solution containing two kinds of cationic surfactants (CTAB and CTPAB), AgNO3 and ascorbic acid. The resulting AuNRs are 6–9 and 16–45 nm in diameter and length, respectively, and the yields can reach 85%. Since then, several improved systems for the seed-mediated synthesis were proposed, in which a few sophisticated experimental conditions, including hydroquinone and ascorbic acid were used as weak reducing agents, to regulate the concentrations of AgNO3 and gold seeds. Researchers have also adjusted the volume of hydroquinone and the concentration of HAuCl<sub>4</sub>. Accordingly, the yields of the AuNRs can reach 79%-90%.[28-30]

Compared with the seed-mediated method, the seedless-based one is simple on the experimental processes, which gets rid of time-consuming and additional seed production procedures. Qualitatively, in a seedless synthesis system, gold "seeds" are considered to be produced *in situ* in the presence of strong reducing agents (NaBH<sub>4</sub>). Furthermore, the nucleation rate relates to the ratio of weak (ascorbic acid) and strong (NaBH<sub>4</sub>) reducing agents. Under CTAB molecules' guidance, the symmetry is broken and rod shaped products are obtained.<sup>[21,31]</sup> However, due to the chemical processes being fast and complex, the optimal synthesis conditions can only be obtained by experimental exploration.

In this study, we systematically investigate seedless synthesis of AuNRs with diameters ranging from 5 nm to 10 nm. It has been found that several experimental conditions, including the chain length of the used cationic surfactants, and the concentrations of used ascorbic acid, NaBH<sub>4</sub>, and AgNO<sub>3</sub> can profoundly affect the obtained products. Under optimal conditions, the yields of the obtained several AuNRs with different diameters can exceed 90% and even reach almost 100%. The conversion of gold precursors to AuNRs was estimated to be 70%—77% as measured by absorption

spectroscopy and inductively coupled plasma mass spectrometry.

### 2 Experimental

#### 2.1 Materials and Measurements

#### 2.1.1 Chemicals

Chloroauric acid trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) was purchased from J&K Scientific. CTAB, ascorbic acid, NaBH<sub>4</sub>, and AgNO<sub>3</sub> were obtained from Sinopharm Chemical Reagent Limited Corporation. Fuming HCl (37%) was acquired from Merck Chemical Technologies. Each experiment used freshly prepared NaBH<sub>4</sub> and ascorbic acid. All chemical reagents were directly used without further purification. Ultrapure water was used to prepare all aqueous solutions.

#### 2.1.2 Characterizations

The morphology of the AuNRs was characterized by an HT-7800 Hitachi microscope (Japan) at an accelerating voltage of 100 kV. Ultraviolet-visible absorption spectra were measured by an ultraviolet-visible spectrophotometer (UV-Vis, U-2910, Hitachi Japan). The concentration of gold atoms in AuNRs was measured by an inductively coupled plasma-mass spectrometer (ICP-MS, 5110, Agilent). The length and diameter of the AuNRs were measured with Nano Measure software and at least 450 AuNRs were counted for each sample. Calculation of AuNRs yields: in three sets of parallel experiments, at least 600 AuNRs prepared in each set of experiments were taken each time to calculate the yield of AuNRs (yield=number of AuNRs/total number of gold nanoparticles).

### 2.2 Preparation of AuNRs with Different Diameters by Seedless Method

#### 2.2.1 5.65 nm AuNRs

To a CTAB (5 mL, 0.14 mol/L) solution, HAuCl<sub>4</sub> (2.5 mL, 1 mmol/L) was added and stirred until the color of the solution changes from yellow to red and then to orange. After adding AgNO<sub>3</sub> (250  $\mu$ L, 4 m mol/L) and HCl (4  $\mu$ L, 37%) in turn, the ascorbic acid (35  $\mu$ L, 100 mmol/L) solution became colorless. Finally, cold NaBH<sub>4</sub> (10.0  $\mu$ L, 10 mmol/L) was added to the solution. The reaction was placed in a constant temperature water bath at 30 °C and allowed to grow for 5 h. The obtained AuNRs have a diameter of 5.65 nm.

#### 2.2.2 6.42 nm AuNRs

The method was the same with that in Section 2.2.1. The

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concentration of ascorbic acid used was increased from 100.0 mmol/L to 128.6 mmol/L. The diameter of the prepared AuNRs was 6.42 nm.

#### 2.2.3 7.45 nm AuNRs

The method was the same with that in Section **2.2.1**. The concentration of ascorbic acid was increased to 114.3 mmol/L, and the amount of NaBH<sub>4</sub> was reduced to 7.5  $\mu$ L. The diameter of the prepared AuNRs was 7.45 nm.

#### 2.2.4 7.80 nm AuNRs

The method was the same with that in Section **2.2.1**. The concentration of ascorbic acid was increased to 128.6 mmol/L, and the amount of NaBH<sub>4</sub> was reduced to 7.5  $\mu$ L. The diameter of the prepared AuNRs was 7.80 nm.

#### 2.2.5 8.49 nm AuNRs

The method was the same with that in Section **2.2.1**. The concentration of CTAB was increased to 0.20 mol/L, while the concentration of ascorbic acid was increased to 128.6 mmol/L, and the amount of NaBH<sub>4</sub> was reduced to 7.5  $\mu$ L. The diameter of the prepared AuNRs was 8.49 nm.

#### 2.2.6 9.54 nm AuNRs

The method was the same with that in Section **2.2.1**. The concentration of CTAB was increased to 0.20 mol/L, while the concentration of ascorbic acid was increased to 142.9 mmol/L, and the amount of NaBH<sub>4</sub> was reduced to 7.5  $\mu$ L. The diameter of the prepared AuNRs was 9.54 nm.

# 2.3 Effects of Reaction Conditions on the Size and Yield of AuNRs

#### 2.3.1 Surfactant Chain Length

The method described in Section **2.2.4** for the preparation of AuNRs was used. The effect of surfactant chain length on the size and yield of AuNRs was investigated by using 5 mL of 0.20 mol/L C<sub>12</sub>TAB, C<sub>14</sub>TAB and C<sub>16</sub>TAB, respectively, keeping all other conditions constant.

#### 2.3.2 CTAB Concentration

The method of preparing AuNRs in Section **2.2.4** was used. The effect of CTAB concentration on the size and yield of AuNRs was explored using 0.10, 0.14, 0.18 and 0.22 mol/L CTAB, respectively.

#### 2.3.3 NaBH<sub>4</sub> Concentration

The method for the preparation of AuNRs in Section **2.2.4** was used. While 3.2, 6.4, 9.6, 12.8, 19.2, 25.7 and 32.1  $\mu$ mol/L NaBH<sub>4</sub> (corresponding additions: 2.5, 5.0, 7.5, 10.0, 15.0, 20.0, and 25.0  $\mu$ L, respectively) were used to investigate the effects of NaBH<sub>4</sub> concentration on the size and yield of AuNRs.

#### 2.3.4 Ascorbic Acid Concentration

The method for the preparation of AuNRs in Section **2.2.4** was used. The effects of ascorbic acid concentration on the size and yield of AuNRs were investigated using 78.6, 85.7, 100.0, 114.3, 128.6, and 149.2 mmol/L ascorbic acid, respectively.

#### 2.3.5 AgNO<sub>3</sub> Concentration

The method used in Section **2.2.4** for the preparation of AuNRs was used. And 0, 25.7, 51.3, 77.0, 102.6, 128.3, 153.9, 179.2, and 205.2  $\mu$ mol/L AgNO<sub>3</sub> (the corresponding additions of 0, 50, 100, 150, 200, 250, 300, 350, and 400  $\mu$ L) were used as the AgNO<sub>3</sub> concentrations to investigate the effect of AgNO<sub>3</sub> concentration on the size and yield of AuNRs.

### **3 Results and Discussions**

Fig. 1 shows representative TEM images of six kinds of AuNRs, of which the diameters are  $(5.65\pm0.64)$ ,  $(6.42\pm0.43)$ ,  $(7.45\pm0.41)$ ,  $(7.80\pm0.54)$ ,  $(8.49\pm0.91)$  and  $(9.54\pm0.61)$  nm. All the products can well disperse on TEM copper grids and exhibit distinct rod shapes. The production yields of the six AuNRs products are 92% to almost 100%, indicating the effectiveness of the proposed fabrication system.

To better understand the as-prepared synthesis system, the effects of several experimental conditions, including the chain length of the used cationic surfactants, and the concentrations of used ascorbic acid, NaBH<sub>4</sub>, and AgNO<sub>3</sub> have been investigated successively.

#### 3.1 Chain Length of Cationic Surfactants

In the past, cationic surfactants with different alkyl chain lengths have been used to prepare silver nanoparticles.<sup>[32]</sup> As shown in Fig. 2, A–C and Table S1 in the Electronic Supplementary Information (ESI), as the chain length of the employed cationic surfactants decreases from 16 to 14 to 12 carbon atoms, the AuNRs yields correspondingly drop from almost 100% to 92.3% to 61.2%. These results indicate that

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wavelength position of the former is at 508-520 nm and is positively related to AuNRs' diameter. While for the longitudinal plasma resonance, the wavelength shifts to longer wavelength with the increase of the lengthdiameter ratio.[34] In terms of the present AuNRs (Fig. 2, B and C), due to their smaller diameter (6.42 and 7.8 nm), the wavelength of the transverse plasma resonance is 510 nm, which is some shorter than that of the AuNRs with 15 nm (515 nm) in diameter.[35] While for the product shown in Fig. 2A, because of lots of gold spheres, the corresponding wavelength displays an obvious bathochromic-shift. According to our recent quantitative study of the cationic surfactants on AuNRs' surface,[34] two surfactant molecules form a double-layer by hydrophobic interactions of their alkyl chains, which

also plays template effects for guiding

Fig. 2 TEM images (A—C) and corresponding UV-Vis absorption spectra (D) of AuNRs prepared by changing the chain length of the surfactant in the reaction solution

(A) C<sub>12</sub>TAB; (B) C<sub>14</sub>TAB; (C) C<sub>16</sub>TAB.

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longer carbon chains facilitate rod-shaped particle production. Fig. 2D shows the LSPR spectra of the three products. AuNRs exhibit two LSPR bands coming from transverse and longitudinal plasma resonance, which are located at short and long wavelengths, respectively.[33] The

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Au particles to rod shape. Conceivably, for the used cationic surfactants, longer alkyl chains can provide stronger hydrophobic interactions and more effectively form the double-layer molecules, causing higher production yields for AuNRs production.

Fig. 1 Representative TEM images of six AuNRs with diameters of (5.65±0.64) nm (A), (6.42±0.43) nm (B), (7.45±0.41) nm (C), (7.80±0.54) nm (D), (8.49±0.91) nm (E) and (9.54±0.61) nm (F)



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#### 3.2 CTAB Concentrations

During synthesis processes, as the used CTAB concentrations are enhanced from 0.10 mmol/L to 0.22 mmol/L, the diameters of the obtained AuNRs increase from 6.10 nm to 8.70 nm. All the main obtained products are distinctly rod-shaped as described in the TEM images (Fig. 3, A-D) and the typical two weak and strong extinction bands (Fig. 3E). Furthermore, CTAB concentrations also affect the AuNRs yields, which can reach almost 100% as 0.14 mol/L CTAB is utilized; in contrast, in the presence of 0.22 mol/L CTAB, AuNRs yield is only 86.5%. (Table S2 in the ESI)

It is generally recognized that CTAB molecules have two effects on AuNRs growth, although it needs to be further demonstrated. First of all, the dissociated  $Br^-$  anions are selectively adsorbed on the specific lattice planes of the Au seeds, which can lead to the oriented growth of the Au

seeds.<sup>[32]</sup> For CTA<sup>+</sup> chains, their polar tips bind onto the Au surface [probably (110) face, due to the matched size between the polar tips and the distance of Au – Au] by CTA<sup>+</sup>-Br<sup>-</sup> electrostatic attraction effects;<sup>[36,37]</sup> and the other ends, namely alkyl chains can interact with another CTAB chains by hydrophobic effects and form a double layer for guiding and stabilizing the AuNRs.<sup>[38]</sup>

When the concentrations of the added CTAB molecules are low (<0.10 mol/L), the limited stabilizing effects cause the yields of rod-shaped products to decrease.<sup>[31]</sup> As CTAB concentration is increased to 0.18 mol/L, the guiding and stabilizing effects are just appropriate, resulting in high yields of AuNRs (Fig. 3, B and C). As CTAB molecules are further increased to 0.22 mol/L, AuNRs yields are decreased again (from 98.0% to 84.5%). The possible reason is that excess CTAB molecules can be adsorbed to more crystal faces of the Au seeds, leading to the decreased effects for the guiding growth of rod-shaped products.



Fig. 3 TEM images (A—D) and UV-Vis absorption spectra (E) of AuNRs prepared by changing the concentration of CTAB in the reaction solution and the corresponding trend image (F) of the diameter, length, volume of AuNRs (A) 0.10 mol/L; (B) 0.14 mol/L; (C) 0.18 mol/L; (D) 0.22 mol/L; (F) the error bars are only provided for the optimal conditions.

#### 3.3 NaBH<sub>4</sub> Concentrations

As shown in Fig. 4H, as the added NaBH<sub>4</sub> increases from 3.2  $\mu$ mol/L to 32.1  $\mu$ mol/L, the obtained AuNRs exhibit a gradual decrease in their diameters. By the employment of 3.2, 6.4, 9.6, 12.8, 19.2, 25.7 and 32.1  $\mu$ mol/L NaBH<sub>4</sub>, AuNRs with diameters of (8.32±0.11), (7.92±0.31), (7.80±0.54), (6.42±0.41), (5.94±0.11), (5.56±0.34) and (5.15±0.48) nm are correspondingly obtained (Table S3 in the ESI). During the synthesis, the effects of NaBH<sub>4</sub> are the reduction of Au

cations and *in situ* formation of seeds, which are responsible for subsequent rod-shaped particle growth. Qualitatively, as less NaBH<sub>4</sub> is added, fewer gold seeds are produced, which is in favor of larger rod products. In contrast, more NaBH<sub>4</sub> can reduce more gold seeds and produce smaller products. At the same time, the amounts of the added NaBH<sub>4</sub> also affect the yields of the AuNRs. As described (Fig. 4, A and F), too low or too high NaBH<sub>4</sub> can cause a decrease in the rodshaped particles. That is to say, for high yields of AuNRs products, there are optimal amounts for the used NaBH<sub>4</sub>. The exact reason is needed for further study.

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Fig. 4 TEM images (A—G) of AuNRs prepared by changing the concentration of NaBH<sub>4</sub> in the reaction solution and the corresponding trend image (H) of the diameter, length, volume of AuNRs (A) 2.2 umal/(+ (C) 2.2.4 umal/(+ (U) the error have are able

(A) 3.2  $\mu$ mol/L; (B) 6.4  $\mu$ mol/L; (C) 9.6  $\mu$ mol/L; (D) 12.8  $\mu$ mol/L; (E) 19.2  $\mu$ mol/L; (F) 25.7  $\mu$ mol/L; (G) 32.1  $\mu$ mol/L; (H) the error bars are only provided for the optimal conditions.

#### 3.4 Ascorbic Acid Concentrations

Ascorbic acid is one of the famous weak reducing agents, and its effects are the reduction of Au cations to Au atoms during AuNRs synthesis processes. The reactions probably can be divided into two stages. In the first stage, before NaBH<sub>4</sub> is introduced, ascorbic acid molecules reduce Au<sup>3+</sup> to Au<sup>+</sup> cations. Then, strong reducing NaBH<sub>4</sub> molecules are added, which can reduce Au cations to zero-valent Au atoms and form Au nanoseeds. After such homogeneous nucleation processes, the reaction energy barriers are substantially decreased. As a result, the additional ascorbic acid molecules can further reduce Au<sup>+</sup> to Au atoms and cause the Au seeds to grow and form rod-shaped particles.<sup>[39]</sup>

In the experiments, it is found that all the production yields of the AuNRs can exceed 90% in the presence of 78.6—142.9 mmol/L ascorbic acid molecules. However, the amounts of the added ascorbic acid have obvious effects on the diameters and the length of the products. By adding 78.6 mmol/L ascorbic acid, the obtained AuNRs are 8.10 and 53.23 nm for their diameter and length, respectively. As the added ascorbic acid concentration increases to 85.7 mmol/L, their diameter decreases to 6.42 nm. As ascorbic acid concentrations are further enhanced, AuNRs' diameters gradually increase up to 7.8 nm. At the same time, the lengths of the AuNRs decrease step by step as the added concentrations of ascorbic acid exceed 85.7 mmol/L (Table S4 in the ESI).

For AuNR synthesis, the reduced Au atoms are

deposited on the seed along radial and axial directions simultaneously.<sup>[40]</sup> For the formation of rod-shaped particles, the latter speed is larger than that of the former. During the AuNRs growth, the amounts of the added ascorbic acid can affect the reduced speed of Au cations, which might cause some subtle effects on AuNRs growth dynamics. As a result, the products with different diameters and lengths are correspondingly obtained. Obviously, for revealing their detailed modulation effects on AuNRs growth, additional *in-situ* characterization techniques, for example, *in-situ* absorption spectra, *in-situ*-chromatography, etc., are required.

#### 3.5 AgNO<sub>3</sub> Concentrations

Ag<sup>+</sup> cations are essential for AuNRs growth regardless of seed-mediated or seedless synthesis systems. As shown in Fig. 6A, in the absence of Ag<sup>+</sup>, only 4.6% of AuNRs is obtained. The main products are spherical particles with a diameter of 26.33 nm (Table S5 in the ESI). As 51.3  $\mu$ mol/L AgNO<sub>3</sub> is introduced, distinct elongated particles are observed. Then, with the further enhancement of the added AgNO<sub>3</sub> concentrations, AuNRs with larger length-diameter ratios are obtained. At the same time, the diameters of the obtained AuNRs gradually decrease from 26.33 nm to 6.68 nm. When the concentrations of the added AgNO<sub>3</sub> reach 205.2  $\mu$ mol/L, the diameter of the obtained AuNRs is only 5.95 nm. At the same time, lots of gold spheres are produced.

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Fig. 5 TEM images (A—F) and UV-Vis absorption spectra (G) of AuNRs prepared by changing the concentration of ascorbic acid in the reaction solution and corresponding trend image (H) of the diameter, length, volume of AuNRs (A) 78.6 mmol/L; (B) 85.7 mmol/L; (C) 100.0 mmol/L; (D) 114.3 mmol/L; (E) 128.6 mmol/L; (F) 149.2 mmol/L; (H) the error bars are only provided for the optimal conditions.



Fig. 6 TEM images(A—I) and UV-Vis absorption spectra (J) of AuNRs prepared by changing the concentration of AgNO<sub>3</sub> in the reaction solution and the corresponding trend images (K) of the diameter, length, volume of AuNRs (A) 0 µmol/L; (B) 25.7 µmol/L; (C) 51.3 µmol/L; (D) 77.0 µmol/L; (E) 102.6 µmol/L; (F) 128.3 µmol/L; (G) 153.9 µmol/L; (H) 179.6 µmol/L; (I) 205.2 µmol/L; (K) the error bars are only provided for the optimal conditions.

In AuNRs growth processes, the effects of Ag<sup>+</sup> cations have been considered that Ag<sup>+</sup> cations are reduced to Ag atoms and deposit on Au(110) lattice faces by underpotential deposition effects,<sup>[41]</sup> which guide the Au seeds growth along (001) faces and form rod-shaped particles. In the presence of fewer Ag<sup>+</sup> cations (25.7-128.3 µmol/L), due to incomplete (110) face deposition, the growth rate in a radial direction is also relatively fast. As a result, AuNRs with larger diameters are produced (Fig. 6). Due to this reason, the more Ag<sup>+</sup> cations are added, the thin AuNRs are obtained (Fig. 6, F-I). As the added AgNO<sub>3</sub> solution concentration reaches 205.2 µmol/L, nonnegligible spherical Au particles are produced. The possible reason is that excess Ag<sup>+</sup> cations can cause the formation of spherical soft templates, leading to Au nanospheres.<sup>[42]</sup> As described in Fig. 6J, during the above morphology modulation, the long LSPR peaks gradually shift from 643 nm to 879 nm.

# 3.6 Conversion Rates from Au Precursors to AuNRs

Utilizing ICP measurements, we calculate the molar extinction coefficient ( $\varepsilon$ ) based on Lambert-Beer's law:

 $A = \varepsilon bc$  (1) where *A* is the absorbance of AuNRs at their longitudinal peak positions, *b* is the path length, and *c* is the concentration of the AuNRs. By employing the ICP-MS test and geometric estimation (Table 1), AuNRs' concentrations can be obtained. The molar extinction coefficients of the three measured AuNRs are *ca*. 10<sup>8</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>, which is about an order of magnitude smaller than those of "standard" AuNRs.<sup>[43]</sup>

Accordingly, the conversion rates can be obtained by the ratio of the numbers of Au atoms/cations from AuNRs to the precursors. As described in Table 1, for three kinds of AuNRs products with different diameters and aspect ratios, the conversion rates are 70% - 77%. These results indicate the effectiveness of the seedless systems for the synthesis of AuNRs with 5-10 nm diameters.

# Table 1 Molar extinction coefficient and conversion ofgold precursors of AuNRs

Sample	<i>L</i> /nm× <i>D</i> /nm	Aspect ratio	Conversion rate (%)	ε/ (L·mol <sup>–1</sup> ·cm <sup>–1</sup> )
А	29×6.8	4.2	72.03	1.96×10 <sup>8</sup>
В	34×7.9	4.3	77.57	2.20×10 <sup>8</sup>
С	38.5×8.6	4.5	70.15	2.34×10 <sup>8</sup>

\*L is short for length and D is short for diameter.

# 4 Conclusions

In summary, AuNRs with 5-10 nm in diameter are

Chem. Res. Chinese Universities, 2024, 40(2), 311—319 https://doi.org/10.1007/s40242-024-3289-0 synthesized by seedless method. Several experimental parameters, such as the length of the used cationic surfactants, and the concentration of CTAB, can profoundly affect the product morphology. After optimization, the production yields of AuNRs can exceed 90% to almost 100%. The proposed synthesized system can be employed for the production of high-quality small AuNRs for related research.

#### **Electronic Supplementary Information**

Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s40242-024-3289-0.

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#### **Conflicts of Interest**

XIA Yunsheng is a youth executive editorial board member for Chemical Research in Chinese Universities and was not involved in the editorial review or the decision to publish this article. The authors declare no conflicts of interest.

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