

ARTICLE

High Temperature Seedless Synthesis of Au NRs Using BDAC/CTAB Co-surfactant

Min Li, Lai Wei, Xian Zhang, Xue-feng Yu*

Department of Physics, Key Laboratory of Acoustic and Photonic Materials and Devices of Ministry of Education, Wuhan University, Wuhan 430072, China

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Au nanorods have been successfully synthesized at 90 °C by using hexadecyltrimethylammonium bromide (CTAB) and benzyldimethylammoniumchloride hydrate (BDAC) co-surfactant. At 90 °C, the reaction time was less than 10 s, and the longitudinal surface plasmon absorption band could vary between 680 and 770 nm by adjusting the molar ratio of BDAC to CTAB from 2 to 0.5. At 90 °C, nanorods with a longitudinal surface plasmon absorption peak of 770 nm can be obtained when the molar ratio of BDAC to CTAB was 3:2.

Key words: Au nanorod, Hexadecyltrimethylammonium bromide, Benzyldimethylammoniumchloride hydrate, High temperature

I. INTRODUCTION

Metal nanoparticles (NPs), which largely enhance a local field due to the surface plasmon resonance (SPR) absorption [1-6], have wide applications ranging from nonlinear optics to bio-labeling [7-12]. Especially, Au and Ag nanorods (NRs) have highly anisotropic optical properties and have been extensively discussed recently [13-19]. In general, their optical absorption spectra are characterized by two SPR absorption peaks, corresponding to SPR in transverse mode (perpendicular to the long axis of the rods) and longitudinal mode (parallel to the long rod axis). The longitudinal SPR (LSPR) drastically enhances the photoluminescence of Au NRs [20], making them excellent candidates for applications in labeling and imaging [11,12].

Up to now, hexadecyltrimethylammonium bromide (CTAB) has been one of the most popular surfactants in the synthesis of Au NRs. This CTAB-based method was first reported by Yu *et al.* [21], and was improved by many groups [13,16,22]. Though many methods have been demonstrated, most of the work was performed at temperatures close to room temperature and the reaction times are from several minutes to several hours [13,22]. Although Zijlstra *et al.* reported that Au NRs could be synthesized at over 90 °C by very careful controlling the silver nitrate concentration, the LSP peak maximum of Au NRs only reaches 670 nm, which restricts a great deal of the potential applications [16].

In this work, we present a novel preparation method of Au NRs with different aspect ratios at 90 °C by using a binary surfactant mixture of benzyldimethylammoniumchloride hydrate (BDAC) and CTAB, the structure

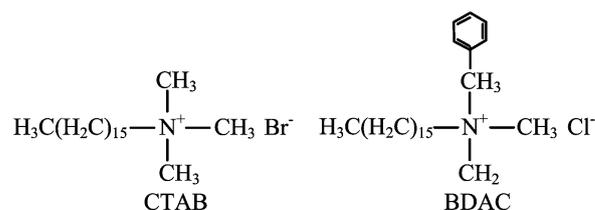


FIG. 1 Structures of CTAB and BDAC. The latter has a bulkier head group.

was shown in Fig.1. At 90 °C, we obtained the final reaction products within 10 s. The LSPR absorption band could vary between 680 and 770 nm by adjusting the BDAC to CTAB molar ratio from 2 to 0.5. This rapid seedless synthesis presents an attractive method for large-scale production of Au NRs. Considering that CTAB surfactant has been widely used in synthesis of many other rod-like nanoparticles such as CdS [23], CdSe [24], Ag [25], Fe [26], and ZnO [27], our method offers a new strategy to improve these surfactant-based syntheses.

II. EXPERIMENTS

A. Materials

All chemicals were purchased from Aldrich (WI, USA) and used as received without further purification. Doubly-distilled water was used for all aqueous solutions.

B. Preparation of Au NRs

Typically, the experiments were carried out as follows. The binary surfactant mixture (0.1 mol/L) was prepared by adding appropriate amount of

* Author to whom correspondence should be addressed. E-mail: yxf@whu.edu.cn

CTAB/BDAC solution with BDAC to CTAB molar ratio from 0.5 to 2. The mixtures were then dissolved by sonication for 20 min. The growth solution was prepared by adding 0.5 mL of 5 mmol/L HAuCl_4 and 0.1 mL of 4 mmol/L AgNO_3 to 4.5 mL surfactant mixture. Then the growth solution was immersed in a heat bath throughout the experiment to get a constant temperature during the growth. After the temperature of the growth solution reached 90 °C, 30 μL of 0.1 mol/L ascorbic acid and 1 μL of 0.01 mol/L NaBH_4 were added. The solution color changed from yellow to red-brown within 10 s, indicating the formation of Au NRs.

C. Characterization

Transmission electron microscopy (TEM) images were acquired with a JEOL 2010 HT transmission electron microscope (operated at 200 kV). TEM samples were prepared by placing 2 μL of the Au NRs solution on a copper grid and drying at room temperature. The absorption spectra of the prepared solutions were measured by using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The samples were measured against water as reference. All samples were loaded into a quartz cell for measurements.

III. RESULTS AND DISCUSSION

A. The production of Au NRs

The synthesis here was based on the seedless growth method previously reported by Jana *et al.* [13]. A high temperature of 90 °C was used to increase the growth rate and a mixture of surfactant (CTAB and BDAC) was used to induce larger aspect ratios. AgNO_3 was added to increase the NR yield and a mixture of strong (NaBH_4) and weak (ascorbic acid) reducing agents was also added. NaBH_4 initiates nucleation and ascorbic acid helps the NPs grow. Size control can be achieved by controlling the nucleation rate [13]. The nucleation rate was controlled by changing the ratio of weak (ascorbic acid) and strong (NaBH_4) reducing agents in the strong and weak reducing agent mixture. An approximate nucleation rate could result in anisotropic NPs [13]. In this work, 30 μL of 0.1 mol/L ascorbic acid and 1 μL of 0.01 mol/L NaBH_4 were employed.

In general, the reaction time of CTAB-based Au NR synthesis is greater than 20 min at room temperature, while the reaction time in this work was within 10 s at 90 °C. The results agree with that of Zijlstra *et al.* who observed an increase in growth rate of about 3 orders of magnitude at 97 °C [16]. The final products (shown in Fig.2) exhibit a shape similar to those synthesized at room temperature. Moreover, the aspect ratios of the NRs can be adjusted, and the maximum aspect ratio is about 4:1 (shown in Fig.2(b)). This rapid seedless

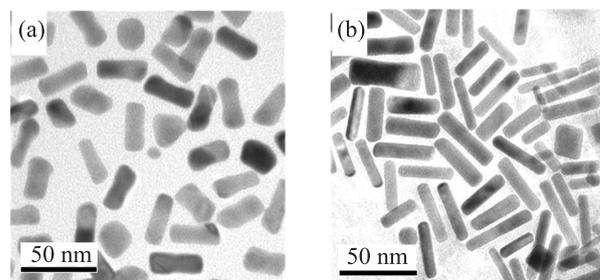


FIG. 2 TEM images of Au NRs prepared at 90 °C with SPR band at (a) 710 nm and (b) 770 nm. The molar ratio of BDAC to CTAB was (a) 3:2 and (b) 2:1, respectively.

method presents a more attractive method for large-scale production of NRs.

The tunable LSPR absorption bands of Au NRs in the visible and near infrared (NIR) region of the absorption spectra could open up opportunities for applications in photonics, chemical and biochemical sensing, and imaging. For example, it was reported that small changes in aspect ratio could result in great changes in transmitted colors [28]. The longer rods scatter red or orange light, while shorter rods scatter yellow or blue-green color. This is because both the LSPR and TSPR absorption peaks of the short Au NRs are in the visible and NIR region. Short Au NRs scatter more visible light and are brighter than long Au NRs, giving them applications in optical sensing and imaging. This work may provide an alternative route to synthesize Au NRs with different SPR bands for applications in optical sensing and imaging.

B. The effect of temperature on NR synthesis

To study the effect of temperature on NR growth, the initial conditions for each reaction are identical. The seedless growth method previously reported by Jana *et al.* is adopted in this study [13].

Figure 3 (a) and (b) show the absorption spectra of the solutions synthesized by using CTAB or BDAC/CTAB co-surfactant at different temperatures. As can be seen from Fig.3 (a) and (b), when using CTAB surfactant, the LSPR peak shifts from 800 nm to 710 nm as the synthesis temperature increases from 25 °C to 90 °C, indicating the formation of NRs with a lower aspect ratio. When using BDAC/CTAB co-surfactant, the LSPR peak shifts from 720 nm to 770 nm as the synthesis temperature increases from 25 °C to 90 °C, indicating the formation of NRs with a larger aspect ratio. It is suggested that at 90 °C the BDAC/CTAB co-surfactant was found to be more suitable for Au NR synthesis than the CTAB surfactant. In Fig.3(c), we show the evolution of the LSPR peak of NR synthesized at different temperatures ranging from 50 °C to 90 °C. The LSPR peak showed no obvious

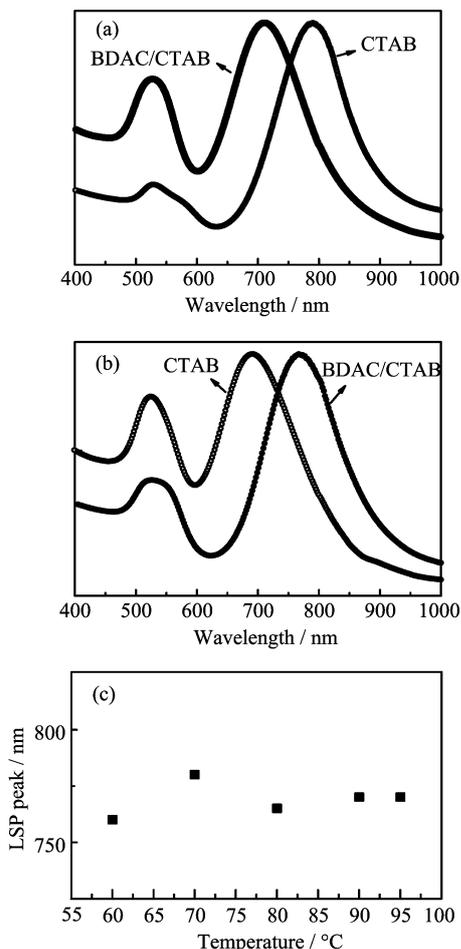


FIG. 3 Absorption spectra of Au NRs synthesized by using CTAB or BDAC/CTAB co-surfactant at (a) 25 °C and (b) 90 °C, and (c) LSPR peak of Au NRs *vs.* synthesis temperature, respectively. In these solutions, the concentration of HAuCl_4 , AgNO_3 , NaBH_4 , and ascorbic acid was kept constant.

change when different temperature was used. However, we observed an obvious increase in growth rate with the increasing of the synthesis temperature. The results agree with Zijlstra *et al.* that of [16]. We notice that the NR yield is low at temperatures below 50 °C when using the BDAC/CTAB co-surfactant.

C. The effect of the co-surfactant on NR synthesis

At room temperature, different LSPR peak positions of Au NRs can be obtained by changing the AgNO_3 concentration [22]. The AgNO_3 concentration is crucial for the formation of NRs and can not be changed widely at high temperatures [16]. In this work, the aspect ratios are tuned by changing the molar ratio of BDAC/CTAB in the co-surfactant mixture. Figure 4 shows the absorption spectra of the Au NRs produced in BDAC/CTAB surfactant mixture at 90 °C. In these so-

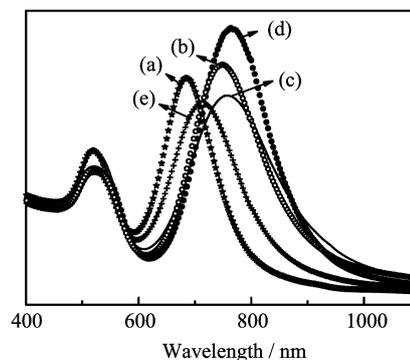


FIG. 4 Absorption spectra of Au NRs synthesized by using different ratios of BDAC to CTAB with different SPR bands. (a) 1:2, 680 nm, (b) 3:4, 745 nm, (c) 1:1, 758 nm, (d) 3:2, 770 nm, and (e) 2:1, 715 nm.

lutions, the concentration of HAuCl_4 , AgNO_3 , NaBH_4 , and ascorbic acid is kept constant, while the molar ratio of BDAC to CTAB changed from 0.5 to 2. It can be seen that as the ratio of BDAC to CTAB was increased, the LSPR absorption peak was red shifted, indicating formation of NRs with larger aspect ratio. But on further increasing beyond 1.5, the aspect ratio of NRs became smaller, as can be seen from a blue-shift of the LSPR wavelength. Indeed, using a growth solution containing BDAC without CTAB, only spheres were formed at high temperatures. In addition, we tried to adjust the aspect ratio of the NRs by changing the concentration of NaBH_4 , but a low rod yield resulted when the NaBH_4 concentration left the optimum value even slightly. Although here we point out the proper ratio of BDAC to CTAB is 3:2, it should be noted that the ratio would be slightly changed if different concentration of AgNO_3 or NaBH_4 was used.

Surfactant is widely used in the synthesis of Au NRs or NPs. Surfactants such as oleic acid [29] and CTAB [13,16,21,22,] have been used to grow NRs. CTAB has been one of the most popular surfactants in the synthesis of Au NRs. The shape and size of CTAB surfactant is important in controlling the final shape of Au NRs. Surfactants form elongated or wormlike micelles at higher concentrations with the addition of suitable additives [28]. Additives such as BDAC [22], heptane, sodium hydroxide, cyclohexane [30], and acetone, were found to be useful to synthesize Au NRs with different shapes, aspect ratios and yields. It is reported that using suitable additives can result in the rod-like micellar structure [31] or further elongate the micelles or enlarge the micelle size, increasing the yield and the aspect ratio of Au NRs [22].

One key point that helps Au NR formation is the symmetry-breaking according to Jana *et al.* [13]. The cylindrical micelle induced symmetry breaking in the growing NP. The NP would detach from the micelle surface because of its comparatively larger mass when the NP is larger than a certain size (5-10 nm). The

Ag⁺-surfactant complex could promote the attachment between the NP and the micelle surface. Under this condition, Au⁺ in the micelle were directed along the elongated micelle surface and caused the “Au-embryo” to grow in one dimension, resulting in symmetry breaking [13,28].

Another important factor leading to NR formation is the addition of the cationic surfactant which forms rod-like micelles above its critical micelle concentration (CMC). A high concentration (0.1 mol/L) is usually required for NR growth. The micelle concentration of CTAB determines the shape of the NPs. If it is below the CMC, the reduction primarily results in nanospheres. Only above CMC, anisotropic shape develops as the major product [13,28]. However, the micelles of CTAB are temperature dependent. If the temperature increased over 50 °C, the micelles would be destroyed intensively [13,16], resulting in a very low NR yield (as shown in Fig.3(b)). In contrast, by using the BDAC/CTAB co-surfactant with a proper ratio at 90 °C, much higher NR yield (over 95%) was obtained and the LSPR band maximum of the Au NRs reached 770 nm in this work (shown in Fig.2(b)). The results indicate that the BDAC/CTAB co-surfactant, as a flexible template, is more suitable for NR synthesis at high temperatures. Previous reports showed that in a mixed surfactant system of BDAC and CTAB, the CMC dropped dramatically compared to the CTAB system [28]. Similarly, BDAC here, as a co-surfactant, lowered the CMC of the surfactant solution, promoting the formation of micelle with anisotropic shape at high temperatures. As a result, higher yield and longer NRs were obtained by using such co-surfactant system at the temperature of 90 °C.

D. The effect of AgNO₃ concentration on NR synthesis

We observed that, in the absence of AgNO₃, ~90% Au spheres were obtained. The addition of an appropriate concentration of AgNO₃ increased the Au NR yield, and this result is consistent with the work of El-Sayed's group [22]. The addition of AgNO₃ in the growth solution is important for NR synthesis at elevated temperatures. AgNO₃ is believed to slow the growth of the NRs, resulting in NRs with better aspect ratio [16]. Choosing an optimum AgNO₃ concentration becomes important at high temperatures. Addition of a high concentration of AgNO₃ resulted in a low rod yield and main spheres at temperatures above 50 °C. A low AgNO₃ concentration resulted in short NRs at temperatures above 50 °C. The optimum AgNO₃ concentration used in this study was 4 mmol/L, which resulted in formation of NRs at the temperature of 90 °C. This result is consistent with the work of Zijlstra's group [16]. It should be noted that the AgNO₃ concentration should be carefully controlled and should not be changed significantly.

The characteristic Ag SPR band of ~400 nm did

not appear after adding AgNO₃ into the mixture of BDAC/CTAB, HAuCl₄, ascorbic acid, and NaBH₄, indicating that the silver ions are not reduced (shown in Fig.2). To date, the effect of AgNO₃ on Au NR synthesis remains unclear [22]. Murphy *et al.* proposed that AgNO₃ formed AgBr (Br⁻ from the CTAB molecule) and was absorbed on different facets of Au particles with different strengths, resulting in the formation of NRs [31,32]. Nikoobakht *et al.* proposed that the CTAB surfactant acted as a soft template, and AgBr decreased the charge density of CTAB molecules that were absorbed on Au facets and the repulsion between neighboring headgroups decreased, which then led to the formation of an elongated CTAB template [22]. Liu *et al.* recently reported that silver acted as a surface-structure-specific surfactant and silver deposits selectively on the {110} facet of Au NRs, slowing down the growth of this facet [33].

High-temperature Au NR synthesis helps to resolve two important problems. First, the restriction of slow batch synthesis limits the potential commercial application of Au NRs. Fast high-temperature synthesis provides a better system for rapid Au NR synthesis to satisfy potential commercial applications. In this work, high-temperature synthesis resulted in growth of Au NRs within 10 s, which might help develop rapid NR synthesis. Second, Au NRs could form at high temperatures, which suggests that using a thermally activated reducing agent is possible. For example, using thermally activated reducing agents, metal nanoparticles are synthesized in ethylene glycol at elevated temperatures [34,35]. This rapid seedless growth presents an attractive method for large-scale production of Au NRs.

IV. CONCLUSION

In summary, we synthesized Au NRs at 90 °C by using the BDAC/CTAB co-surfactant mixture. The BDAC/CTAB co-surfactant was found to be more suitable for Au NR synthesis at high temperatures than the CTAB surfactant. At 90 °C, we observed that the reaction time was within 10 s, and the LSPR absorption band of the Au NRs was adjustable from 680 nm to 770 nm by changing the molar ratio of BDAC to CTAB in the co-surfactant solution. This method showed excellent batch-to-batch reproducibility while the AgNO₃ concentration was carefully controlled. Although Au NRs with longer aspect ratio can be obtained at room temperature, this rapid seedless growth presents an attractive method for large-scale production of Au NRs, and this co-surfactant-based method may be extended to other surfactant-based metal NR synthesis.

V. ACKNOWLEDGMENT

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