

# Gold Nanorods: A Journey Towards Successful Synthesis

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## ABSTRACT

The journey towards the successful synthesis of gold nanorods (AuNRs) presented here identifies significant challenges, contributes to the elucidation of the complexity of synthesis and the manufacture of “home made” AuNRs. The issues discussed here offer valuable knowledge for nanotechnologists who are making their first steps into AuNR synthesis or experienced AuNR chemists who are confronted by problems in replication of these nanoparticles.

**Keywords:** gold nanorods, seeded growth, challenges

## 1 INTRODUCTION

Engineered gold nanoparticles (AuNPs) are receiving considerable research interest due to their unusual size-related properties; for instance, very small AuNPs are catalytically active and small AuNPs are brightly coloured but not golden. Colloidal AuNRs are of particular interest since their colours are tunable to cover almost the entire visible and NIR region of the electromagnetic spectrum, depending primarily on the nanorods' aspect ratio. Although a vast number of peer-reviewed AuNRs synthesis protocols have been published, have you ever found it difficult to successfully reproduce AuNRs with a particular aspect ratio in your own facilities? This paper outlines a journey from failures to successes, and shares strategies for tackling challenges of the synthesis of AuNRs.

## 2 CHALLENGES OF SEEDED GROWTH NANOROD SYNTHESIS

Colloidal AuNRs gain their optical properties from *localised surface plasmon resonance* (LSPR) effects.

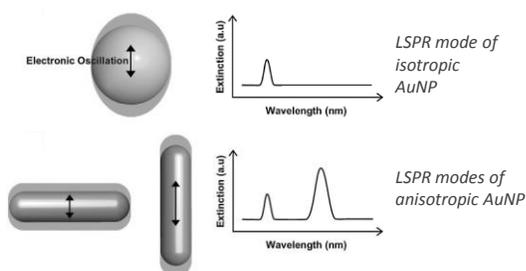


Figure 1: LSPR modes of isotropic and anisotropic AuNP. Graphic adapted from [1].

When interacting with the electric field of light the conduction electrons of the nanostructure separate collectively from the metal core and coherently oscillate within the particle boundaries resonating with the optical frequencies of light in the visible and infrared regions. Depending on size LSPR spectral peaks of isotropic AuNPs occur typically at 515–545 nm. Depending on aspect ratio, anisotropic AuNPs resonate at 515–545 nm (transverse LSPR wavelength) and at longer wavelengths for the longitudinal LSPR band.

This work is motivated by the experience of nil to poor reproducibility of previously published one-step seed-mediated AuNR synthesis protocols of a particular aspect ratio in our laboratory. The wet chemical syntheses investigated here are derived from Murphy's pioneering work requiring at least two pots [2]. Pot 1 contains very small gold seeds resulting from the reduction of gold(III) by a strong reductant ( $\text{NaBH}_4$ ) and being often stabilised by cetyltrimethylammonium bromide (CTAB) or trisodium citrate (TSC). Pot 2 contains the particle growth solution which consists commonly of a saturated CTAB solution and  $\text{Au}^+$  ions (from gold(III) reduced by a weak reducing agent (ascorbic acid)), and often  $\text{Ag}^+$  ions. Transfer of a certain amount of the contents of pot 1 into pot 2 leads to formation and subsequent deposition of  $\text{Au}^0$  onto  $\text{Au}\{111\}$  facets of the preformed gold seeds. A bilayer of the growth directing agent CTAB is responsible for blocking  $\text{Au}\{100\}$  and  $\text{Au}\{110\}$  crystal facets leading to longitudinal growth [3,4]. Three major issues affecting nanorod synthesis are discussed here: influence of ambient temperature, choice of dilute  $\text{NaBH}_4$  solution and removal of excess CTAB from the nanorod colloid.

## 3 EXPERIMENTAL

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , cetyltrimethylammonium bromide (CTAB), sodium borohydride ( $\text{NaBH}_4$ ) in triethylene glycol dimethyl ether and  $\text{NaBH}_4$  powder were purchased from Aldrich. Trisodium citrate (TSC) was purchased from Sigma. Ascorbic acid and 2,6-dihydroxybenzoic acid were purchased by Merck. Sodium salicylate (SA) was purchased from BDH.

### 3.1 Influence of Ambient Temperature

New Zealand has winter in June–August and summer in December–January. The ambient temperature in the laboratory in winter ranges from 18–21 °C and in summer from 21–23 °C.

CTAB ( $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3^+\text{Br}^-$ ) is a cationic surfactant molecule with a hydrophobic tail and a hydrophilic headgroup consisting of a quaternary ammonium cation and bromide as the counterion. The solubility of CTAB in  $\text{H}_2\text{O}$  is 0.1 M at 40 °C [5].

**Surfactant solution at 40–60 °C:** A saturated CTAB solution (or a surfactant solution with very similar properties [6]) is essential for the nanorod synthesis and is present in the growth solution and sometimes in the seed solution as well [3]. The saturated CTAB solution is transparent and colourless at 40–60 °C.

**Growth solution at 27–30 °C:** The growth solution should be ideally conditioned to 27–30 °C to control the rate of nanorod growth and to achieve the desired aspect ratio [3]. At reaction temperatures < 25 °C CTAB precipitates rapidly which inhibits the longitudinal growth. Reaction temperatures of 30–80 °C form rather short and broad nanostructures [7].

**Seed solution at 20–30 °C:** Seed solutions containing CTAB requires gentle warming of 23–30 °C. Without CTAB but with TSC, the preparation of the seed solution is not temperature critical.

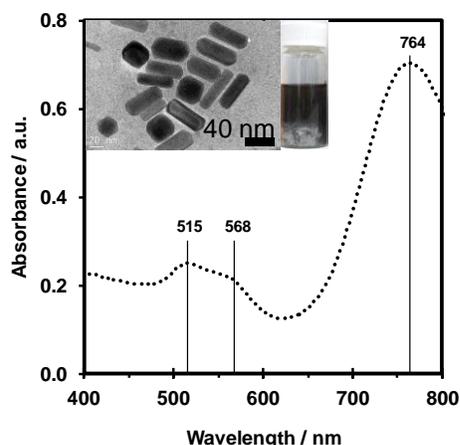


Figure 2: Visible spectrum of AuNRs synthesised with a controlled reaction temperature of 27–30 °C. Insert: Transmission electron micrograph of AuNRs of different aspect ratios and blueish grey sample with precipitated CTAB.

**Nanorod synthesis requires temperature control:** Synthesis attempts at ~19 °C without control of the reaction temperature (by e.g. hotplate, waterbath) were unsuccessful due to reasons outlined above. Controlled experiment temperatures facilitate reasonably regular nanorod growth as shown in Figure 2. The transverse resonant spectral peak is located at 515 nm. The longitudinal resonance peak is at 764 nm. The peak at 568 nm comes from shorter and broader AuNPs.

### 3.2 Choice of Dilute $\text{NaBH}_4$ Solution

The importance of quality of CTAB<sup>1</sup> for successful AuNR syntheses is documented, but other chemicals such as  $\text{NaBH}_4$ , appear to play a less critical role.

$\text{NaBH}_4$  acts as strong reducing agent for the formation of very small gold seeds (< 5 nm). As shown by Gole [9], the nanorod's aspect ratio does not necessarily depend on seed size or the nature of the capping agent.

**Form of  $\text{NaBH}_4$ :**  $\text{NaBH}_4$  is commercially available as a 2.0 M solution in triethylene glycol dimethyl ether or as pure solid. Is there a difference in the performance of these different forms as reductants for AuNP synthesis? To compare both compounds, solutions of each with a concentration of 0.01 M were made up. The 2.0 M  $\text{NaBH}_4$  solution in triethylene glycol dimethyl ether was diluted in absolute ethanol. Solid  $\text{NaBH}_4$  was dissolved in distilled water to give a 0.01 M solution.

**Synthesis of gold seeds:** The synthesis of very small gold seeds followed Ye's *et al.* protocol [10] at 30 °C. The hotplate's temperature sensor was positioned in a separate 25 ml-glass vial filled with 15 ml of water that was stirred at 400 rpm to avoid direct contact of the sensor with the gold containing solution. On addition of  $\text{NaBH}_4$  the colour in the reaction vial changed from deep yellow to pale brown due to AuNP formation. Typically, the pale brown seed solution was aged for two hours or until the decomposition of excess  $\text{NaBH}_4$  by water is completed (i.e. seed solution stops effervescing) before it was added to the pre-prepared growth solution.

Figure 3 shows the absorption spectra of the two forms of the pale brown seed solutions with almost identical optical properties (no LSPR).

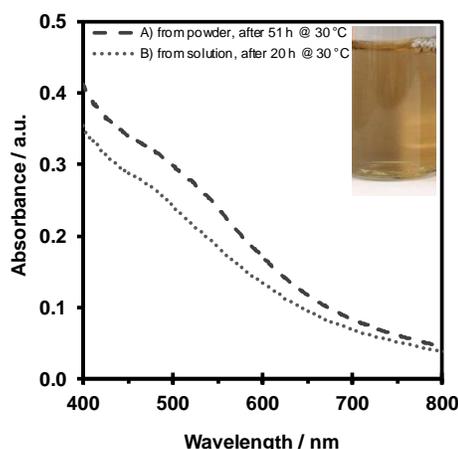


Figure 3: Absorption spectra of seeds synthesised by dilute  $\text{NaBH}_4$  solution from solid  $\text{NaBH}_4$  and from triethylene glycol dimethyl ether solution. Photo: Seed AuNPs are pale brown.

<sup>1</sup> CTAB's source as well as impurities is important. Smith [8] provides information about reliable products and their providers for AuNR synthesis.

This indicates that the original form of the  $\text{NaBH}_4$  has no influence on the seed formation within the first 24 h when stabilised by CTAB.

Further investigations are needed to evaluate the influence of triethylene glycol dimethyl ether solvent and ethanol on nanorod growth.

### 3.3 Removal of Excess CTAB

The removal of excess CTAB after AuNR synthesis is required for biocompatibility. Care has to be taken at this stage since removal of too much CTAB results in growth of nanorods beyond the desired dimensions. Overgrowth occurs when the capping agent does not efficiently block the Au{100} and Au{110} facets and the nanorod grows over time, not in longitudinal direction, but in transverse direction [11].

**Centrifugation:** We have tested four different types of centrifuge. A small micro centrifuge for laboratories holding up to eight 1.5 ml-microtubes without control over speed nor temperature did not separate AuNRs and solution. A *Eppendorf Centrifuge 5702 R* at 4,000 RCF (relative centrifugal force) holding up to four 50 ml-tubes did not separate nanostructure from solution either. Ultracentrifugation of 50 ml-samples at 100,000 RCF for 10 minutes at controlled 20 °C with a *Beckman Coulter Optima L-100 XP* did separate AuNPs from solution but simultaneously plated metallic gold on the inside of the tubes.

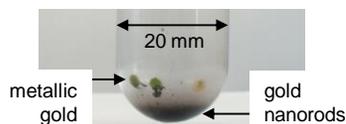


Figure 4: Ultracentrifuge tube after 10 min at 100,000 RCF at 20 °C. AuNRs are in the bottom, metallic gold is plated on the wall and supernatant is clear.

*Eppendorf MiniSpin® Plus* provides almost optimum conditions for up to twelve 1.5 ml-microtubes. The separation of gold nanostructures by density is effective at 10,000 RCF for 5–35 minutes but without complete separation of AuNPs from solution, i.e. the red supernatant contains surfactant and lower density AuNPs. We consider this result as inadequate. At 10,000 RCF the sample warms noticeably over 20–35 minutes resulting in undesired overgrowth with subsequently altered optical properties of the AuNRs.

We conclude that separation by centrifugation at 10,000 RCF should be limited to 35 minutes, although the supernatant is likely to be still coloured due to AuNPs of smaller particle size (lighter weight).

**Filtration:** The colloidal AuNRs were produced according to Ye *et al.* [10] using sodium salicylate as an additive at 30 °C. The sample was allowed to cool to ambient temperature and then kept at 4 °C overnight. The

final sample containing colloidal AuNRs and crystalline CTAB was filtered via a filtration column using Whatman filter papers 4, 2 and 50 as well as a fibrous glass filter (GF).

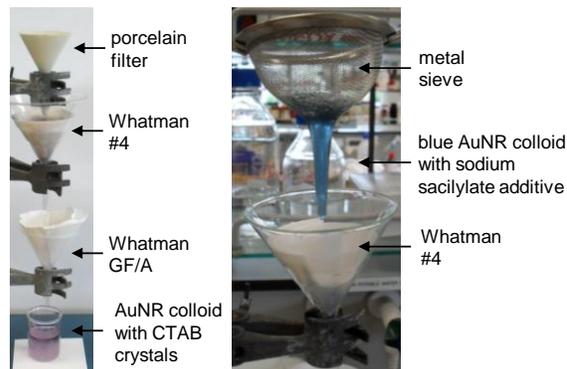


Figure 5: Left: Filtration column of lilac colloidal AuNRs with crystalline CTAB. Right: Filtration column of blue AuNRs. Sodium salicylate is highly viscous at ~21 °C.

Figure 5 shows two filtration columns. The left image shows CTAB crystals in the lilac AuNR colloid in the collecting vessel. It is possible that the GF/A became perforated and allowed the CTAB crystals to pass. It is worth repeating this filtration without bending the filter by using a filter cup. The right image shows that the sodium salicylate additive stabilises the AuNRs well. Its viscous nature at ~21 °C slows the filtration speed.

To crystallise more CTAB, the sample was frozen at -20 °C. The freezing process proceeds from the outside to the core removing free solvent (water). The nanorods assemble in the centre of the ice leaving colourless ice around the coloured core.

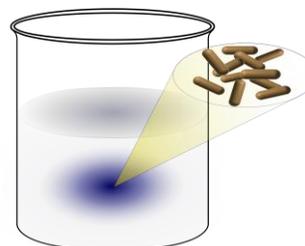


Figure 6: Schematic of AuNPs in CTAB solution assembling in the centre of the sample at -20 °C. The dense core in the otherwise clear ice represents blue AuNRs.

**Dialysis:** Although dialysis is time consuming it is very effective in removing unwanted material. Here, cellulose tubing *Membracell MD44-14* with a molecular mass threshold of 14 kDa was employed. The colloidal AuNR were produced as described by Ye *et al.* [10] with 2,6-dihydroxybenzoic acid as the additive. The visible absorbance spectrum is shown in Figure 7. The absorbance after 22 h and 39 h at 30 °C is almost identical with the

transverse resonance peak at 542 nm and the longitudinal resonance peak at 739 nm. This data indicates completed growth and stable AuNR formation. The sample was cooled to 4 °C overnight to precipitate excess CTAB. The precipitation was partly removed by Whatman 50 filter paper (filtrate was still “soapy”). The filtrate was transferred into the dialysis tubing which was placed in 800 ml of slowly stirring distilled water at 30 °C. The water was exchanged after 16.5 h and after 18 h. The dialysis was then considered to be completed since the water did not foam upon shaking (note: other samples might require more frequent exchanges of water). The transverse as well as the longitudinal peak show red-shifts of 2 nm and 4 nm, respectively—indicating a slight alteration of the AuNR’s aspect ratio—and decreased intensities. After 3 months at ~20 °C the purple AuNR colloid is “soapy” again because CTAB detached from the AuNR surface and dissolved. The AuNR slightly shortened as represented by a further red-shift and intensity decrease of the longitudinal peak.

Other samples without additive show significant overgrowth when dialysed.

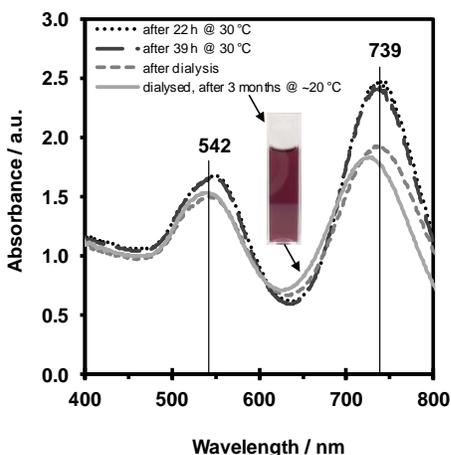


Figure 7: Visible spectra of AuNRs after 22 h and after 39 h. Then the suspension was dialysed and left for 3 months. The final colloid is purple.

In conclusion, the dialysis of CTAB/2,6-dihydroxybenzoic acid stabilised AuNRs removing excess surfactant without significant alteration of the AuNR’s aspect ratio. The stabilising surfactant diffuses from the AuNRs surface into solution over time.

## 4 CONCLUSIONS AND SUMMARY

The synthesis of seed mediated AuNRs requires commitment and skill.

A controlled reaction temperature is the key for controlled nanorod growth. The ideal range is 22–30 °C.

Dilute sodium borohydride solution made from both crystalline powder and triethylene glycol dimethyl ether solution form small gold seeds reliably.

CTAB should be purchased from suppliers as cited in the literature [8]. The nature and amount of impurities of CTAB is significant for nanorods in order to achieve a controlled aspect ratio.

Saturated CTAB solutions are necessary for nanorod formation, however, removal of excess CTAB is essential for AuNRs e.g. in biological applications. Moderate centrifugation (10,000 RFC for 5–35 minutes) removes excess CTAB. AuNPs of lower density will remain in supernatant, i.e. the recovery of AuNPs from the supernatant is incomplete. Dialysis removes excess CTAB reliably from the entire AuNR colloid but overgrowth appears. Filtration with paper and glass filterpapers seems to be insufficient for excess CTAB removal but has to be studied further.

We were able to identify critical issues which influence the synthesis of seed-mediated AuNRs. We used published synthesis protocols as a starting point and modified these procedures to our convenience with the knowledge gained from the experiments above.

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