



High conversion of HAuCl_4 into gold nanorods: A re-seeding approach



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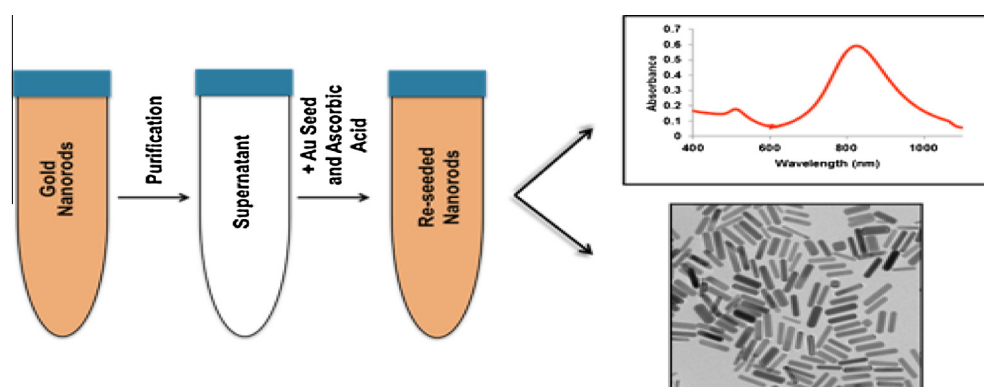
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GRAPHICAL ABSTRACT



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ABSTRACT

Gold nanorods with varying aspect ratios have been utilized in recent years for a wide range of applications including vaccines, surface enhanced Raman spectroscopy (SERS) substrates, and as medicinal therapeutic agents. The surfactant-directed seed mediated approach is an aqueous based protocol that produces monodisperse nanorods with controlled aspect ratios. However, an inherent problem with this approach is poor efficiency of gold conversion from HAuCl_4 into nanorods. In fact only ~15% of gold is converted, motivating the need for alternate synthetic protocols in order to make the process more scalable and efficient as gold nanorods progress toward commercial applications. In the current study, we have significantly improved this conversion by growing rods in several iterations of supernatant solutions that were previously discarded as waste. Inductively coupled plasma mass spectrometry (ICP-MS) data indicates ~14% gold conversion per nanorod solution with a total recovery of ~75%. Gold nanorods prepared in consecutive supernatant solutions generally have slightly increased aspect ratios and maintain stability and monodispersity as measured by UV-vis and TEM. The increased nanorod yield minimizes gold waste and results in a greener synthetic approach.

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1. Introduction

Gold nanorods have been successfully employed in numerous biological applications, including vaccines, photothermal therapy, and drug delivery [1–3]. Additionally, they have been employed

as surface enhanced Raman spectroscopy (SERS) substrates [4,5] and sensors [6]. This, combined with the growing interest in this synthetic approach and extreme gold prices (~\$1300/oz), results in mounting pressure to improve the synthetic efficiency in an effort to minimize gold waste. Much of the interest in metallic nanoparticles stems from their interesting size- and shape-dependent optical properties. Largely, these studies have focused on gold since they maintain strong Plasmon bands (a collective oscillation of electrons on the metal surface) in the visible to near-infrared (NIR) region of the electromagnetic spectrum [6–8]. Early work in the field focused on the synthesis of spherical nanoparticles, however, particles having a variety of morphologies including cubes, stars, nanoshells and nanorods are now readily prepared [8–10]. Gold particles having a rod-like shape are of particular interest since they possess 2 Plasmon bands (transverse and longitudinal) that may be tuned in the visible to NIR by altering nanorod aspect ratio [7].

Spherical nanoparticles are prepared by the rapid reduction of Au^{3+} to Au^0 in the presence of a strong reducing agent such as sodium borohydride. While this process efficiently converts nearly 100% of Au^{3+} or Au^{1+} into Au^0 spheres, this assumption does not hold for nanorods [11,12]. An aqueous seed-mediated approach is commonly employed that utilizes a growth directing agent to promote the desired rod-like morphology [6–8]. The synthesized nanorods are highly monodisperse and their aspect ratios easily tuned by the addition of small amounts of AgNO_3 . A report by Guyot-Sionnest suggests that in close proximity to the nanorod surface, Ag^{1+} is reduced to metallic Ag^0 resulting in the formation of monolayers or submonolayers of Ag^0 on the gold surface [13]. This is believed to result from underpotential deposition (UPD) of Ag^{1+} by ascorbic acid at a lowered reduction potential [12–15]. Additionally, there have been 2 other proposed mechanisms allowing for aspect ratio control: (i) a possible CTA-Br- Ag^+ complex acting as capping agent with preferential binding to a specific gold face and [16] (ii) silver interacting with bromide altering the shape of the CTAB micelle and thus its behavior as a soft template [7]. While there is evidence to support all 3 approaches it is still unclear which mechanism dominates or if it is a combination of all 3 working in harmony.

Unlike their spherical counterparts, the rod growth occurs kinetically much slower and with the use of weaker reducing agents, resulting in significantly less efficient gold conversion. Orendorff et al. reported only ~15% of initially introduced Au^{3+} is transformed into gold nanorods [12]. His report further suggests a feasible mechanism of nanorod growth and termination whereby the rate of Ag^0 layer deposition on side versus end faces of the nanorod dictate final aspect ratio [12]. Recently, several reports of higher conversion of gold into low aspect ratio gold nanorods in one-pot synthetic approaches measured by changes in spectral data and TEM have been reported [17–19].

In the current study, we investigate the conversion of previously disposed of supernatants containing unreacted Au^{1+} , growth directing agent, and ascorbate into gold nanorods. It should be noted that all nanorods solutions must always be centrifuged post synthesis in order to remove these unreacted species. Failure to remove the unreacted reagents results in morphological changes to the nanorods over time. Briefly, originally prepared gold nanorod solutions are centrifuged and their supernatants saved. These supernatant solutions are subsequently dosed with 4 μL ascorbic acid, re-seeded and allowed to sit undisturbed overnight resulting in new rod growth. This process results in growth of gold nanorods through 5 iterations of recycling the previously disposed of supernatant solutions, yielding ~75% total conversion as measured by inductively coupled plasma mass spectrometry (ICP-MS) analysis. Furthermore, this approach provides maximum versatility whereby each supernatant solution provides a “new” “one-

pot” growth solution. By altering silver nitrate additions to these solutions, there is the potential to grow rods of varying lengths with each re-seeding event. To the best of our knowledge, this is the first quantitative report of gold conversion into nanorods through multiple re-seeds of supernatant growth solutions.

2. Materials and methods

2.1. Chemicals

Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate, ascorbic acid, sodium borohydride (NaBH_4) and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich. Gold standard solution used for ICP-MS analysis was purchased from Inorganic Ventures. All chemicals were used as received. All reactions were performed using ultra purified 18 megaohm water.

2.2. Gold nanorod preparation

Gold nanorods with an aspect ratio (A.R.) of ~3 were prepared in the presence of CTAB following a seed-mediated approach as previously reported [3,12]. Briefly, to a 2.5×10^{-4} M chloroauric acid solution containing 0.1 M CTAB was added 600 μL of 0.01 M ice-cold sodium borohydride under vigorous stirring for 10 min resulting in ~1.5 nm spherical “seed” particles. After a minimum of 60 min, 12 μL of these seed particles were added to a growth solution containing 9.5 mL of 0.1 M CTAB, 60 μL of 0.01 M silver nitrate, 5×10^{-4} M chloroauric acid and 55 μL of 0.1 M ascorbic acid. Rod growth was allowed to proceed overnight and nanorod solutions were purified by centrifugation at 10,000 rpm for 30 min. All nanorods were resuspended in 10 mL deionized water. Supernatants containing unreacted CTAB, Au^{1+} , $\text{Ag}^{1+}/\text{Ag}^0$, and ascorbic acid were removed and saved for subsequent re-seeding events. For each seeding event 5, 10 mL samples were prepared.

2.3. Re-seeded gold nanorod solution preparation

Gold nanorod growth in supernatant solutions was accomplished by the addition of 4 μL of 0.1 M ascorbic acid and 12 μL seed to 10 mL of supernatant. Rod solutions were allowed to sit overnight and purified as described above. This procedure was applied through 5 iterations.

2.4. Ultraviolet-visible spectroscopy (UV-vis)

All gold nanorod solutions were analyzed via UV-vis spectroscopy to assess particle integrity. For each seeding event spectra were collected on the 5, 10 mL samples then mixed and measured again. All spectra were collected on an Agilent 8453 UV-Vis spectrophotometer or an Agilent Cary 5000 UV-Vis-NIR spectrophotometer.

2.5. Transmission electron microscopy (TEM)

TEM images were collected on a Phillips CM20 scanning transmission electron microscope with a 100 kV operating voltage. Nanorod samples were drop cast onto TEM grids and desiccated overnight prior to imaging.

2.6. Inductively coupled plasma mass spectroscopy (ICP-MS)

For ICP-MS analysis samples were prepared with 50 μL of the purified gold nanorod solutions and digested in 2 M hydrochloric acid. All ICP-MS experiments were collected in triplicate for each

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