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Kinetically controlled fabrication of gold nanorods and investigation of their thermal stability via in-situ TEM heating

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Abstract. Size controlled CTAB-capped AuNRs with various aspect ratios (ARs) ranging from 1.63±0.13 to 4.12±0.25 were synthesized following a modified seed-mediated method. Their thermal stability was examined by in-situ TEM heating. The results revealed a structural change from rods to spheres with increasing temperature. At lower temperatures < 300ºC, the AR decreased rapidly and, for temperatures >600ºC, particles became increasingly spherical. This behaviour occurred at temperatures lower than the melting point of bulk gold supporting a surface diffusion mechanism with material diffusing from the tips and redepositing at the middle of the rods. The rate of change in AR appeared to increase for thinner AuNRs.

1. Introduction

Gold nanorods (AuNRs) play an important role in various applications due to their shape-dependent optical properties which can be tuned into the near infrared (NIR) region for the purposes of in-vivo photothermal therapy and ultrasound imaging which take advantage of the NIR window in biological tissue [1]. AuNRs exhibit two surface plasmon resonances: transverse and longitudinal [1, 2]. The longitudinal plasmon resonance has been found to be very sensitive to the aspect ratio (AR) of the rods, thus controlling the AR via a facile synthesis procedure is of importance. However, there are reports of a decrease in the AR of AuNRs during exposure to ultrafast pulsed laser radiation and thermal heating [3]. Hence the thermal stability study of AuNRs is of interest both fundamentally and for their use in specific medical applications.

2. Experimental Procedure

2.1 Synthesis of CTAB-capped AuNRs

In this work, a seed mediated method following Nikoobakht and El-Sayed [4] was used to obtain homogeneous AuNRs with various ARs; kinetic control via pH adjustment was introduced in order to slow down the growth rate and achieve a homogenous distribution of AuNRs. The synthesis involved 2 main steps: seed growth and growth in solution described below.

1.) *Seed solution,* 5 mL of 0.2 M CTAB was gently mixed with 5 mL of 0.5 mM of $HAuCl_4$. Then, 0.6 mL of 2 hr aged ice-cold 0.01 M $NaBH_4$ was rapidly injected and mixed by shaking. The solution was left for 2 hr.
2.) *Growth solution,* 10 mL of growth solution containing 5 mL of 0.2 M CTAB and 5 mL of 1 mM $HAuCl_4$ was first prepared in 5 different vessels. Then, 4 mM of $AgNO_3$ was added in differing amounts (150, 200, 250, 300, 350 µL) in each vessel and gently mixed in order to obtain different AR rods (denoted samples 1-5 respectively). Kinetic control was achieved via addition of 12 µL of 12 M HCl and gentle mixing. Next, 70 µL of 0.0788 M of ascorbic acid was mixed into the growth solution resulting in a colourless appearance. The final step was to

rapidly inject 12 µL of seed solution into the growth solution without any mixing. This was incubated at 30℃ for 5 hr.

2.2 Materials Characterization and TEM heating experiment

AuNR samples were initially centrifuged twice and redispersed with the same amount of Milli-Q water to remove the excess CTAB. They were then characterized by UV-vis spectroscopy, and TEM. 1 mL of AuNRs was put in a UV-vis cuvette and examined in a Perkin-Elmer lambda35 model spectrophotometer to obtain the optical absorption spectrum from 400 to 900 nm. All TEM images were obtained in bright field mode from a FEI Tecnai G2 TEM/STEM operating at 200 kV. TEM samples were prepared by dropping 2 µL of AuNRs suspension onto holey carbon film 400 mesh copper TEM grids and naturally dried at room temperature. The thermal stability of AuNRs was studied via in-situ TEM. The samples were prepared by dropping 2 µl of centrifuged AuNRs onto a Si_3N_4 heating chip (DENS solutions) which was then allowed to dry. The chip was loaded into the in-situ DENS heating holder and loaded into the TEM. The chip was heated from room temperature up to 1000ºC, applying a 50ºC increase every 5 minutes. The morphology of the rods in the centre of the heating chip were monitored.

3. Results and discussion

3.1 Synthesised CTAB-capped AuNRs

The kinetically controlled modified synthesis method of CTAB-capped AuNRs produced well-controlled and reproducible AuNRs with various ARs. The colour of the dispersion gradually changed over 20-30 min depending on the aspect ratio of the rods. Figure 1(a) illustrates the colour differences of CTAB-capped AuNRs and their corresponding UV-vis spectra. The samples exhibited a red-shift of the absorption spectra as a function of increasing AR. The longitudinal plasmon resonances of the synthesized rods ranged from the visible region (575 nm) to the NIR (800 nm) according to their AR. Statistical measurements of particle size (200 particles per sample) from TEM images were undertaken using ImageJ software. The results showed that the AR of AuNRs increased as the amount of $AgNO_3$ employed in the synthesis increased. The ARs of AuNRs were 1.63±0.13, 2.14±0.22, 2.92±0.25, 3.43±0.32, 4.12±0.25 for samples 1-5 respectively, as seen in figure 1(b). This shows the longitudinal plasmon mode is very sensitive to the AR, with only a small change in resulting in a significant shift of the absorption spectra.

The absorption spectra also exhibited a transverse plasmon resonance band located at around 520 nm, which did not vary significantly between different samples, in agreement with literature. This transverse absorption mode represents the oscillation of electrons over the short axis of the rods and the absorption maximum was similar to that of spherical particles which had a peak resonance at around 520 nm. However, in sample 5, the transverse peak (orange colour) was broad indicating that various sizes of spherical particles were produced. The presence of AuNRs were confirmed by HRTEM and selected area electron diffraction (SAED). An SAED pattern of a group of AuNRs (inset 2(a)) showed fcc Au lattice reflections of (111), (200), (220), and (311). In figure 2(b), HRTEM showed a lattice spacing of 0.148 nm along the rod axis which can be assigned to the (220) spacing of fcc Au.

3.2 TEM heating experiment

AuNRs with different ARs were investigated by in-situ TEM heating. The results illustrated a structural change of AuNRs with increasing temperature, as shown in figure 3. The aspect ratio clearly started changing, albeit with only a small decrease, at relatively low temperatures ca. 100ºC. More significant changes were observed at higher temperatures, with the rod length decreasing and the rod width increasing. The rate of change of AR, the slope of the graph in figure 3(b), was large for temperatures up to 300ºC and then reduced and became relatively constant at higher temperatures. For temperatures >600ºC, particles became increasingly spherical for all rods monitored. There were some variation in results with some rods exhibiting a significant change in AR at high temperatures, e.g. < 700ºC for rods 1, 2 and 3.

Longer rods were found to be more unstable and exhibited a higher rate of change of AR with temperature than shorter rods. The change in AR depended on the surface area to volume ratio [5]; thinner rods (rods 1-4) exhibited a more rapid decrease in AR as compared to thicker rods (rods 5-7). For rods with different lengths but the same width, the longer rods showed more a significant change

with temperature than the shorter rods. Interestingly for rod 4, which is thinnest rod with an AR~3.82(L/W;28.34/7.41nm), the surface of AuNR started melting and diffused from the tip to the middle of the rod at ca. 150℃. At 250℃, a significant decrease in length was observed. At higher temperatures the rate of change increased and the rod transformed into a sphere at about 800℃. Initial room temperature TEM images were compared with those at the end of heating profile to calculate the particle volume change. Assuming a cylindrical rod with two hemi-spherical endcaps, the estimated initial volume was 1180.29 ± 0.09 nm^3 whilst the spherical particle volume after heating was 1134.98 ± 0.05 nm^3. This perhaps indicates a slight change in volume which may occur during to surface melting via evaporation or diffusion onto the support film. The thermal transformation mechanism of rods was revealed by heating at a lower temperature for a longer period of time (figure 4). This revealed evidence for surface melting and surface diffusion at temperatures lower than the melting point of bulk gold arising from the minimization of surface energy [6]. The tips of rods, with a large radius of curvature and hence higher surface energy, were most reactive with material diffusing and redepositing towards the middle of the rods, resulting in a decrease in aspect ratio.

Overall the studies revealed that rods with aspect ratios of about 4.0 - 4.5, with a surface plasmon resonance lying at about 800 nm, would be a good candidate for nanomedical applications, both in terms of its optical properties and thermal stability; the useful ranges of temperatures, whereby heating did not significantly change optical properties, were up to 100 ºC.

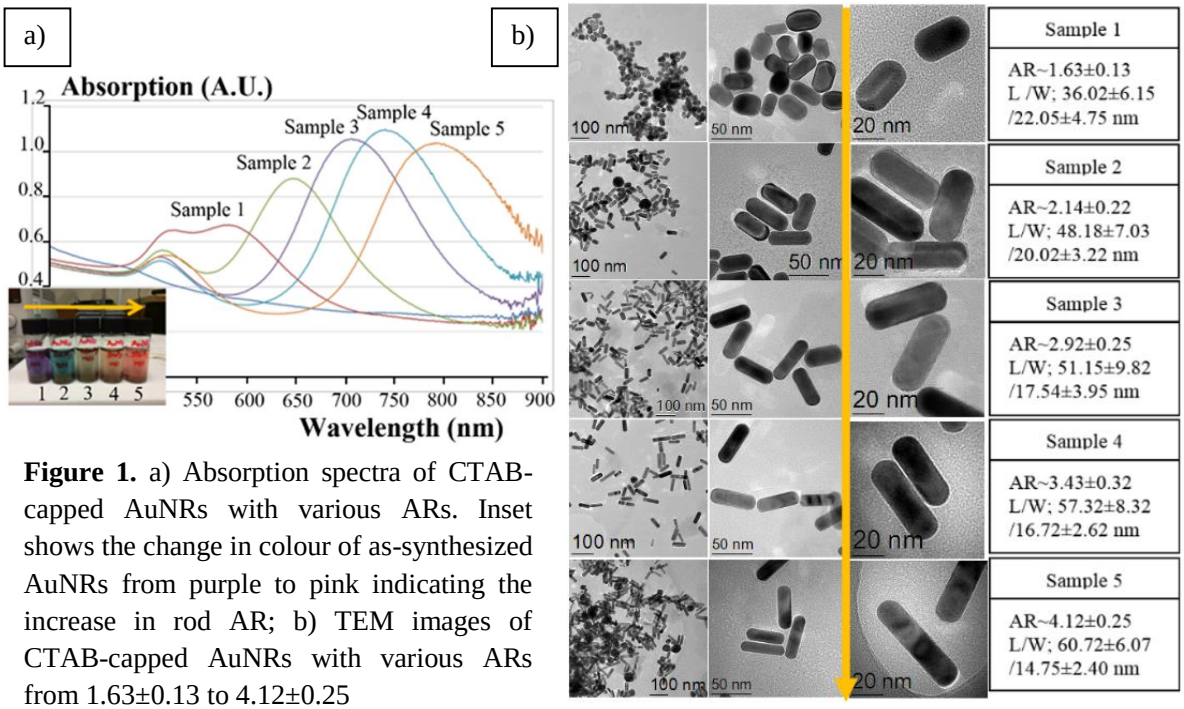

Figure 1. a) Absorption spectra of CTAB-capped AuNRs with various ARs. Inset shows the change in colour of as-synthesized AuNRs from purple to pink indicating the increase in rod AR; b) TEM images of CTAB-capped AuNRs with various ARs from 1.63±0.13 to 4.12±0.25

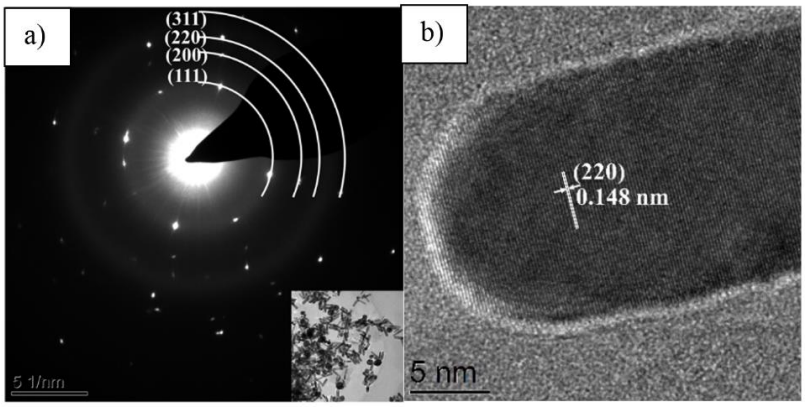

Figure 2. a) Electron diffraction pattern of a group of AuNRs shown in the image inset; b) HRTEM image of AuNRs, showing [220] direction along the rod axis

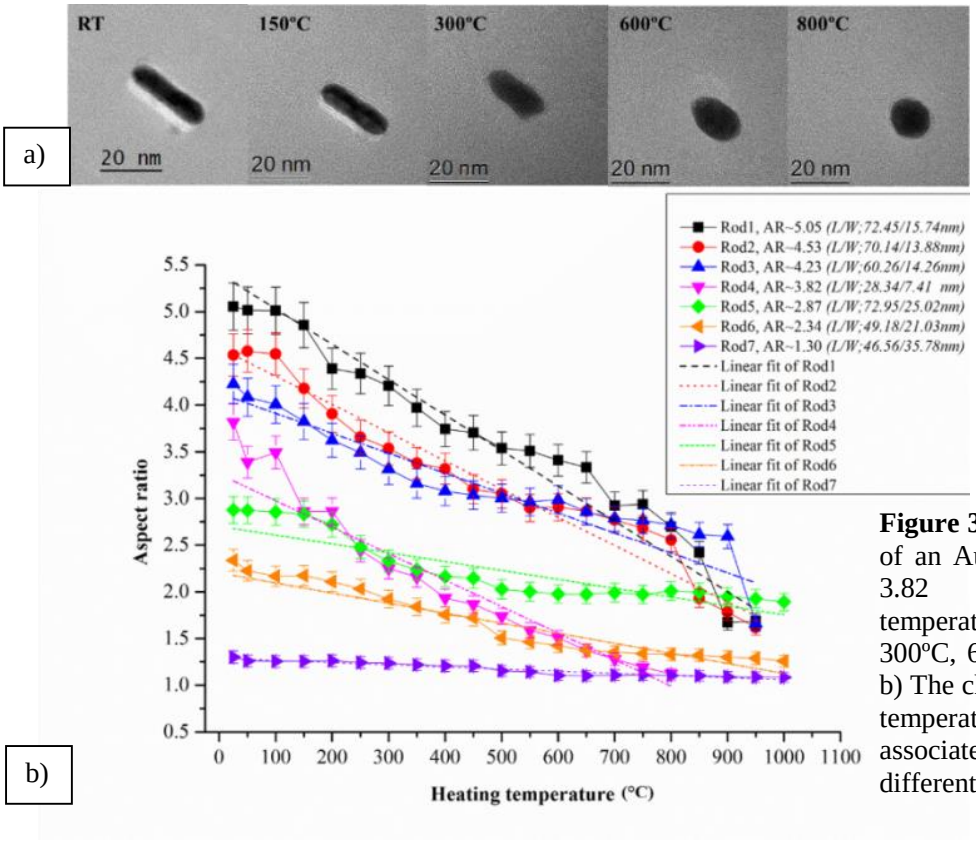

Figure 3. a) TEM images of an AuNR with AR of 3.82 at different temperatures: RT, 150ºC, 300ºC, 600ºC and 800ºC. b) The change in AR with temperature and associated linear fits for different AR rods

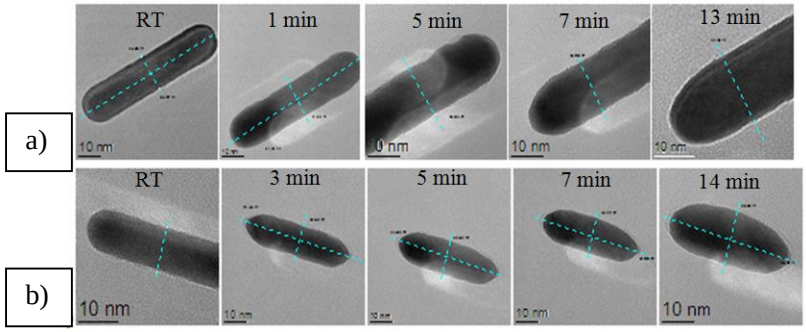

Figure 4. Low temperature heating experiment: TEM images of an AuNR at a) 100ºC and b) 150ºC for 15 mins, illustrating the transformation mechanism arising from surface diffusion from tip and redeposition at the middle of the rods

4. Conclusion

Size controlled AuNRs with various ARs were reproducibly synthesised following a modified seed-mediated method together with pH adjustment. After heat treatment via in-situ TEM heating, there was a structural change from rods to spherical particles which depended on the exact rod morphology. These findings are important for the application of AuNRs in photothermal therapy and ultrasound imaging, which require no change in optical properties during heating. This study attempts to define a usable temperature range for AuNRs in such applications which could be then simulated by modelling for a given laser power.

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