Two-step synthesis of high aspect ratio gold nanorods

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Received 7 July 2005; accepted 17 October 2005

Abstract: We describe a very simple, two-step synthetic method to prepare gold nanorods with extremely high aspect ratios (> 20) and average lengths of more than 1000 nm. The method is based on a seed-mediated growth in presence of the surfactant cetyltrimethylammonium bromide. The length and aspect ratios of the nanorods can be manipulated by varying the surfactant concentration.

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Keywords: Gold, nanorods, surfactant, cetyltrimethylammonium bromide

1 Introduction

Gold nanoparticles have been widely studied because of their unusual optical, catalytic and electronic properties and they have been proposed as future building blocks in nanotechnology [1–5]. Their properties are very different from the corresponding bulk material. The size and shape of the nanoparticles greatly influences their properties [5] for example, spherical gold nanoparticles exhibit a single plasmon resonance in the visible region of the spectrum while rodlike particles exhibit a longitudinal and transversal plasmon resonance [6]. Hence, a lot of effort has been put into the development of synthetic methods that yield control over size and shape. The design of rodlike particles especially, has been the subject of intense research. Several methods to prepare gold nanorods have been reported in literature. For example, they can be synthesized in rigid templates such as nanoporous matrices or in the presence of surfactants by electrochemical or seed-
mediated growth methods [7–14]. Surfactant based methods are usually considered as
being more practical for large-scale synthesis. A recent report used a multi-step seed
mediated growth method to obtain gold nanorods with aspect ratios as high as 18 and
lengths of a few 100 nanometers [12, 13]. Another group reported the synthesis of gold
nanorods with aspect ratios of 10 in a two-step method using a binary surfactant mixture
[14]. The latter method yields pure nanorods in contrast to the former where a mixture
of differently shaped particles is obtained.

In this communication we use a surfactant based two-step method to prepare gold
nanorods with extremely high aspect ratios (> 20) and average lengths of more than a
micrometer. Our method is a simple modification of the procedures described in references
11, 12, and yields a mixture of spherical, triangular and rodlike nanoparticles with the
predominant formation of rodlike particles at high surfactant concentrations. Changing
the surfactant concentration was shown to vary the length of the nanorods formed.

2 Experimental

The seed solution was prepared by mixing 20 mL of a $2.5 \times 10^{-4}$ M HAuCl$_4$.3H$_2$O
and $2.5 \times 10^{-4}$ M Na$_3$ citrate in water with 400 $\mu$L of an ice cold and freshly prepared solution
of 0.1 M NaBH$_4$ in water. The colour of the solution immediately changes from yellow to
orange.

The growth solution was prepared by adding an appropriate amount of cetyltrimethyl-
lammonium bromide (CTAB) (to yield overall CTAB concentrations of $10^{-3}$, $10^{-2}$, 0.1
and 1 M, respectively) to a 10 mL solution of $2.5 \times 10^{-4}$ M HAuCl$_4$.3H$_2$O in water. To
dissolve all the CTAB, the solution was heated slightly, but after dissolution the solution
was cooled down to room temperature (20 °C) again, except in the case of 1 M CTAB so-
lution which was kept at 35 °C to prevent precipitation of CTAB. A 40 $\mu$L of 0.1 M L(+)-
Ascorbic acid was then added to the solution. The bright yellow solution immediately
turned colourless, due to the formation of a Au(I) complex with CTAB.

The nanorods were then prepared by adding 25 $\mu$L of the seed solution to 10 ml of
the growth solution. After gentle mixing, the solution was allowed to stand for several
hours to complete the growth of the nanorods.

3 Results and discussion

The advantage of the method we describe here over the one reported by Jana et. al. is that
we were able to synthesize long nanorods. Moreover, Jana et al. describe a multistep
procedure, requiring several seed- and growth cycles while the method described here
requires only a single seed- and growth step. Hence, we were able to study the role
of the CTAB concentration on the length of nanorods formed. The synthesis of the
nanorods was performed in the presence of different amounts of CTAB, and depending
on its concentration a difference in the amounts and sizes of nanorods were observed.
The UV/Vis spectra of the nanorod mixtures in the presence of $10^{-3}$, $10^{-2}$, and 0.1 M

CTAB are shown in Figure 1. All spectra are quite complex although a transversal and longitudinal plasmon band typical for rodlike particles is clearly seen.

![Fig. 1 UV/Vis spectra of solutions containing nanorods, prepared in the presence of $10^{-3}$ (solid line), $10^{-2}$ (dashed line), and 0.1 M (dotted line) CTAB, respectively.](image)

Two possible mechanisms for rod formation have been proposed in literature: a direct surfactant templating mechanism with or without an electric-field directed growth of gold nanorods [12, 15] and a mechanism suggesting the lowering of the interfacial tension of a specific crystal facet [16]. Since the formation of rods is observed well below the cmc of CTAB, a templating mechanism seems unlikely. However, a clear dependence of rod length on CTAB concentration is observed with the rod length increasing significantly upon increasing CTAB concentration. Moreover, at CTAB concentrations higher than the sphere-to-rod transition [17, 18] both rod diameter and length increase substantially, which seems to suggest that a templating mechanism does influence rod formation.

This was further confirmed by scanning electron microscopy (SEM). A solution of 0.001 M CTAB showed mainly the presence of spherical nanoparticles of 10 nm diameter with only a small amount of nanorods of an average length of 110 nm and width of 30 nm. However, with increasing concentration of CTAB we clearly observe an increase in nanorod formation and nanorod length. Thus, a solution containing 0.01 M CTAB gave nanorods with an average length of 220 nm and 40 nm width while a 0.1M CTAB concentration yielded 400 nm length and 18 nm width. Though the amount of nanorods (as compared to spherical and triangular particles) increases with increasing CTAB concentration, we still observe a small amount of nanoparticles with atypical shapes (Figure 2).

In the presence of 1M of CTAB, the solution containing the nanorods is only slightly colored and the absorption spectrum is rather featureless in the visible and near infrared. Scanning electron microscopy images show the formation of extremely long nanorods with average lengths of over 1 micron and 60 nm in width (Figure 3), with a small amount of atypically shaped particles still present. The absence of significant absorption in the visible and near infrared is due to the fact that nanorod formation shifts the plasmon resonance to lower energies, whereas the high energy plasmon resonance decreases in
Fig. 2 SEM image of gold nanorods prepared in the presence of 0.1 M CTAB.

intensity.

Fig. 3 SEM images of gold nanorods prepared in the presence of 1 M CTAB solution.

The average lengths and aspect ratios of the different nanorods as measured by SEM are summarized in Table 1 for each CTAB concentration. Note the extremely high aspect ratios and nanorod lengths at high CTAB concentration. We are not aware of any other simple surfactant based method that yields gold nanorods of these dimensions and aspect ratios. In this respect, this method could be very useful for large scale-synthesis of nanorods. We do realize however that this synthetic method does not yield pure nanorods and an additional purification step, such as centrifugation, might be necessary.

Acknowledgment

The authors would like to thank Rudy De Vos for SEM measurements. We thank the Fund for Scientific Research-Flanders (FWO-Vlaanderen, Grant G.0297.04), the Katholieke Universiteit Leuven (Grant GOA/2000/03) and the Belgian Government (Grant IUAP P5/03) for financial support. The research of T.M. was financed by a Ph.D. grant from the Institute for the Promotion of Innovation through Science and Technology in Flanders.
Table 1 Average lengths and aspect ratios for nanorods as measured by SEM, for different surfactant concentrations.

(IWT-Vlaanderen).

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