Synthesis of Gold Nanorods by Surfactant-assisted One-step Chemical Reduction Method

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The synthesis of metal nanorods has attracted a great deal of attention due to their unusual roles in the fabrication of nanoscale electronic devices and investigation of quantized conductance and localization effects. This work describes a simple and novel procedure for the fabrication of high aspect ratio gold nanorods under mild conditions.

Gold nanorods were synthesized as follows: first, 0.36 g cetyltrimethylammoniumbromide (CTAB) was dissolved in 5 mL of water and heated up to 80 ℃ under magnetic stirring. Then 5 mL of aqueous solution of $NaAuCl_4$ (0.5 mM) was added and stirred continuously for about 30 min. After that, a controlled amount of tri-sodium citrate (0.034 M) and NaOH (1 M) were added rapidly into this hot solution to initiate the reaction. After the addition of NaOH, the reaction solution became colorless instantly, indicating the reduction of Au^{3+} to Au^{+}. Subsequently, this solution gradually turned pink and pink-purple in a different time period with varying amount of NaOH. The reaction was maintained for 3 h to ensure the complete reaction. The resulting solution was centrifuged at 6000 rpm for 10 min once and at 3000 rpm for several times to remove the surfactants.

NaOH is crucial to the growth of gold nanorods, without which the reduction reaction could not be initiated. Figure 1 shows transmission electron microscopy (TEM) images of gold nanorods prepared by addition of 5, 15, 20, 50 μL of NaOH at 80℃. It is seen that no rods were formed with 5 or 50 μL of NaOH (Figure 1A and Figure 1D). However, gold nanorods with aspect ratio up to 100 were obtained when 15 μL of NaOH was added (Figure 1B). Similar products could be obtained with 20 μL of NaOH (Figure 1C). The nanorods have diameters about 20-30 nm with lengths up to 1-3 μm. Figure 2A shows a typical TEM image of a single gold nanorod with a diameter of about 25 nm and aspect ratio of 48. The ED pattern (Figure 2B) indicates its single crystalline nature.

In order to clarify the growth process of the gold nanorods, the reaction was monitored by fixing the amount of NaOH at 15 μL. It has been observed that large amount of small particles were formed at the initial reaction stage. After 30 min, rod-shaped structures appeared being mixed with those small particles. It should be noted gold nanorods were formed gradually after 60 min by consuming small particles. The nanorods kept growing until 180 min with increased aspect ratios. There are still some particles observed together with the gold nanorods, which needs careful centrifugation to separate.

The synthetic procedure we used to make the gold nanorods is very simple because it could be carried out with one-step without any use of seed or additives. We propose the following mechanism for the nanorod growth: when the $AuCl_4^-$ was reduced by citrate, gold nuclea were formed at the initial reaction stage. These nuclea generally grew to nanoparticles in the absence of surfactant, as well known as Frens synthesis of gold nanoparticles. However, in the presence of CTAB, the gold nuclea grew into nanorod with capping of CTAB on specific crystalline facets. Other factors that influence the growth of the gold nanorods are the reaction temperature and reaction time, concentration of reducing agent and amount of NaOH etc. We found that gold nanorods could be formed over a range of temperatures from 60 to 90 ℃. Among these factors, the pH value is crucial to the growth of gold nanorods probably because it greatly affect the rate of formation of initial gold nuclea therefore affects the growth of gold nanorods. Too fast or too slow reaction rate can only lead to gold nanoparticles. Therefore, high yield gold nanorods and high aspect ratios must be prepared by carefully controlling the reaction conditions. The formation mechanism of gold nanorods and the influencing parameters are still under investigation.

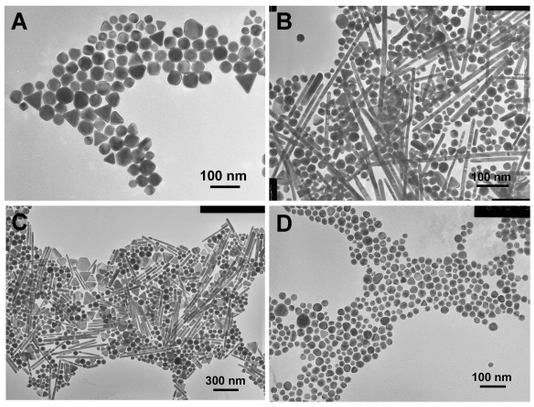

Figure 1. TEM images of gold nanorods prepared with (A) 5, (B) 15, (C) 20, and (D) 50 μL of NaOH.

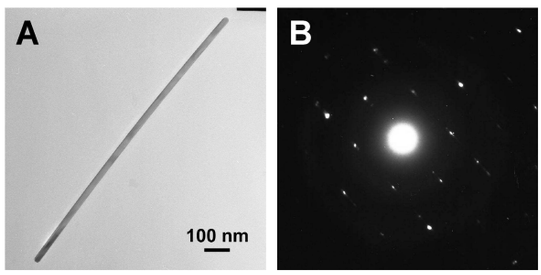

Figure 2. A typical TEM image of gold nanorod (A) and its ED pattern (B).

In conclusion, by carefully controlling the preparation condition, gold nanorods have been successfully synthesized with one-step chemical reduction method using CTAB as shape-inducing surfactant. This process is very simple, without any aid of seed or additives during the formation process, and is expected for synthesis of other metal nanorods.

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