Exploring the Length of Gold Nanorods

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In the synthesis of metal nanoparticles (NPs), control over the shape has been one of the most important and challenging tasks. The shape and crystallographic facets are the major factors in determining not only the catalytic and surface activity of the NPs [1] but also its optical and magnetic properties. By suitable choice of experimental conditions and additives, non-spherical shapes such as disks, rods, wires, tubes and concentric core-shell structures have been successfully synthesized and they are found to possess properties which depend not only on NP size but also their shape and other topological aspects [2].

An interesting case is the study of rod-shaped gold NPs or gold nanorods (Au NRs). One of the features of these rod nanoparticles is the presence of two distinct surface plasmon absorption bands. The transverse surface Plasmon (TSP) band, around 520 nm, is due to the excitation across the short dimension of the NRs while the longitudinal surface plasmon (LSP) band is due to the excitation along the long axis [3]. By changing Au NRs aspect ratio (AR), the LSP resonance band can be tuned from the visible to near infrared (NIR) wavelength [2], a region where interesting biologic tissues are relatively transparent (water window) and can be studied.

The two known approaches in the preparation of Au NRs using surfactants are: the electrochemical [4] or photochemical methods [5] and seed-mediated growth methods [6]. In the electrochemical method, the gold ions are reduced on a platinum electrode in the presence of a solution of surfactant mixture [4] while in the seed-mediated method Au seeds are first synthesized and then used as nucleation sites for the anisotropic growth of Au NRs. Besides the methods mentioned above, other approaches have also been attempted to produce Au NRs, such as bio-reduction [7] and growth of Au NRs directly on mica surface [8].

The seed-mediated growth formation mechanism of Au NRs in CTAB (Cetyl Trimethyl Ammonium Bromide) micellar solution remains a subject of debate, but all mechanism for the growth of Au NRs are based on the crystal growth inhibition, which is closely related to the crystalline structure and thermodynamic stability of the face-centered cubic (fcc) structure of the metallic gold. The use of cationic surfactant CTAB is a crucial parameter in the synthesis of Au NRs following a seed-mediated method. However, the trimethylammonium headgroup alone does not efficiently direct NP growth into rods and silver nitrate plays a crucial role in obtaining Au NRs in high yield. In fact, the kinetics of reduction of gold ions to atomic gold showed that the reduction was slower in the presence of silver nitrate.

In this work, we present the synthesis of bimodal metallic systems including Au and Pt. The influence of different parameters that have crucial influence in the final morphology of Au NRs will be discussed. In detail, the control of the length of Au NRs will be studied by systematically varying both platinum ion and seeds content in the growth solution. Besides, the influence of CTAB concentration on the final morphology of Au NRs will be thoughtfully studied.

Previous results of the approach presented in this work are shown in Figure 1. Au rods of 10 µm can be synthesized in the presence of Pt nanoparticles in aqueous solution. AuNRs with AR of 200 were obtained. This is a noteworthy achievement, since in the bibliography AuNR with aspect ratio from 2.9 to 4.5 have been previously reported by standard routes. Further experiments will offer the perspective of to what extent the NRs can grow in the experimental conditions. The concepts of kinkerdall effect, transmetallization, seeded growth, assisted growth and other will be discussed.

References:

[1] El-Sayed, M.A., Accounts of Chemical Research, 34:4 (2001) p.257-264.

[2] Kelly, K.L., et al., Journal of Physical Chemistry B, 107:3 (2003) p.668-677.

[3] Mohamed, M.B., et al., Journal of Physical Chemistry B, 102:47 (1998) p.9370-9374.

[4] Yu, Y.Y., et al., Journal of Physical Chemistry B, 101:34 (1997) p. 6661-6664.

[5] Esumi, K., K. Matsuhisa, and K. Torigoe, Langmuir, 11:9 (1995) p. 3285-3287.

[6] Jana, N.R., L. Gearheart, and C.J. Murphy, Journal of Physical Chemistry B, 105:19 (2001) p. 4065-4067.

[7] Canizal, G., et al., Journal of Nanoparticle Research, 3:5-6 (2001) p. 475-481.

[8] Mieszawska, A.J. and F.P. Zamborini, Chemistry of Materials, 17:13 (2005) p. 3415-3420.

Figures:

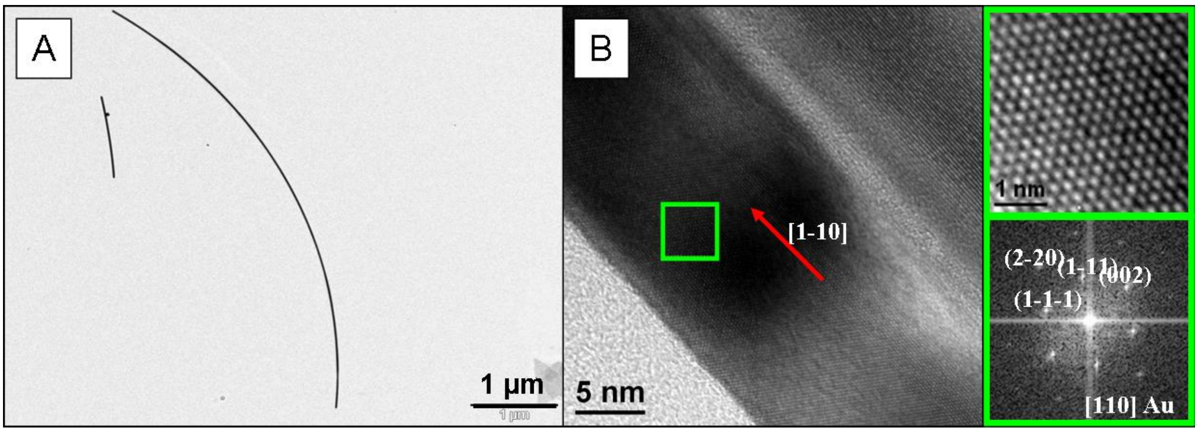

Figure 1: A) TEM image of a 6µm AuNR. B) HRTEM of AuNR with a growth in the [1-10] direction and without defects.