Plasmonic and Structural Effects in the Growth of Ag Triangular Nanoplates.

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Introduction

The shape control of metallic nanoparticles has been a subject of intensive research in the past few years because it provides an alternative way, in addition to size, to tune the properties of a metal[1]. In this work, we present solid experimental evidences of the important role of surface plasmons and structural defects in the anisotropic growth mechanism of photochemically synthesized Ag triangular nanoplates (TNPs).

Results and Discussion

TNPs are synthesized by irradiating silver seeds, following Ref. 1. The use of incident radiation with different wavelengths revealed that two different growth process are present: an initial slow growth (stage I), when small TNPs are formed and a second rapid anisotropic growth (stage II), which begins when the surface plasmon resonance (SPR) peak of the growing TNPs becomes resonant with the incident light.

The correlation of the reaction kinetics, followed by *in situ* Ag+ concentration measurements, with the morphological evolution, obtained by transmission electron microscopy (TEM) and ultraviolet-visible spectroscopy, allowed us to clearly demonstrate the enhancement of the photochemical reaction by excitation of SPR of the growing particles, as evidenced by the change in the reaction rate[1].

To further understand the stage I and the origin of the anisotropic growth in this system, detailed structural characterizations were performed in the early stages of the synthesis (Figure 1). In the initial seeds, several particles containing many parallel twins or stacking faults in the <111> direction were observed, as indicated by X-ray powder diffraction (XRD) and high resolution TEM (HRTEM). The presence of this type of defects is identified by the unusual periodicity of 2.49 Å found in the HRTEM images and the peak at $2\theta = 36^{o}$ in the XRD pattern and are associated to the 1/3{422} forbidden reflections. The same type of defects was also present in all of the TNPs.

The HRTEM observation of intermediate stages revealed that TNP are formed in the early stages of the synthesis by epitaxial anisotropic deposition of Ag photoreduced atoms over the defective seeds present in the initial solution. To confirm these results, we uses Au seeds instead of Ag one since the Au seeds present different types of defects (mainly multiple-twinned particles). These experiments confirmed the striking effect of structural defects in the growth process since no TNP was formed in this case. The use of Au seeds also provided important insights about the role of the capping molecule (i.e., citrate ions) in the anisotropic growth.

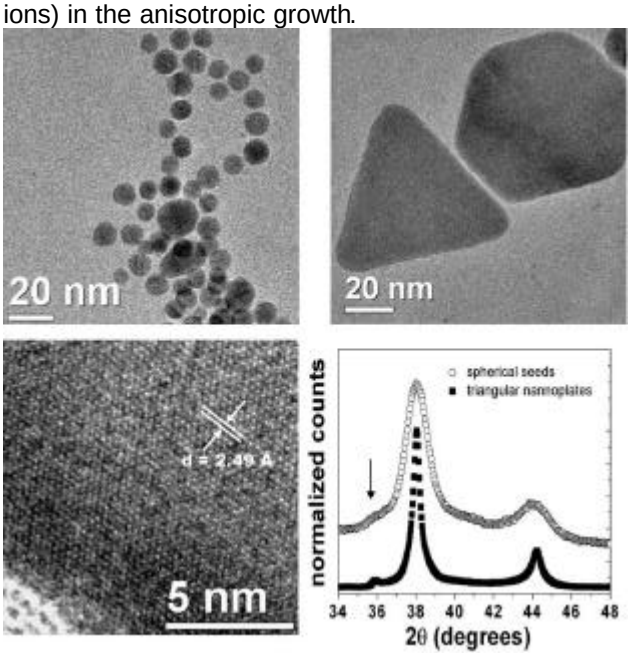

Figure 1. (a) TEM images of Ag seeds; (b) TNP formed by photochemical growth; (c) HRTEM image of a TNP showing the unusual periodicity; (d) XRD patterns of Ag seeds and TNPs. The arrow corresponds to the 2.49 Å periodicity.

Conclusions

This work points out that SPR excitation plays an important role defining the final length of the TNPs, and therefore providing an efficient size control mechanism. However, the shape is defined at early stages of the reaction with the structural defects being one of the main driving forces of the anisotropic growth, shedding new insights about the growth mechanism of anisotropic metal NPs.

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