High-Yield Uniform Synthesis and Microstructure-Determination of Rice-Shaped Silver Nanocrystals

Hongyan Liang, Huaixin Yang, Wenzhong Wang, Jianqi Li, and Hongxing Xu

*J. Am. Chem. Soc.*, 2009, 131 (17), 6068-6069 • DOI: 10.1021/ja9010207 • Publication Date (Web): 13 April 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
High-Yield Uniform Synthesis and Microstructure-Determination of Rice-Shaped Silver Nanocrystals

Hongyan Liang,†,‡ Huaixin Yang,† Wenzhong Wang,*†,‡ Jianqi Li,† and Hongxing Xu*,†,§

Institute of Physics, Chinese Academy of Science, Beijing 100190, China. College of Science, Minzu University of China, Beijing 100081, China. School of Materials Science and Engineering, Shandong University, Jinan 250100, China. and Division of Solid State Physics, Lund University, Lund 22100, Sweden

Received February 9, 2009; E-mail: wzhwang@aphy.iphy.ac.cn; hongxingxu@aphy.iphy.ac.cn

Abstract

In recent years, intensive research has been devoted to synthesis of metallic nanoparticles because of their potential applications in catalysis, photonics and plasmonics, information storage, surface-enhanced Raman scattering (SERS), biological labeling, imaging, and sensing. Numerous studies have demonstrated that the intrinsic properties of metal nanostructures can be effectively tailored by controlling their size, shape, composition, crystallinity, and structure. This is particularly true for silver and gold nanoparticles which have rich optical properties due to the strong surface plasmon resonances (SPRs), while SPRs strongly depend on the parameters mentioned above. Particular emphasis recently has been focused on the control of shape, because in many cases it is crucial to obtain preferred optical properties. However, the nature of crystallinity of gold or silver at the nanometer scale causes the shapes of its nanostructures to be faceted. Recently, a method for coating rice-shaped iron oxide nanoparticles as templates with thin gold shell to produce rice-shaped gold core-shell nanoparticles has been reported to have a rice-like shape. But for pure noble-metal nanocrystals, only a deformed nanostructure possibly caused by etching silver crystal nanobars has been reported to have a rice-like shape. In this communication, we report the large scale preparation of silver nanorices with uniform shape in high yield by a facile polyol route. The increasing stacking faults of FCC coexisting with HCP at the surfaces and round ends. Due to their anisotropy, the UV/vis spectrum (Figure 1c) taken from the suspension of nanorices is characterized by two peaks in the visible and NIR region, which are caused by transverse and longitudinal plasmon resonance, respectively.

Figure 1. (a) Low- and (b) high-magnification SEM images of the as-prepared silver nanorices. (c) UV/vis spectrum of nanorices.

A drop of the suspension of particles was placed on a piece of silicon wafer for scanning electron microscopy (SEM) studies. Figure 1a and b show low- and high-magnification SEM images of a typical sample. These images show that a large quantity of rice-shaped nanoparticles with a narrow size distribution was achieved. Figure 1b indicates that the nanorices have nearly smooth surfaces and round ends. So it is clear that FCC and HCP phases coexist in nanorices.

Figure 2a and 2b show respectively a bright-field TEM image of an individual nanorice with a diameter of ~50 nm and the corresponding electron diffraction (ED) pattern taken along the [110] zone axis direction of the cubic notation. Detailed analysis

Figure 2. (a) TEM image of the silver nanorices. (b) XRD pattern from the same batch of sample.
The complicated stacking faults along the long axis of the rice can be perhaps rationalized in terms of oriented particle attachment as discussed by Murray et al. In fact, products obtained from the earlier stages of our reaction often contain particles with similar microstructure features but a smaller size and length/width ratio. These multiple stacking faults in other systems can determine different morphologies of silver nanoparticles, e.g., transformation of silver platelets to bipyramids and twinned cubes. In our case, there are probably two reasons to determine the rice shapes. The increase of stacking fault density is responsible for the decrease of diameter; this size—microstructure correlation has been previously reported by Li et al. In their case, the twinning periodicity is linearly proportional to the diameter of individual ZnSe nanowires. The surface energy plays an important role in determining the crystal structure of the tip area. The metastable HCP phase has a more stable surface configuration at a certain shape and size range, and an increasing ratio of surface atoms at the tip favors the HCP phase existing.

In summary, uniform silver nanorices can be synthesized on a large scale by a polyol process without the introduction of shape-selected seeds. Nanorices exhibit two plasmon resonance peaks in the visible and NIR regions respectively due to their anisotropy. XRD patterns demonstrated that the HCP phase coexists with the FCC phase in nanorices. The TEM study shows that the microstructures of nanorices are characterized by the intergrowth of FCC and a small amount of HCP phase, high density of stacking faults, and multimode modulations. Considering the complex morphology and correlative novel crystal structure, silver nanorices should be important for both theoretical investigations and practical applications.

Acknowledgment. This work was supported by NSFC under Contract No. 10625418, by MOST under Contract Nos. 2006DFB02020 and 2007CB936800, by CAS projects of “Bairen” and KJCX2-YW-M04, and by “985” and “211” projects.

References


Figure 3. (a) Low magnification TEM image of a typical nanorice with alternate stripes of light and dark. (b) The corresponding ED pattern. (c and d) HRTEM images come from the square-enclosed regions in (a).