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Communication

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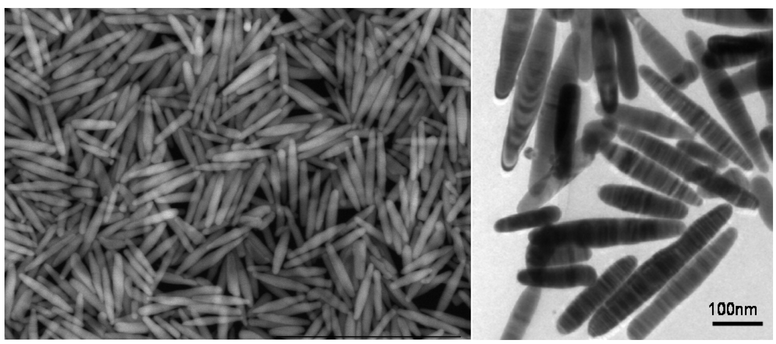

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High-Yield Uniform Synthesis and Microstructure-Determination of Rice-Shaped Silver Nanocrystals

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In recent years, intensive research has been devoted to synthesis of metallic nanoparticles[1] because of their potential applications in catalysis,[2] photonics and plasmonics,[3] information storage,[4] surface-enhanced Raman scattering (SERS),[5] biological labeling, imaging, and sensing.[6] Numerous studies have demonstrated that the intrinsic properties of metal nanostructures can be effectively tailored by controlling their size, shape, composition, crystallinity, and structure.[7] 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 was devised.[8] 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.[9] 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 tip of the nanorice can reduce the surface energy[10] that favors the rice-shaped nanostructure. This mechanism breaks the natural law of crystallinity for faceted noble-metal nanostructures, which may shed new light onto the synthesis of novel noble-metal nanostructures without the limitations of crystallinity by designing the stacking sequence of different crystalline phases.

The silver nanorices were synthesized according to the following procedure which was called a polyol process: 0.5 mL of 1 M $AgNO_3$ aqueous solution and 2.5 mL of 1 M poly(vinyl pyrrolidone) (PVP, $M_w \approx 40\,000$, the concentration was calculated in terms of the repeating unit) aqueous solution were added to 25 mL of a poly(ethylene glycol) 600 (PEG 600) solution in a flask under stirring. The flask was transferred to an oil bath and heated at 100 °C for ~8 h, and then the gray silver colloid was obtained. During our synthesis process, no shape-selected seeds were introduced. To examine the reproducibility of this method, the same synthesis was performed more than 10 times, and nanorices with similar size and morphology were achieved in high yield in each case. It is noted that in comparison with the synthesis method for nanobars,[9] a lower temperature was adopted, PEG was used as a reducing agent rather than EG, and no NaBr was added in our experiment.

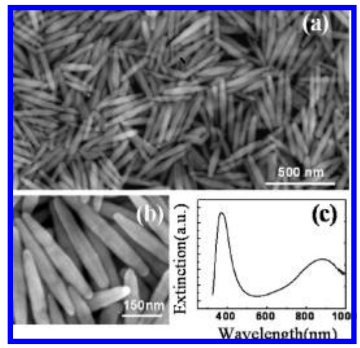

Figure 1. (a) Low- and (b) high-magnification SEM images of the as-prepared silver nanorices. (c) UV/vis spectrum of nanorices.

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. 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.[9]

A transmission electron microscope (TEM) image of nanorices is shown in Figure 2a. A fascinating feature is that alternate stripes of light and dark in a complex manner along the long axis direction appear in most nanorices. Figure 2b is the XRD pattern of nanorices. Except for three typical diffraction peaks which can be indexed to the Ag FCC phase, a peak of the HCP phase with low intensity also is present. So it is clear that FCC and HCP phases coexist in nanorices.

Figure 3a and 3b 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

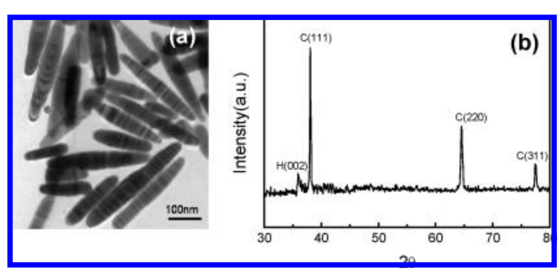

Figure 2. (a) TEM image of the silver nanorices. (b) XRD pattern from the same batch of sample.

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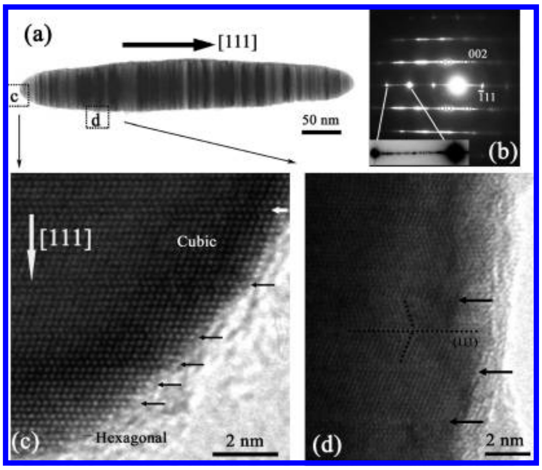

Figure 3. (a) Low magnification TEM image of a typical nanorice with alternate stripes of light and dark. (b) The corresponding ED pattern. (c and d) HRTEM images come from the square-enclosed regions in (a).

demonstrates that the alternate stripes of light and dark appear along the cubic [111] direction, i.e., the growth direction. The stripe contrast in the TEM image and complex diffraction spots in the ED pattern can be well interpreted by the intergrowth of the FCC phase with a small amount of the HCP phase, nanoscale FCC (111) twinning structure, and multimode structural modulations arising essentially from the complicated stacking sequence. Figure 3b shows the ED pattern with visible diffuse diffraction spots streaking along the [111] axis direction, indicating the presence of stacking faults and other planar defects in this nanocrystal. Most of the main diffraction spots can be easily indexed by the (111) twinning structure commonly observed in the FCC systems as briefly denoted by the small circles. The inset of Figure 3b shows a series of weak spots between the (3−3−3) and (2−2−2) main spots with a large magnification, in which the weak spots caused by the HCP phase and multimode modulations can be clearly recognized.

A better and very clear view of the atomic structure for a variety of local defects has been obtained by high-resolution TEM (HRTEM) observations. Figure 3c and 3d show the HRTEM images taken from the square-enclosed regions in Figure 3a, respectively. They both indicate that the nanorices are not crystallized in the conventional single crystal or 5-fold-twinning crystal[11] which often grows along the [110] direction. Figure 3c demonstrates the growth direction of nanorices is along the [111] direction accompanied by complicated stacking faults as marked by arrows. It is important to point out that the HCP phase is present in the top area as marked in Figure 3c. Another notable feature of the as-prepared nanorices is the typical (111) twinning structure with the size as small as a few nanometers commonly appearing in our samples as indicated by dashed lines in Figure 3d.

Based on our TEM observations, we could briefly summarize a statistical result regarding the correlation between shape and microstructure. It is noted that the microstructures in the middle region and elliptical shape ends of the nanorice are very different. The intergrowth and stacking faults occur randomly in the middle part of the nanorice. Coexistence of nanoscale twinning and different types of stacking faults are often recognizable as shown in Figure 3d. With the steady decrease of diameter in the vicinity of the elliptical end, the density of stacking faults increases apparently for the FCC structure and a hexagonal configuration often appears at the tip.

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.[12] 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,[13a] or nanoprisms.[13b] 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.;[13c] 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,[10] 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 the 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.

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