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Crystal structure and optical properties of silver nanorings

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We report the polyol synthesis and crystal structure characterization of silver nanorings, which have perfect circular shape, smooth surface, and elliptical wire cross-section. The characterization results show that the silver nanorings have well-defined crystal of singly twinned along the whole ring. The spatial distribution of the scattering of a silver nanoring with slanted incidence reveals the unique focus effect of the nanoring, and the focus scattering varies with the incident wavelength. The silver nanorings with perfect geometry and well-defined crystal have potential applications in nanoscaled photonics, plasmonic devices, and optical manipulation. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3117504]

Nanostructured noble metals have increasingly attracted much interest due to their unique size- and shape-dependent electronic and optical properties.[1–18] The optical properties of metal nanostructures are dominated by the surface plasmon (SP) resonances, which would induce the absorption or scattering of incoming light and localized electromagnetic field enhancement. So their practical applications in nanoscaled photonics and plasmonic devices are expected to increase rapidly.[1,2] Silver has a very small imaginary part of the dielectric constant and very high electrical conductivity, which lead to the excellent optical and electronic properties of silver nanostructures, such as large local field enhancement in silver nanoparticles (NPs),[3,4] small propagation loss of SP and electron in silver nanowires (NWs).[5,6] These excellent properties have motivated extensive studies to synthesize silver NPs with various shapes (such as nanocubes, nanobars, nanorices, and nanoprisms)[19–21] and one-dimension silver NWs.[22,23]

Silver NWs with singly twined or fivefold twined crystalline structure prepared by polyol method have well-defined crystal and surface structure to support SP propagation comparing with the one prepared by lithography techniques,[6,22] and have been used as SP propagation waveguides,[9] plasmonic resonators,[10,11] and exciton-plasmon interaction converters.[12–14] Compared with NWs, metal nanorings are particularly attractive due to their highly tunable plasmonic ability depended on the size of the ring and the polarization and angle of incidence.[15–18] Several methods have been proposed to prepare silver and gold nanorings by using lithography techniques and nanostructure templates,[15,24–26] but the growth of silver nanorings with perfect geometry and well-defined crystal is a hard challenge.

Recently, we have reported the polyol synthesis of silver nanorings and exciton-plasmon interactions between the quantum dots and silver nanorings.[27] In this letter, we reported the optimization of growth conditions for the silver nanorings with different diameters, carefully characterized the singly twinned crystal behaviors of whole silver nanoring. We also investigated the variations in SP enhanced scattering patterns of a single silver nanoring as the incidence wavelength.

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The synthesis method of Ag nanorings is very similar to that of the singly twined Ag NWs (nanobeams)[6] and the details have been reported elsewhere.[27] In the presence of poly(vinyl pyrrolidone) and sodium bromide (NaBr), Ag nanorings were synthesized by reducing silver nitrate ($AgNO_3$) in ethylene glycol solution with magnetic stirring. We changed the volume of 22 mM NaBr here. The reaction mixtures obtained at different reaction times were washed with ethanol several times. The absorption spectra were recorded by ultraviolet-visible-near-infrared spectrophotometer (Varian Cary 5000) using quartz cuvettes with an optical path of 1 cm at room temperature. The final products contained silver NPs, while NWs and nanorings were characterized by scanning electron microscopy (SEM) (FEI Sirion 200 SEM) and transmission electron microscopy (TEM) (JEOL 2010HT). The scattering patterns of Ag nanorings were recorded by a spectrometer (Acton SpectraPro 2500i) with liquid nitrogen cooled charged-coupled device (Princeton SPEC-10).

As shown in Figs. 1(a) and 1(b), the Ag nanorings have

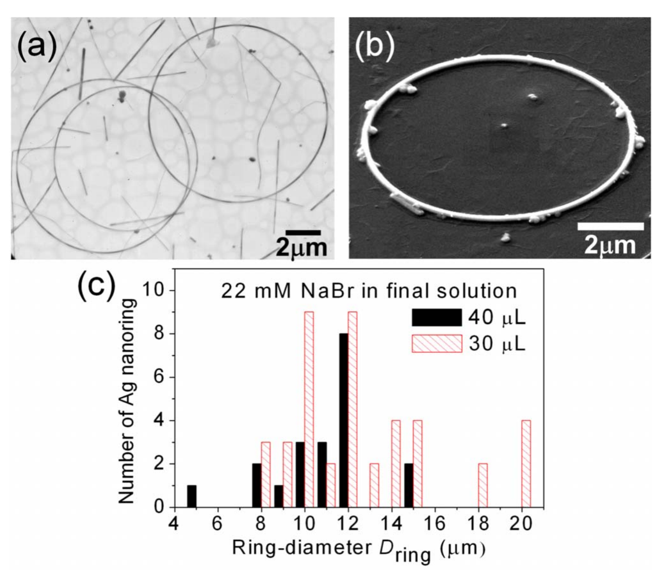

FIG. 1. (Color online) (a) TEM and (b) SEM images of silver nanorings. (c) Size distribution of ring diameter of final synthesized Ag nanorings with different concentration of NaBr.

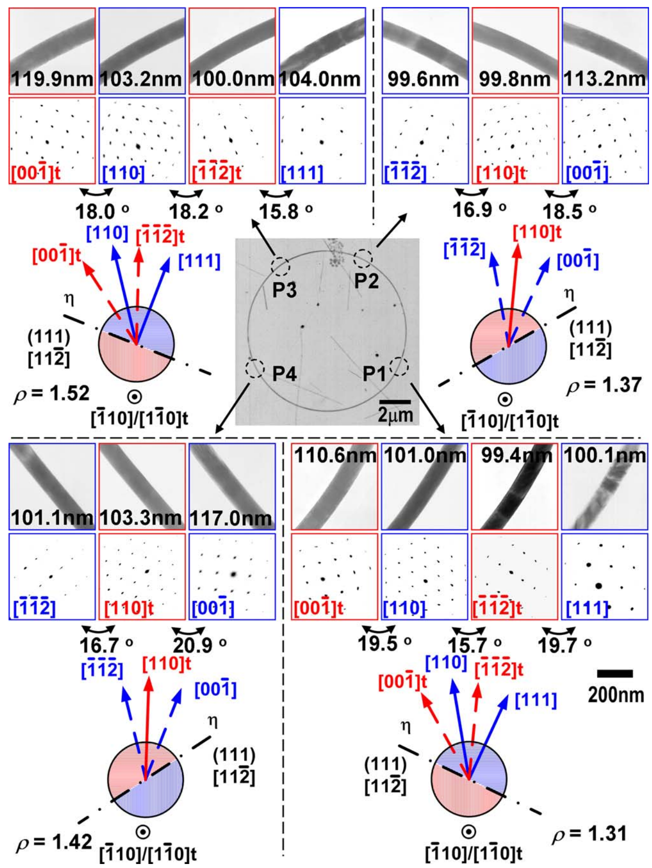

FIG. 2. (Color online) TEM images and SAED patterns of four different points on a silver nanoring. The insets on each image display the wire diameter and zone axis index. The biarrows under the SAED images show the rotating angle between the zone axes. The schematic illustrations of the cross-section exhibit the zone axes (solid and dashed lines), twinning plane (dashdot) and growth axis direction. The solid and dashed lines express the zone axes in different twin variants. ρ expresses the estimated ellipticity of the cross-section.

perfect circular shape with smooth surfaces. Figure 1(a) is the TEM image of three Ag nanorings with ring diameter of 8.2, 9.9, and 10.3 μm, respectively. Figure 1(b) shows an Ag nanoring with ring diameter of ~6.9 μm and wire diameter of ~165 nm. The silver nanoring has a circular wire cross-section with ellipticity of ~1.3,[27] distinct from the pentagonal silver NWs,[22] but it is similar to the singly twined silver NWs.[6] Figure 1(c) shows the ring-diameter distribution of silver nanorings synthesized by adding different concentration of NaBr. The size distribution of ring diameter is in the range of 4.8–20 μm.

To determine the crystal structure of silver nanorings, we have performed electron diffraction analysis on a silver nanoring from different tilting angles by using TEM. The corresponding morphology images and selected-area electron diffraction (SAED) patterns are shown in Fig. 2. At the point of P1 on the nanoring, four typical zone axes of $\langle 001\rangle$, $\langle 110\rangle$, $\langle 112\rangle$, and $\langle 111\rangle$ could be indexed. The angle between the $\langle 110\rangle$ and $\langle 001\rangle$ zone axes is about 19.5° which is different with 90° in single crystal face-centered cubic (fcc) structure, but is consistent with the $(111)[11\bar{2}]$ type twin in fcc metals.[28] The same results are obtained on the other points of the same ring in Fig. 2. It indicates that the silver nanoring has a well-defined singly twinned crystal structure along the whole ring, and the ring grows along the $\langle 110\rangle$ direction and

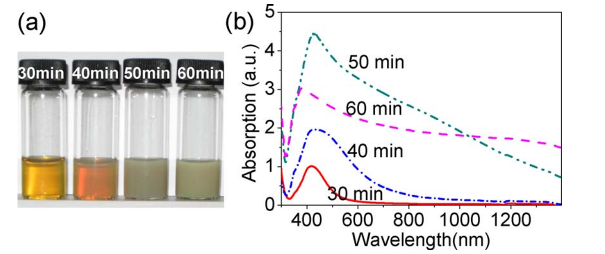

FIG. 3. (Color online) (a) Photograph and (b) absorption spectra of the reductive reaction mixtures at 30, 40, 50, and 60 min.

the (111) twinning plane is parallel to the growth direction. At each point, the wire diameter varies with the tilting angle, which matches the elliptical wire cross-section, and the estimated average ellipticity of the circular cross-section is about 1.41.

Careful analysis of the SAED patterns indicates that the direction of the twinning plane varies along the nanoring. Based on the experimental data, Fig. 2 shows the schematic illustrations of the twin variants, zone axes, twinning plane, and growth axis direction in the cross-section of each point. The $\langle 001\rangle$ axis direction relative to the $\langle 110\rangle$ axis is different at different points, which implies that the twinning plane twists along the ring. The silver nanorings with stable twinning plane have also been found in the final reaction mixture (data not shown). It is reported that the singly twinned silver NWs synthesized by the similar method would twist randomly.[6] The varying twinning plane in some silver nanorings is induced by the uncertain twisting along the nanoring.

At present, we do not completely understand the growth mechanism of silver nanorings. For the silver nanorings with the properties of the singly twinned crystal structure, the elliptical wire cross-section and the random twisting of twinning plane are very similar to the singly twinned silver NWs synthesized by the polyol method. We propose that the ring shapes are possibly derived from the self-connection and self-concrescence of the two ends of a silver NW.[27] In the presence of Br^-, the singly twinned silver NWs could be formed through the anisotropic growth of seeds with a single twin, which are remained when Br^- preferentially etch away multiply twinned seeds.[6] The soft silver NWs with long aspect ratio is easy to bend due to the strong magnetic stirring. Then the silver NWs self-connect possibly and grow into nanorings, and the connection point would be covered and grown smoothly due to the lateral growth via a process known as Ostwald ripening.[22]

As the growth of silver NPs, NWs, and nanorings at different synthesis stages, the color of the reductive reaction mixtures varied from bright yellow to red and then opaque gray-yellow due to the shape-dependent SP resonance absorption [Fig. 3(a)]. Figure 3(b) shows the absorption spectra of the reaction mixtures obtained at different reaction time. The absorption peaks at around 420 and 380 nm are caused by the SP resonances of silver NPs and long NWs.[22] The reaction mixtures at 60 min have a broad band strong absorption ranging from 400 to 1400 nm, which are attributed to the longitudinal SP resonance of silver NWs and nanorings.

Silver nanorings exhibit unique scattering patterns with slanted illumination. The plot in Fig. 4(a) is the scattering intensity spatial distribution in pseudo color mode of a single

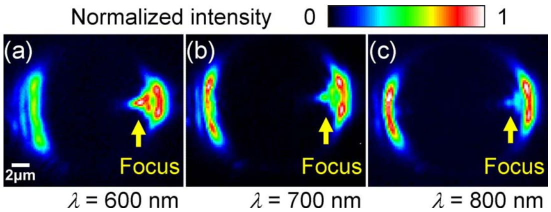

FIG. 4. (Color online) Spatial distribution of scattering from a single silver nanoring with the slanted incident angle of 60° and the incident wavelength (a) $\lambda=600(\pm 10)$, (b) $\lambda=700(\pm 10)$, and (c) $\lambda=800(\pm 10)$ nm.

silver nanoring with ring diameter of ~ 19.8 μm illuminated with incident angle of 60°, which was recorded by using white light source with a narrow bandpass filters at the wavelength $600(\pm 10)$ nm. Besides in the scattering from the surface of silver nanoring, there is a unique focused scattering in the nanoring and at the far side of the nanoring. This focused scattering effect induced by SP is very similar to the SP focus behavior of the silver circular disk.[29,30] The scattering at the two ends of the ring are caused by the surface scattering and the SP induced field enhancement. To further investigate the focused behaviors of the scattering from single nanoring, we also recorded the scattering patterns by using narrow-band ($\sim$10 nm) light source with different wavelengths with the center wavelength $\lambda=700$ and 800 nm [Figs. 4(b) and 4(c)]. As the illuminating wavelength increases, the focused scattering intensity in the focus region decreases.

In summary, we have demonstrated the polyol synthesis and structure characterization of silver nanorings. The silver nanorings have perfect circular shape, smooth surface, and elliptical wire cross-section. The characterization results show that the silver nanorings have well-defined crystal of singly twinned along the whole ring, and there is a varying twinning plane in some nanorings. These high-quality silver nanorings with perfect geometry and crystalline structure have unique plasmonic properties of SP resonance absorption and scattering. Especially, they exhibit a unique tightly focused scattering in the nanoring. We believe that these silver nanorings should find the applications in the area of nanoscaled photonics, plasmonic devices, and optical manipulation.

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