Aligned Gold Nanorods in Silica Made by Ion Irradiation of Core–Shell Colloidal Particles**

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Metal nanoparticles embedded in glass have stimulated the interest of scientists and artists for several centuries because of their linear and nonlinear optical properties.[1] Crucial elements for control of these properties are the nanocrystal size, shape, interparticle distance, and the dispersity of these parameters. While most of these parameters are often well controlled, *shape* is a factor that has not been much addressed. Anisotropically shaped metal nanoparticles have several interesting optical properties due to the fact that the surface plasmon resonance bands split up for orientations along major and minor axes. For a large enough size aspect ratio, plasmon bands may shift well into the infrared, thus enabling the use of metal nanostructures in telecommunication applications in that wavelength range. In addition, anisotropic metal particles show reduced plasmon relaxation times[2] as well as enhanced nonlinear response[3] when compared to spherically shaped particles, and may thus be used as building blocks in a variety of optical devices.

Several techniques have been developed to fabricate rod-shaped metal nanoparticles using, e.g., lithographic means[4] or anisotropic growth. Recently, we have demonstrated that ion irradiation can also be used to modify the shape of nano-materials.[5] For example, silica colloids with diameters in the 100–1000 nm range show dramatic anisotropic plastic deformation under mega-electron-volt ion irradiation, changing their shape from spherical into oblate ellipsoidal. This ion-beam-induced anisotropic deformation effect is known to occur for a broad range of amorphous materials,[6] but has not been observed for crystalline materials, including metals.

In this letter we show that polycrystalline Au colloids can be deformed by ion irradiation *indirectly*, if they are embedded in an amorphous silica glass matrix that does deform under the ion beam. To do so, we have irradiated colloidal core–shell particles composed of a 14 nm diameter Au core surrounded by a 72 nm thick SiO_2 shell with 30 MeV Cu or Se ions. By irradiating ensembles of these particles we were able to fabricate arrays of aligned Au nanorods that showed evidence for split plasmon bands that are characteristic for anisotropic metal nanoparticles.

Figure 1a shows a transmission electron microscopy (TEM) image of a Au–silica core–shell particle before irradiation. It is spherically shaped, with the 14 nm diameter Au core centered inside. Figure 1b shows a TEM image after 30 MeV Se irradiation at a fluence of 2×10^{14} cm^{-2}, with the ion beam 45° off normal. The image was taken along the normal, and the arrow in Figure 1b indicates the ion beam direction projected onto the surface.

Clearly, after irradiation, neither the silica shell nor the Au core are spherically shaped. The deformation of the silica shell is consistent with our earlier work on ion beam deformation of pure silica colloids (i.e., formation of an oblate particle, with the minor axis parallel and two major axes perpendicular to the ion beam). The ~20 % expansion of the major axis of the particle in Figure 1b is similar to that observed after 16 MeV Au irradiation at a fluence of 4×10^{14} cm^{-2}.[7]

Figure 1b also shows that the Au core has deformed, but in an entirely different manner: a major axis is observed along the ion beam and a minor axis perpendicular to the beam. The initially 14 nm diameter Au core has deformed into a rod with apparent dimensions of 6 nm by 38 nm. Correcting for the 45° projection of the TEM image relative to the ion beam direction, the major axis is as large as 54 nm (size aspect ratio ~9). Assuming cylindrical symmetry, we can derive from the TEM image that the volume of the Au particle does not change during the deformation, within an error bar of ±20 %.

Reference measurements were also performed, in which 14 nm diameter Au colloids, not surrounded by a silica shell, were irradiated with 30 MeV Se ions, and no deformation was observed. These data indicate that the deformation of the Au core is related to an effect imposed by the silica shell.

To study this in more detail, a series of core–shell particles was made with different silica shell thicknesses (and identical Au cores) in the range 15–72 nm. No measurable deformation of the Au core was observed for silica shells thinner than 26 nm. A second additional observation, of similar nature, is that for core–shell particles of equal size and shell thickness, the deformation of the metal core depends on the local surroundings of the particles: particles that are stacked two or three layers thick and are in contact before irradiation exhibit significantly larger deformation of the metal core than isolated particles. A TEM image of an ensemble of deformed particles is shown in Figure 2 (30 MeV Se, 2×10^{14} cm^{-2}). An

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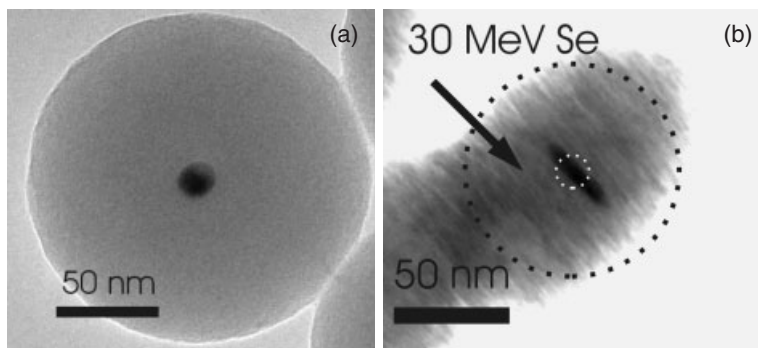
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Figure 1. TEM images of core–shell colloids composed of a 14 nm diameter Au core surrounded by a 72 nm thick silica shell a) before irradiation, b) after 30 MeV Se ion irradiation at an angle of 45° to the normal at a fluence of 2×10^{14} cm^{-2}. The ion beam direction projected onto the surface is indicated by an arrow. The original spherical perimeter is indicated by the dashed circle.
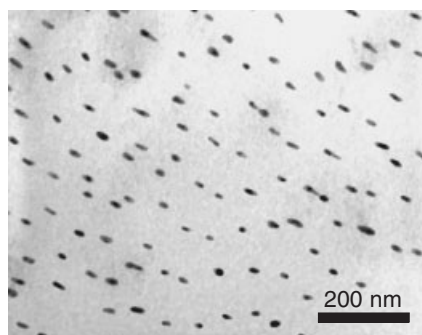
Figure 3 (inset) shows a TEM image of an isolated core–shell particle that is deformed after 30 MeV Se irradiation at the same high fluence of 5×10^{14} cm^{-2}. As can be seen, the metal core has now evolved into a dumbbell-like structure, i.e., two small spheres connected by a thin rod. The rod is aligned along the ion beam axis. The main panel of Figure 3 shows a TEM image after irradiation of a thick layer of colloids with the same fluence. Due to the contact, larger deformation of the Au core is induced, and in this case the Au core has broken up into a collection of smaller spheres, randomly distributed in the silica colloid.

Preliminary optical transmission measurements were made under normal-incidence conditions on core–shell colloids, with 14 nm diameter Au cores
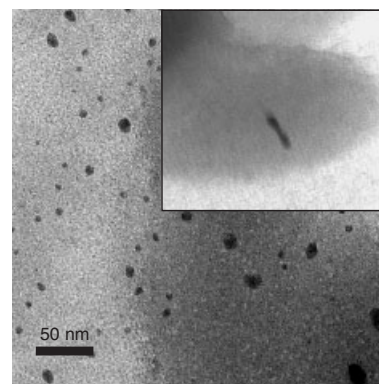

Figure 2. TEM image of an ensemble of touching core–shell colloids after 30 MeV Se ion irradiation at a fluence of 2×10^{14} cm^{-2}. Aligned Au nanorods with varying size aspect ratios are observed.

Figure 3. TEM image of an irradiated ensemble of touching colloids, irradiated to a fluence of 5×10^{14} cm^{-2}, in which larger deformation is observed. In this case, the Au nanorods have broken up. The inset (same scale as main panel) shows an image of a core–shell colloid after 30 MeV Se ion irradiation to a fluence of 5×10^{14} cm^{-2}. A dumbbell-like nanostructure has formed.

array of aligned nanorods is observed, with size aspect ratios that vary across the image, due to the varying degree of interparticle contact throughout the structure. From these two independent experiments (varying shell thickness and varying colloid contact) we conclude that the Au core deforms more efficiently as more silica surrounds it.

To explain the shape change of the Au core due to the silica shell we propose the following indirect deformation scenario. Each individual ion impact in silica leads to the formation of a thermal spike that leads to an in-plane strain perpendicular to the ion beam.[8] In planar (constrained) films the combined strain of all individual ion impacts leads to the build up of a macroscopic stress that can be as large as several hundreds of mega-pascals.[9] In freestanding silica colloids this leads to anisotropic expansion perpendicular to the beam, as also observed here for the silica colloid. In the core–shell colloids studied here the lateral stress fields surrounding each individual ion track in silica also act on the Au core. Metals are known to be relatively soft under ion irradiation, as evidenced, e.g., from the low radiation-induced viscosity.[10] Thus with an in-plane stress acting on the soft core, it may flow in the out-of-plane direction, i.e., along the direction of the ion beam.

and 39 nm thick shells, that were allowed to dry on a fused silica substrate (0.5 mm thick) to a thickness of 10–20 layers. The sample was immersed in an index-matching fluid to avoid light scattering due to the silica shells, so that only the extinction due to the Au cores remains. Figure 4 shows extinction spectra derived form the transmission data after background subtraction. Fitting a Lorentzian line shape to the main peak for the unirradiated sample gives a central wavelength of 529 nm. This is in good agreement with the surface plasmon resonance of Au nanoparticles embedded in a silica matrix.

After irradiation with 2×10^{14} cm^{-2}, 30 MeV Cu ions directed 20° off normal, a broad shoulder has developed on the long-wavelength side (600–650 nm). In addition, the central wavelength of the main feature has slightly blue-shifted to a wavelength of 521 nm. The small blue shift and large red shift are characteristic for elongated Au nanoparticles. The size aspect ratio estimated from the shifts[11] is ~4.6, taking into account the 20° viewing angle.
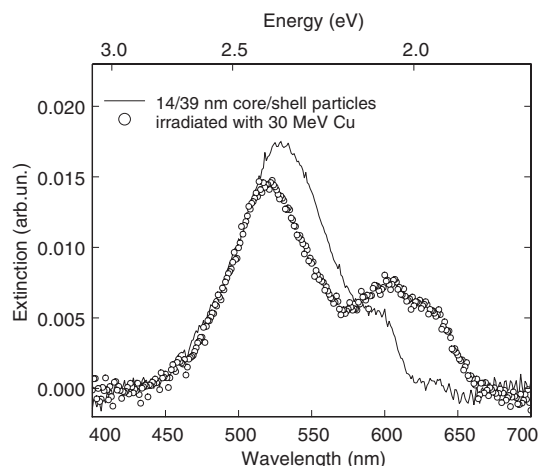
Figure 4. Optical extinction spectra for ensembles of core–shell colloids with 14 nm diameter Au cores and 39 nm thick shells embedded in an index-matching fluid. Data are shown before and after irradiation with 30 MeV Cu ions. A broadening of the plasmon absorption band is observed, which is attributed to the formation of Au nanorods.

In conclusion, mega-electron-volt ion irradiation of colloidal silica particles containing an Au core leads to a deformation of the shell into an oblate ellipsoid and of the Au core into a nanorod. The Au deformation is attributed to the in-plane mechanical stress in the silica shell acting on the radiation-softened Au core. The Au nanorods have size aspect ratios as large as nine for intermediate fluences; they break up for higher fluences. Preliminary optical extinction data show surface plasmon resonance shifts characteristic for anisotropic Au nanorods. As anisotropic deformation is known to occur in a variety of (amorphous) hosts, several other combinations of core and shell materials may be ion-beam-shaped as well.

Experimental

Materials: Colloidal core–shell particles were prepared in solution using a method described elsewhere [12]. A few drops of the solution were allowed to dry on a quartz substrate. Scanning electron microscopy (SEM) and Rutherford backscattering spectrometry were used to confirm that at least ten layers of colloidal particles covered the surface of these substrates. It was also evident that the colloid layer thickness varied across the samples due to inhomogeneous deposition and drying conditions. A few drops of a diluted solution were dispersed on a 10 nm thick Si_3N_4 membrane which allowed transmission electron microscopy (TEM) of individual particles.

Ion Irradiation: The particles were irradiated with 30 MeV Cu or Se ions to fluences in the range $2–4 \times 10^{14}$ ions cm^{-2}. During irradiation the samples were clamped to a liquid-nitrogen-cooled Cu block. Some irradiations were done at normal incidence, others with the ion beam 20° or 45° tilted away from the normal. 6 MV tandem accelerators in Rossendorf and Montreal provided the ion beams. Following irradiation the colloids were examined by SEM (5 keV electron beam), TEM (200 keV electron beam), and optical transmission measurements.

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Porous Tin Oxides Prepared Using an Anodic Oxidation Process**

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The formation of self-ordered porous oxide by an anodization process has been studied for several decades. To date, however, only a few metals, for instance Al[1] and Ti,[2] have been successfully oxidized to form highly ordered porous oxide structures such as honeycomb or nanotubular structures. Porous anodic alumite has been widely used as a template for preparation of many functional materials in nanostructured forms for optical, electronic, magnetic, and electrochemical applications,[3–5] whereas porous anodic titanate could be used for catalytic and gas-sensing applications.[6]

Tin oxide is a semiconductor that has been widely used for various applications, including solid-state gas sensors, optical devices, and lithium secondary batteries.[6–8] A variety of preparation methods have been explored to fabricate nanostructured tin oxides to dramatically improve the desired functionality. In particular, one-dimensional (1D) tin oxide structures such as nanoribbons, nanotubes, and nanorods have been successfully synthesized by a high-temperature thermal oxidation process[9,10] and low-temperature solution-based synthesis[11] for highly sensitive gas sensors in many applications. However, 1D porous tin oxides have not yet been synthesized. In

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