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Photothermal reshaping of prismatic Au nanoparticles in periodic monolayer arrays by femtosecond laser pulses

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Prismatic gold nanoparticles in the periodic monolayer arrays prepared with nanosphere lithography technique can be reshaped with femtosecond laser pulses at different powers and wavelengths. As the power density of 400 nm femtosecond laser increases, the prismatic particle tips begin to round and the overall particle shape changes from a prism to a sphere with a tripod intermediate. The formation of the tip-rounded nanoprisms is probably due to the dewetting properties of gold on quartz surface and the low melting temperature at the tips. The formation of the tripod nanoparticles is attributed to the inhomogeneous heating and lattice rearrangement of the as-deposited nanoparticles to a metastable state, which is more stable than the prismatic shape but less stable than the spherical shape. With 800 nm femtosecond laser irradiation, only tip-rounded nanoprisms are observed and no spherical nanoparticles are formed at the laser powers used. This is most likely due to the blueshift of the plasmon absorption band for the transformed particles, so that they cannot absorb the required energy to overcome the barrier to make the spherical shape. With 700 nm femtosecond laser irradiation, the tip-rounded and the tripod nanoparticles are formed and few spherical particles are observed at the higher laser power density. From the results of this work, it is shown that by changing the wavelength and power density of the femtosecond laser, one can control the final shape of the particles formed from the original prismatic nanoparticles. © 2005 American Institute of Physics. [DOI: 10.1063/1.2132515]

I. INTRODUCTION

Great interest has been directed lately to the interaction between noble-metal nanoparticles and lasers. Pulsed-laser-based time-resolved transient absorption spectroscopy provides a powerful tool to measure the electron-phonon and phonon-phonon relaxation dynamics in thin metal films and small metal particles. Combined with ultrafast x-ray-diffraction experiment, the laser-induced lattice motion of nanoparticles has been directly observed. In particular, silver and gold nanoparticles have been studied extensively as they show a strong surface-plasmon absorption band in the visible region, whose maximum is highly sensitive to the particle's size, shape, the environment around them, and the coupling between the nanoparticles. These distinct properties prompt the surface-plasmon-based applications in environmental and biological sensing.

The irradiation of metallic nanoparticles with a pulsed laser results in ultrafast temperature rises of the nanoparticle lattice (within a few picoseconds when using femtosecond laser pulses) while the temperature of the environment remains constant initially. Since the phonon-phonon relaxation time is usually on the order of 100 ps, pulsed laser irradiation can lead to size and shape changes of the nanoparticles before the deposited laser energy is given to the surrounding medium. This introduces other important chemical and physical applications of the short-pulsed laser in the preparation and modification of nanoparticles. A distinct merit of ultrafast laser pulses is their extremely high intensities at substantially reduced laser energy, which makes the processing of a material with ultrafast laser inherently different from the traditional thermal processing. Metallic nanoparticles have been synthesized with pulsed laser ablation of metallic bulk material in solution and pulsed laser deposition on substrate. It is also found that pulsed laser is a convenient tool to control the size and shape distributions of an inhomogeneous nanoparticle sample in colloidal solution, on substrate, or in glass matrix. Recently, aggregated iron oxide nanoparticles were directly formed on a bulk steel surface with pulsed laser irradiation.

Most of the studies carried out so far have been focused on the laser irradiation of nanoparticles randomly distributed in solution, on substrate, or in glass matrix. Due to the Gaussian distribution of the laser-pulse energy, the focus point on the sample has the highest power density in the center of the focus point and the lowest power on its edge. Most of the studies use the total laser-pulse energy as the control parameter and measure the transmission electron microscope (TEM) image of the irradiated products, which only gives an average result of the effect of the pulsed laser irradiation especially for solution samples. A more detailed study is needed to build the relationship between the nanoparticle shape and the "true" irradiation power density that induces those changes.

We report here on a more detailed study of a femtosecond-laser-induced photothermal reshaping of a monolayer two-dimensional array of highly monodisperse periodic gold prismatic nanoparticles. Assuming the laser...
pulses have a Gaussian distribution, different laser irradiation intensities induce shape and optical property changes that can be determined accurately with scanning electron microscope (SEM) and microabsorption measurements. Using a femtosecond laser as the irradiation source, we find tripod-shaped gold nanoparticles formed when 400 and 700 nm lasers are used at an appropriate power density, while no tripod-shaped gold nanoparticles are found when we use laser pulses at 800 nm. The spherical shape is the most thermodynamically favored particle shape because it has the lowest surface energy compared with other shapes, which makes the gold tripodal nanoparticle quite unusual. Apparently, the gold nanoparticle is not totally melted, which makes the transformation of the prismatic nanoparticle direct to the spherical shape. Our results suggest that the energy barrier of the transformation of gold nanoparticles from prismatic to tripod shapes is smaller than that from prismatic to spherical shape. The lowest surface energy compared with other shapes, which thermodynamically favored particle shape because it has the minimum energy. Thus it is kinetics rather than thermodynamics that determines the nanoparticle shape transformation, just like their formation.

II. EXPERIMENTAL SECTION

A. Sample preparation

Periodic arrays of silver and gold nanoparticles are prepared using the nanosphere lithography (NSL) method. Commercially available monodisperse polystyrene (PS) suspensions were purchased from Duke Scientific Corp. and used as received. The diameters of the spheres used in our experiments were 0.45 μm. Quartz slides (Technical Glass Products, Inc.) are used as the substrate and were cleaned in piranha solution (3:1 H2SO4:30% H2O2) at 80 °C for 1.5 h. The quartz slides were placed in a solution of 5:1:1 H2O:NH4OH:H2O2 and were sonicated for 1 h. A 5 μl PS suspension solution was deposited on the quartz slide, which was tilted to disperse the suspension solution evenly on the substrate. The substrate was slowly immersed in distilled water. A monolayer of PS spheres was formed on the surface of the water. One drop of 2% deocylsodiumsulfate surfactant was then added to the water and an ordered monolayer of PS spheres was formed. A clean substrate was used to pick up the PS sphere monolayer. After the evaporation of the water, the PS sphere monolayer forms and covers all of the substrate. The mask was then mounted in a thermal evaporator (Denton DV-502A) to deposit 30- or 50-nm-thick silver or gold (99.999%, Alfa Aesar) in the spaces between the spheres. The thickness of the deposited metal was monitored by a quartz-crystal thickness monitor (Inficon). After deposition, the PS spheres were removed by sonication in absolute ethanol. The formed silver and gold prismatic monolayer nanoparticle arrays were checked using a SEM.

B. Femtosecond laser setup

In the femtosecond laser system, a frequency-doubled Nd: vanadate laser (Coherent Verdi) was used as the pump for the Ti:Sapphire laser system (Clark MXR CPA 100). This generated laser pulses of 100 fs duration (FWHM) with energy of 1 mJ at 800 nm at a repetition rate of 1 kHz. The 400 nm laser was generated by the second harmonic of the 800 nm fundamental. The 700 nm laser was produced with the optical parametric oscillators [travelling-wave optical parametric amplifier of superfluorescence (TOPAS) generators from Light Conversion, Vilnius, Lithuania].

C. Laser intensity dependence of the absorption spectra and SEM images

The samples were irradiated with femtosecond laser pulses for 3 min. The size of the laser spot used (150–250 μm in diameter) was larger than the resolution of the microabsorption experiments (3.75×3.75 μm²) and the SEM images recorded (1.50×1.50 μm²). It was possible to observe the changes of the absorption spectra and the SEM images as a function of the distance from the center of the laser pulse. Thus, for any laser power, the laser intensity decreases as a function of the distance from the spot of the maximum value. For any specific total pulse energy (which can be changed by adding neutral density filters), a study of the effect of energy on the nanoparticle shape can be examined.

We assumed that the energy of a laser pulse has a Gaussian distribution. The transverse profile of the optical intensity of a Gaussian laser beam is

\[ I(r, z) = \frac{2P}{\pi w_z^2} \exp \left(-2 \frac{r^2}{w_z^2} \right), \]

where \( P \) is the total power in the beam and \( w_z(0) \) is the beam radius. The smallest beam radius \( w_0 \) occurs at \( z=0 \), where the Gaussian beam has a flat phase profile.

The radius and power distribution of the laser pulse were determined from the SEM measurement of the laser irradiation spot. In Eq. (1), \( w(z) \) is the only unknown and can be calculated by assuming that the sample is placed at \( z=0 \). The radius of the irradiation spot on the sample then changes with the power of the laser beam. Under two different total powers \( P_1 \) and \( P_2 \), the laser power intensity \( I(r_1) \) at the edge of the laser irradiation spot 1 is equal to the intensity \( I(r_2) \) at the edge of the laser irradiation spot 2. So we have

\[ \frac{2P_1}{\pi w_0^2} \exp \left(-2 \frac{r_1^2}{w_0^2} \right) = \frac{2P_2}{\pi w_0^2} \exp \left(-2 \frac{r_2^2}{w_0^2} \right), \]

thus,

\[ w_0^2 = -2 \ln \frac{P_2}{P_1} \left( r_1^2 - r_2^2 \right). \]

\( r_1 \) and \( r_2 \) can be measured from the SEM image of the two laser irradiation spots where the array nanoparticles have the same changes. Then the power intensity at any radius \( r \) is given by

\[ I(r) = \frac{2P}{\pi w_0^2} \exp \left(-2 \frac{r^2}{w_0^2} \right). \]

The microabsorption spectrum is recorded on SEE 1100 microspectrometer in the transmission mode and the examined area is 3.75×3.75 mm² (50×objective lens). With the microspectrometer, the laser irradiation spot can be viewed directly, which allows us to record the absorption spectra of
the laser-irradiated spot with a spatial resolution of the examined area. A series of absorption spectra and SEM images are taken from different parts of a laser irradiation spot with different distances $r$ to the center of the spot, which correspond to different laser power intensities $I(r)$ calculated by Eq. (4).

III. RESULTS AND DISCUSSION

A. Photothermal reshaping of prismatic Au nanoparticles with 400 nm femtosecond laser

A series of irradiation experiments with 400 nm femtosecond laser was performed on a sample made with 0.45 μm polystyrene spheres by the NSL technique. The size of the as-deposited array nanoparticles is 103.7 ± 6.8 nm in the bisector based on more than 500 particles from the SEM image. The thickness of the array nanoparticles is 30 nm monitored by quartz-crystal thickness monitor. In Fig. 1, the spectrum represented by filled black square (■) shows that the prismatic array nanoparticles have a strong absorption band with a maximum at 850 nm before laser irradiation. The SEM image [Fig. 2(a)] shows the nanoparticle array sample before laser irradiation. The microabsorption spectra also show a weak band around 500 nm on the blue side of the main plasmon resonance band. The weak surface plasmon band in the microabsorption spectrum was also observed by Mohamed from triangular gold nanoplatelets. Based on the absorption spectrum and discrete dipole calculations of silver prism nanoparticles, Jin et al. assigned the strong plasmon absorption band to in-plane dipole resonance. Another two weak bands at 340 and 600 nm were assigned to out-of-plane and in-plane quadrupole resonances, respectively. Due to the similarity of the particle shape in our case, it is likely that the weak plasmon resonance band in our gold array sample results from the in-plane quadrupole resonance transition and the strong absorption bands shown in Fig. 1 are the in-plane dipolar transitions.

There is also a dip around 500 nm which results from the gold film or large defects formed during the sample preparation. The absorption spectrum increases below 500 nm, which is due to the absorbance of the electron transitions from the Au 5d band to empty 6sp bands above the Fermi level (interband transitions). So with 400 nm laser light, both of the free electrons and the 5d electrons can be excited.

As shown in Fig. 1, the in-plane dipolar transition bands blueshift as the power density of the laser irradiation increases from 0 to 3.2 W/cm², which may be due to the laser photothermal annealing of the prismatic array nanoparticles. Similar phenomena have been observed for thermal annealing and solvent treatment of the Ag prismatic array nanoparticles. In the thermal annealing experiment, Jensen et al. found that the silver nanoparticles change from triangular to elliptical shape after annealing at 300 °C for 1 h. This shape change results in a blueshift of the surface-plasmon...
absorption maximum of more than 200 nm. In the solvent treatment, a 100 nm blueshift of the absorption peak was observed after exposure to two solvent cycles of water and methanol. Atomic Force Microscope (AFM) measurements of the sample before and after the solvent exposure revealed that the height of the particle increased 4 nm and the tips of the nanoparticles became round. Both of these changes induce a blueshift of the surface-plasmon absorption maximum. Figure 2(b) is a SEM image of the sample after irradiation by 400 nm femtosecond laser at 3.1 W/cm², which clearly shows the rounding of the nanoparticle tips. This is due to the dewetting properties of gold on a quartz surface and a lower melting temperature at the tips due to the size-dependent surface melting temperature.

As the power density increases above 3.5 W/cm², the intensity of the absorption bands decreases due to the loss of the gold material as the particle becomes smaller. The spectra also show a tail at the red side of the dipolar plasmon absorption maximum, which may be due to the large defects on the sample that are hard to change under this laser power density. Quite interestingly, we found tripod-shaped particles when we measure the SEM image in the same region as shown in Fig. 2(c). The spherical shape is the most thermodynamically favored particle shape with a lower surface energy than any other shape, which makes the gold triodapal nanoparticles quite unusual. Apparently, the gold nanoparticle is not totally melted, else it would make the transformation of the nanoparticles from prismatic direct to the spherical shape [Fig. 2(d)]. It is obvious that the tripodal shape has lower surface energy than that of the prismatic shape.

We first think the tripodal nanoparticles are formed due to the inhomogeneous heating of the prismatic array nanoparticles. Novotny et al. found that the illumination of a gold nanoneedle with 810 nm monochromatic waves in water induces a strong E-field enhancement (=3000) around the tips of the nanoneedle. This induces a temperature gradient around the tip due to the inhomogeneous absorption of the light energy. A maximum of ΔT=11.1 K was found inside the tip at the location of the maximum absorption. With the discrete dipole approximation (DDA) method, Kelly et al. found that the E-field contours for a Ag nanoprism has maximum enhancement around its tip when it was irradiated with 770 nm light (corresponding to the dipolar resonance absorption). While the E-field enhancement has a maximum at the sides of the Ag prism when it was irradiated with 460 nm light (corresponding to the quadrupole resonance absorption). In our experiment, the prismatic gold nanoparticle array sample has dipolar resonance absorption at 850 nm and quadrupole resonance absorption at 570 nm. We believe that the 400 nm femtosecond laser irradiation will induce a more enhanced E-field at the sides of the prismatic gold nanoparticles because it is close to the quadrupole resonance absorption. Thus, the sides will be hotter than the tips of the prismatic gold nanoparticles. The tripod will be formed from the prismatic nanoparticles by the loss of Au at the sides or contraction induced by surface tension at the sides. However, the tips of the array nanoparticles will maintain their shape or only have slight annealing effect as we observed in Fig. 2(c).

![Graph showing absorption spectra](image)

**FIG. 3.** (Color online) Microabsorption spectra of a periodic monolayer array of prismatic gold nanoparticles after irradiation with 800 nm femtosecond laser at different intensities. The numbers in the plot correspond to different power densities (W/cm²) of the examined region on the substrate within the laser profile calculated by assuming that the energy in the laser pulse has a Gaussian distribution. The arrow shows that the energy density goes from low to high as one moves from the edge to the center of the laser irradiation profile on the array. The diameter of the laser spot on the array is 250 μm.

As the power density of laser irradiation reaches 3.9 W/cm², we find that the dipolar absorption band at 850 nm completely disappears, while an absorption band at 540 nm appears. The SEM image taken in the same region shows that a spherical gold nanoparticle array is formed with the diameter of the particle around 70 nm. The formation of the spherical shape suggests that the absorbed irradiation energy is sufficient to melt the entire particle to form the most thermodynamically stable shape. In aqueous solution, a 70 nm gold nanosphere will give surface-plasmon absorption at 553 nm. The small difference between the surface-plasmon absorption maxima is a result of the difference in the dielectric constants of the surrounding environment.

The absorption band around 540 nm disappears when the power density of the laser irradiation is increased above 4.5 W/cm². The SEM image measured in this area shows that most of the nanoparticles have disappeared due to the ablation of the gold array nanoparticles.

**B. Photothermal reshaping of prismatic Au nanoparticles with 800 nm femtosecond laser**

Using 400 nm laser at appropriate power density, we can reshape the prismatic gold array nanoparticles to tripod shape and finally to spheres. Upon using an 850 nm laser as the irradiation source to excite the dipolar surface plasmon, Schatz’s calculation showed that the tips absorb more of the incident laser light than the sides of the prismatic array nanoparticles. This induces a higher temperature at the tips than at the sides. As a result, the tips of the array nanoparticles are rounded.

Figure 3 shows a change in the absorption spectra due to...
the irradiation of the gold prismatic nanoparticle with 800 nm femtosecond laser pulses. As the power density increases, the dipolar resonance absorption band initially broadens (3.3 W/cm$^2$) and then forms two populations at 3.6 W/cm$^2$, one with a peak at 750 nm and the other at 850 nm with an absorption dip at 800 nm. This split absorption spectrum results from the absorption of the reshaped particles and the unchanged particles. As the power density increases to 4.5 W/cm$^2$, the absorption band at 850 nm decreases while the band at 750 nm increases. This indicates that the prismatic nanoparticle with an absorption at 850 nm photothermally changes to a particle with a shorter absorption maximum at 750 nm.

The SEM images taken in the same area further support this explanation. Figure 4(a) is recorded within the area that has a power density of 2.1 W/cm$^2$. No obvious shape change is observed and the absorption spectrum only blueshifts slightly, as shown in Fig. 3. Figure 4(b) is from the area that has a laser energy density of 3.0 W/cm$^2$. The image shows that the tips of the smaller particle are rounded, which causes the broadening of the absorption spectrum. As the power density increases to 4.5 W/cm$^2$, the tips of most of the particles become rounded, thus the absorption at 750 nm increases (Fig. 3).

As the power density increases further to 5.0–5.6 W/cm$^2$, the plasmon absorption bands at 750 nm drops in intensity dramatically, while their maxima do not change. This suggests that the shape of the nanoparticles does not change but rather the particle density decreases (the particles that have an absorption band at 750 nm). From the SEM images of the area [Figs. 4(d) and 4(e)], we can see that some of the particles are removed from their original location and touch each other, which will shift the plasmon absorption band substantially because of the increase in the size of the jointed nanoparticles. This leads to a decrease in the absorption at 750 nm as observed. We also observe that some of the particles are turned on their sides. The calculation on silver prismatic nanoparticle by Kelly et al. shows that only the weaker out-of-plane plasmon resonance absorption will be excited when the polarization of the incident light is along the z axis of the particle (perpendicular to the prism surface). Both of these two effects cause a decrease in the dipole resonance absorption of the array nanoparticles at 750 nm.

When the power density of the laser irradiation increases to 5.9 W/cm$^2$, most of the array nanoparticles leave their original positions and form large aggregates. This decreases the absorption at 750 nm further and increases the absorption at the red side of the plasmon band (>820 nm).

When we use 800 nm light as the irradiation source (close to the dipolar resonance absorption), the E-field enhancement will be around the tips of the prismatic nanoparticles. Then the tips of the nanoparticles will absorb more light energy and their temperature will increase more than those of the sides of the nanoparticles. This gives rise to heating the tips and thus gives rise to rounding them up.

From the SEM measurement (Fig. 4), we do not observe spherical nanoparticles in the array even when the power density is increased to 5.9 W/cm$^2$. This is most likely due to the fact that rounding the tips leads to shifting the surfaceplasmon band to ~750 nm. Thus, the absorption of the particles at 800 nm becomes weak. This decreases the probability of heating the nanoparticles as a result of exposure to the 800 nm laser pulses. The observation that most of the particles are removed from their original positions suggests that the absorbed energy is sufficient to break the nanoparticle-substrate “bonds” but not sufficient to overcome the barrier to form the spherical shape.

C. Photothermal reshaping of prismatic Au nanoparticles with 700 nm femtosecond laser

Since the nanoparticles weakly absorb the 800 nm laser after the tips of the nanoparticle are rounded, we used a 700 nm laser as the irradiation source. Figure 5 shows the changes in the absorption spectra with increasing power density of the femtosecond laser pulses. The plasmon band blueshifts to 750 nm by increasing the laser power density from 1.8 to 2.8 W/cm$^2$. As the power density increases to 3.0 W/cm$^2$, another band at 660 nm appears. Then the band at 660 nm continuously increases when the laser power den-
very weak. The reason that the plasmon bands stop shift in their original position and forming aggregates when we excite the array nanoparticles with the 800 nm laser. Again, the reason that the plasmon bands stop shift is that the particles stop changing as their plasmon absorption maximum to 750 nm. Then the relatively smaller populations result from the absorptions of the reshaped particles and the unchanged particles.

The difference with 700 nm laser irradiation is that initially all of the particles start changing together, bringing the absorption maximum to 750 nm. Then the relatively smaller nanoparticles reshape faster than the big ones to form two populations because the 700 nm laser is located at the shoulder of the blue side of the plasmon absorption spectrum [represented by (\(\nabla\)) in Fig. 5].

The band at 660 nm continuously decreases as the power density increases from 3.6 to 6.0 W/cm\(^2\), which is also observed when we excite the array nanoparticles with the 800 nm laser. Again, the reason that the plasmon bands stop shift is that the particles stop changing as their plasmon absorption maxima shift to 660 nm (the absorption at 700 nm is very weak). The intensity of the absorption decreases because some of the particles are tuned on their sides with the incident light parallel to the particle surface or removed from their original position and forming aggregates [Figs. 6(d)–6(f)]. Both of these changes decrease the number of particles that absorb at 660 nm. The band at 750 nm not only decreases in intensity but also shifts to longer wavelength as a result of forming larger aggregates. From Fig. 6(e) and 6(f) we can see some nanospheres formed. This is likely due to two-photon absorption. The nanoparticles absorb enough energy which changes the entire nanoparticle to spherical shape.

We also see tripod-shaped gold nanoparticles formed at 3.1 W/cm\(^2\), even though it is not as obvious as the tripod formed when we use 400 nm laser. Both the dipole and quadrupole resonances have absorption at 700 nm initially (black line in Fig. 1), but the dipole resonance has more absorption than the quadrupole resonance as the dipole band shifts to 750 nm (at 2.8 W/cm\(^2\)). This tripodal shape formed from the prismatic nanoparticles cannot simply be explained only by the inhomogeneous heating mechanism of the gold nanoparticles by laser irradiation of different wavelengths. Another possible explanation is the lattice rearrangement of the as-deposited gold prismatic array nanoparticles.\(^{65}\) The gold tri-podal nanocrystals had been successfully synthesized in solution with a chemical reduction method at room temperature.\(^{66}\) The formation of the anisotropic tripod structure was attributed to the equalized stabilization of the \{110\} and \{111\} surfaces of the precursor.\(^{66}\) Another experiment performed by Hao et al.\(^{67}\) showed that the gold tripod can be formed within a mixture solution of sodium citrate and 30% H\(_2\)O\(_2\). The citrate method is one of the most well-known methods for the synthesis of spherical gold nanoparticles.\(^{68}\) In this method, citrate acts not only as a
reducing agent to reduce HAuCl₄, but also as the capping material to stabilize the gold nanoparticles. With the citrate method, a gold spherical nanoparticle can be formed with narrow size distribution. With the assistance of the H₂O₂ at room temperature, the gold tripod can be formed with as high as 40%–50% yield. So with the same citrate as the capping agent, both of the gold spherical and tripodal nanoparticles can be synthesized. This supports our results that the tripod shape is a metastable state of gold nanoparticles on their path to the stable spherical shape.

IV. CONCLUSIONS

The monolayer periodic gold prismatic array nanoparticles can be reshaped by using femtosecond laser pulses from the prismatic shape to a tip-rounded triangular, to a tripod shape, and finally to a spherical shape by increasing the H₂O₂ at room temperature, the gold tripod can be formed with as high as 40%–50% yield. So with the same citrate as the capping agent, both of the gold spherical and tripodal nanoparticles can be synthesized. This supports our results that the tripod shape is a metastable state of gold nanoparticles on their path to the stable spherical shape.

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