Single laser pulse reshaping of Au Nanoparticles

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ABSTRACT

Samples of suspended gold nanoparticles in the diameter range 10 nm to 100 nm were subjected to a single 7 ns pulse from a 532 nm laser to determine the effects of laser power on particle size distribution, mean size, and morphology. For 60 nm particles, a laser pulse of 10 mJ/cm^2 was sufficient to produce observable changes. In the range 10 mJ/cm^2 – 72 mJ/cm^2 dynamic light scattering indicated very little change in mean particle size, but a more than threefold reduction in the polydispersity index. Transmission electron microscopy showed that the particles became highly spherical and that there was a growing population of particles < 10 nm in size that could not be detected by the other methods. At higher power, the mean particle size decreased until all particles were < 10 nm in size. These results will be useful for potential therapeutic applications for pulse-heated nanoparticles and demonstrate the use of a simple laser treatment for modifying and improving nanoparticle properties.

Keywords: gold nanoparticles, dynamic light scattering, laser heating, transmission electron microscopy, electrospray dynamic mass analysis

1 INTRODUCTION

Gold nanoparticles (NPs) have a wide variety of applications in biosensing, health diagnostics and therapeutics. A common fabrication method produces Au NPs in a colloidal suspension using a method based on the reduction of a gold salt by citrate[1-2]. Methods continue to be developed for improving the size and shape uniformity[3]; however, fabricated NPs tend to be faceted and not highly spherical[4]. We present results that show that the faceted NPs from a commercial gold colloid can be converted to highly spherical Au NPs by exposing the colloid to a single 7 ns pulse from a laser.

2 EXPERIMENT

The starting material for this work was a commercially available monodisperse, citrate-stabilized, Au colloid of varying nominal diameters: 10 nm, 20 nm, 30 nm, 60 nm, and 100 nm. Laser exposures were performed with a Q-switched Nd:YAG laser, with the 1064 nm line frequency doubled to produce a 532 nm beam, and with a pulse time measured to be 7.46 ns. The beam profile had a diameter of 4 mm. The experimental techniques used to characterize the nanoparticles were dynamic light scattering (DLS), electrospray-dynamic mass analysis (ES-DMA) which provides particle size distributions, ultraviolet-visible absorption spectroscopy (UV-VIS), and transmission electron microscopy (TEM).

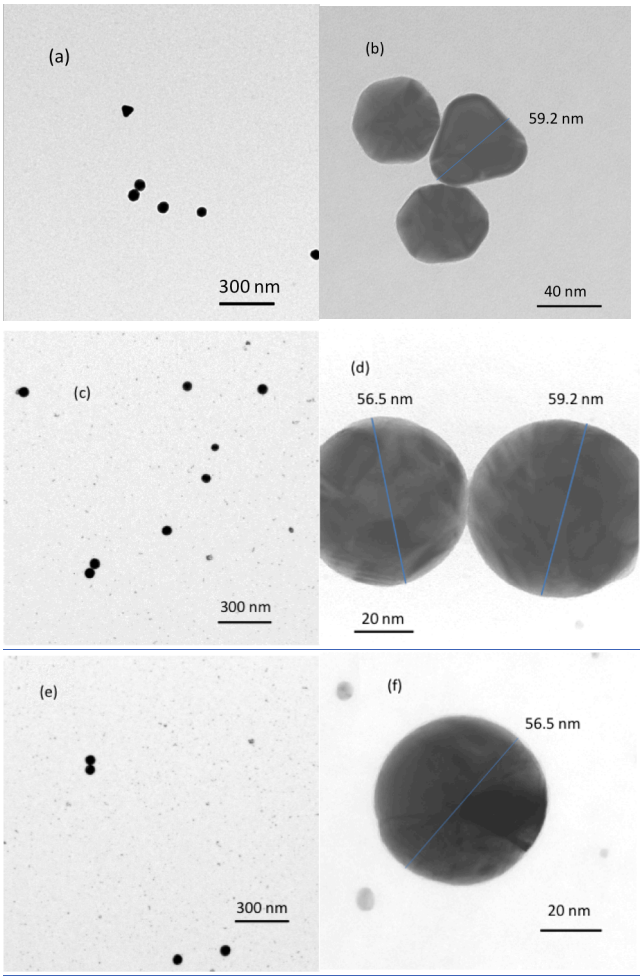

Figure 1. TEM images of the 60 nm diameter NPs (a) and (b), before laser exposure, and exposed to a single pulse of 532 nm laser irradiation at: (c) and (d), 23 mJ/cm^2; (e) and (f), 31 mJ/cm^2.

RESULTS

An example of the reshaping of the NPs by a laser pulse is shown in the transmission electron microscope images in Figure 1 for the case of 60 nm average diameter NPs. The NPs as received (Fig. 1 (a) and (b)) are clearly faceted and exhibit a variety of cross-sections including hexagonal, triangular, and circular. Single pulse exposures at fluences of 23 mJ/cm^2 (Fig. 1 (c) and (d)) and 31 mJ/cm^2 (Fig. 1 (e) and (f)) show the spherical particles that result from the laser treatment. At these fluence levels, there are also present irregular particles typically less than 10 nm in diameter, which result from ablation off the originating particles. Figure 2 shows the particle aspect ratio distribution before and after a pulse.

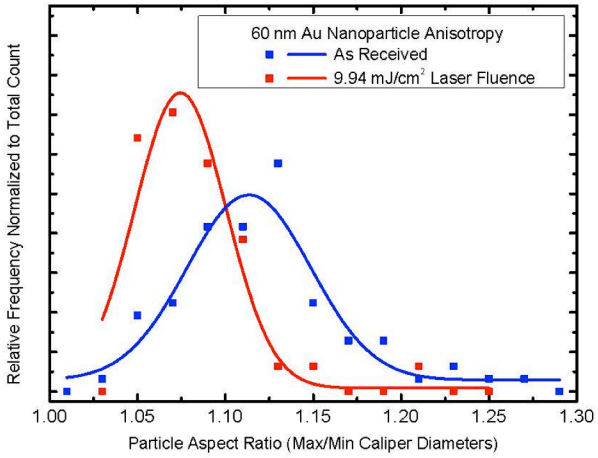

Figure 2. Distribution of particle aspect ratio before and after laser pulse.

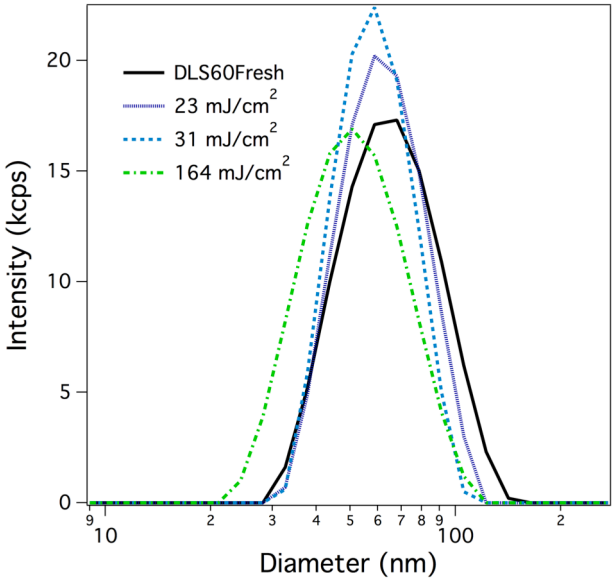

Figure 3. DLS distribution of particle sizes with initial mean diameter of 60 nm for varying energy of exposure to a single pulse of 532 nm laser irradiation. Intensity units are kilocounts per second (kcps) measured by the detector.

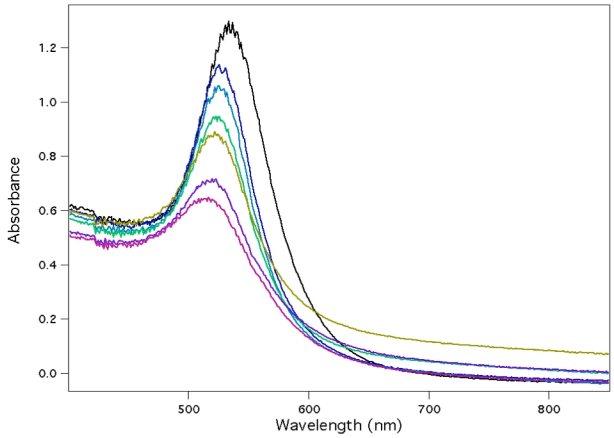

Figure 4. UV-Vis spectra of particles with initial mean diameter of 60 nm for varying energy of exposure to a single pulse of 532 nm laser irradiation. The amplitude of the peak corresponds inversely to the exposure fluence, the largest peak is unexposed, the next largest is 23 mJ/cm^2, and in order of decreasing peak height, 31 mJ/cm^2, 72 mJ/cm^2, 107 mJ/cm^2, 164 mJ/cm^2, and 390 mJ/cm^2.

Dynamic Light Scattering (DLS) measurements showed that there was a tightening of the apparent size distribution as a result of the single laser pulse for pulse fluences below 31 mJ/cm^2. An example for 60 nm particles is shown in Figure 3. Polydispersity index values as low as 0.04 were measured for 60 nm diameter particles. For this fluence range, the average particle size remained unchanged, while the scattering intensity decreased. The threshold for laser effects on the particle decreased with increasing particle size for particles with diameters 10 nm to 60 nm, while the threshold increased for the 100 nm particles. Because the scattering intensity varies strongly with particle size, the smaller <10 nm particles observed with TEM were not detected in this measurement. ES-DMA results indicated very little change in the particle size for fluences below 31 mJ/cm^2. At higher fluences the DLS distribution broadens and aggregated species are observed.

UV-vis spectra of particles with initial mean diameter of 60 nm for varying fluence of the laser heating pulse are shown in Figure 4. The absorption maximum shifts to shorter wavelength and is of reduced amplitude as the laser pulse fluence is increased. The shift in the UV absorbance to smaller wavelength with pulse fluence, can be attributed to a dependence of absorbance on particle shape[5]. For example, nanorods show an increase in absorption peak energy with decreasing aspect ratio[6]. At higher pulse fluence, the particle size decreased, which also resulted in a shift to higher energy for UV-Vis absorbance.

CONCLUSIONS

While previous work has shown that a laser can melt and reshape gold nanorods[7], the present results show a simple process to create highly spherical NPs from Au

colloids fabricated by traditional methods. Optimization of the process conditions can possibly eliminate the irregular <10 nm particles we have observed, or they can be separated from the treated colloid by a variety of methods. This work also suggests that a simple laser pulse treatment may be useful for modifying coatings on NPs, or altering alloy NPs.

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