

# Visible Laser Induced Fusion and Fragmentation of Thionicotinamide-Capped Gold Nanoparticles

Hiroaki Fujiwara,<sup>†,‡,§</sup> Shozo Yanagida,<sup>†,||</sup> and Prashant V. Kamat<sup>\*,‡</sup>

Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan, and Notre Dame Radiation Laboratory, Notre Dame, Indiana 46556-0579

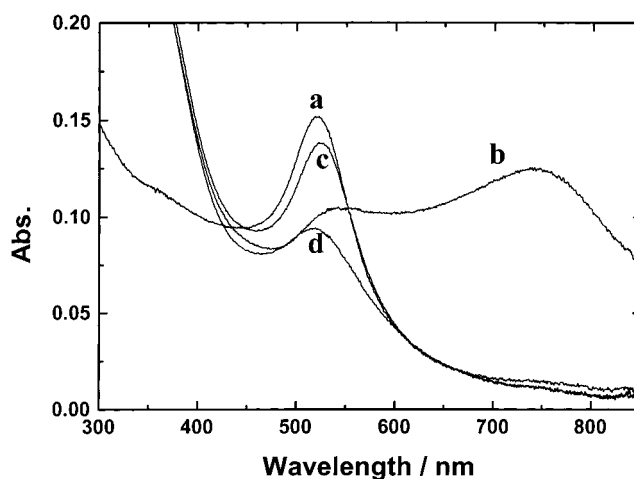
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Thionicotinamide-capped gold nanoparticles undergo fusion as well as fragmentation upon laser pulse excitation (532 nm). The aggregation effect which is induced by thionicotinamide also disappears following laser pulse excitation. The morphological changes induced by thermal and photochemical effects were found to influence the optical properties of these particles.

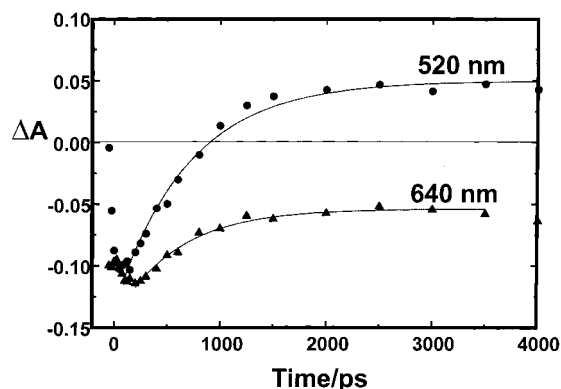
Self-assembled monolayers (SAM) of organic compounds containing thio or amino functional groups provide a unique way to organize molecules and semiconductor nanoclusters on gold surfaces (see, for example, refs 1 and 2). Attempts have been made in recent years to modify gold nanoparticles with thio compounds.<sup>3–8</sup> Although recent efforts address the issues related to bulk SAM–gold surfaces, spectroscopic studies related to thio-capped gold nanoclusters<sup>9–12</sup> are rather limited. Interaction of thio compounds with gold nanoclusters in solution often leads to aggregation effects. Such an aggregation is noted by the appearance of a broad band in the red–infrared region. Recent laser-induced photochemical studies of metal nanoclusters have noted interesting photophysical properties such as transient plasmon bleaching, electron ejection, and photofragmentation.<sup>13–17</sup> We report here visible laser induced transformations of thionicotinamide gold nanoparticles and the spectral properties associated with changes in the morphology of these particles.

Gold colloids were prepared by the conventional citric acid reduction of  $\text{HAuCl}_4$  in water with sodium citrate at near-boiling temperature.<sup>18</sup> Surface modification of gold colloids was carried out by adding controlled amounts of thionicotinamide (TNA) to the ruby-colored colloidal gold suspension at room temperature. Transmission electron microscopic examination (TEM) was conducted by applying a drop of the colloid sample to a carbon-coated copper grid. Particle sizes were determined from the photographs taken at a magnification of 150 000 using a Hitachi H600 transmission electron microscope. The laser irradiation was carried out in a quartz cuvette (10 mm  $\times$  2 mm) with continuous  $\text{N}_2$  bubbling. Laser irradiation experiments were performed using a mode-locked, Q-switched Continuum YG-501 DP Nd:YAG laser system (pulse width  $\sim$  18 ps;  $\lambda$  = 532 nm, output 1.5 mJ pulse).<sup>17</sup>

The absorption spectra of gold nanoclusters in aqueous solutions before and after the complexation with thionicotinamide are shown in Figure 1 (spectra **a** and **b**, respectively). The native gold colloids exhibit a prominent surface plasmon band at 520 nm. At relatively high thionicotinamide concentrations



**Figure 1.** (a) Absorption spectrum of 0.5 mM gold colloids in water. Absorption spectra of TNA-capped gold colloids (0.5 mM gold colloidal suspension containing 3 mM thionicotinamide) were recorded (b) before irradiation, (c) 1 min and (d) 30 min after 532 nm laser pulse (pulse width 18 ps, 1.5 mJ/pulse) irradiation, respectively.



**Figure 2.** The absorption–time profiles recorded at (a) 520 nm and (b) 640 nm following the laser pulse (532 nm) irradiation of TNA-capped gold nanoclusters.

\* Author to whom correspondence should be addressed. E-mail: pkamat@nd.edu; or <http://www.nd.edu/~pkamat>.

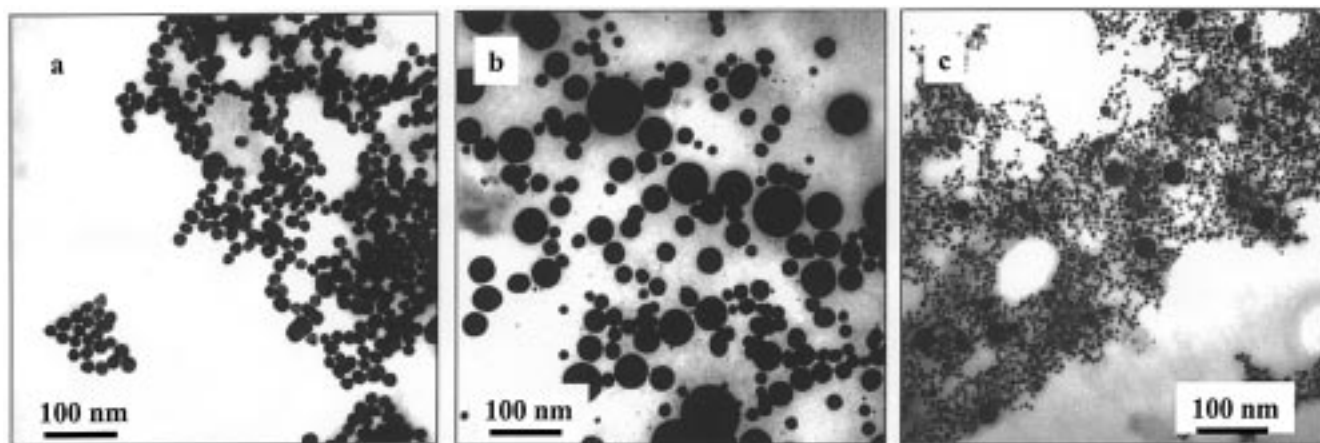
<sup>†</sup> Osaka University.

<sup>‡</sup> Notre Dame Radiation Laboratory.

<sup>§</sup> E-mail: fujiwara@ap.chem.eng.osaka-u.ac.jp.

<sup>||</sup> E-mail: yanagida@chem.eng.osaka-u.ac.jp.

the colloidal suspension turns blue and an absorption band in the red–infrared region ( $\lambda_{\text{max}} \sim 750$  nm) appears. Such a broad band is indicative of aggregation and/or changes in the shape of gold nanoclusters. As indicated earlier,<sup>19</sup> the position of this



**Figure 3.** Transmission Electron Micrographs of TNA-capped gold colloids, (a) before, (b) 1 min, and (c) 30 min after 532 nm laser irradiation.

absorption band strongly depends on the size and shape of the nanoclusters. At relatively high TNA concentrations ( $>1$  mM) the surface charge is neutralized, thus, paving the way for aggregation. Displacement of citric acid by amines on gold surfaces has been demonstrated by atomic force microscopy (AFM).<sup>20</sup>

Upon laser pulse (532 nm) irradiation of a TNA-capped gold nanoparticle suspension for a few minutes, we observe a reversal of color change from blue to ruby-red. The broad absorption band at 750 nm disappears during this laser irradiation experiment (spectrum **c** in Figure 1). Increased absorption at 520 nm associated with the spectral change indicates the restoration of the surface plasmon absorption band. The excitation with a 532 nm laser pulse thus prompts the disappearance of aggregation effects in TNA-capped gold nanoparticles.

Figure 2 shows the absorption–time profiles recorded at 510 and 640 nm. The bleaching observed at these two wavelengths occurs within the laser pulse duration of 18 ps. The bleaching at 640 nm recovers partially during the period of 1 ns. The residual bleaching represents the disappearance of the aggregate band. This absorption–time profile at 640 nm also indicates the duration with which the aggregates of TNA-capped gold nanoparticles undergo physical changes following laser pulse irradiation. On the other hand, 510 nm bleaching which represents the damping of the plasmon band recovers quickly (within 2 ns) and exhibits a residual positive absorption at longer times. The increased (positive) absorbance at 510 nm essentially represents the growth in the plasmon absorption as a result of aggregate breakup. (Details on the transient bleaching phenomenon in gold colloids were reported elsewhere.<sup>13–16</sup>)

To assess the morphological changes caused by the laser irradiation we probed the TNA-capped gold nanoparticle samples using transmission electron microscopy. Some representative examples are shown in Figure 3. Native gold colloids prepared by the citric acid reduction method are nearly spherical in shape with a particle diameter of 15–20 nm. The transmission electron micrograph of TNA-capped gold nanoparticles (Figure 3a) shows the presence of cluster islands, each consisting of several nanoparticles that are in close contact. The sample taken after one-minute laser pulse irradiation (532 nm, 10 Hz, 1.5 mJ) shows the formation of large size particles that are nearly spherical (Figure 3b). These large-size particles which are well separated from each other do not exhibit optical transitions (the absorption band in the red–IR region) that correspond to aggregation effects.

The transmission electron micrographs support the hypothesis that aggregates of TNA-capped nanoclusters undergo fusion to

form larger nanoparticles even under short-term ( $\sim 1$  min) laser irradiation. Although these nanoclusters have grown in size ( $\sim 100$  nm), they are well separated from each other, thus ceasing the aggregation effects on the absorption spectrum. No such changes were seen when unmodified gold colloids were subjected to laser pulse irradiation. When the laser irradiation was continued for 30 min we observed fragmentation of these gold nanoclusters to produce small-size (diameter  $\sim 5$  nm) particles. The fragmentation of TNA-capped and uncapped gold nanoparticles is seen only at high-intensity and/or long-time irradiation experiments.

The results described here indicate that TNA-capped gold nanoparticles are photochemically active and undergo physical changes upon laser irradiation. Photoinduced coagulation<sup>21</sup> and fragmentation<sup>17,22,23</sup> as well as dissolution<sup>24,25</sup> of metal nanoparticles have been reported in previous studies. In the present laser irradiation experiments with TNA-capped gold nanoparticles we observe the formation of larger-size particles during the short-term laser irradiation. We attribute this phenomenon to the melting (fusion) of aggregates to form larger spherical particles during initial stages of laser irradiation. Since surface-modified gold nanoparticles exist as aggregates we expect the energy gained from the absorbed photons to be dispersed as excess heat to the neighboring particles and thus to induce their fusion. Similar laser-induced fusion is not seen in uncapped gold colloids because individual particles are well separated and the heat gained from laser excitation is quickly dumped into the surrounding aqueous medium ( $<200$  ps).<sup>15,16,26</sup>

At high laser intensity and/or long-term irradiation we observe fragmentation of nanoparticles as thermal and photochemical changes continue to propagate. As discussed earlier,<sup>17</sup> photoejection of electrons followed by the charging-up of the surface is a possibility that could lead to the particle fragmentation. The surface-complexed thionicotinamide may also play a role by capturing the photoejected electrons at the gold surface. Picosecond laser flash photolysis experiments are currently being performed to elucidate the photochemical events in the TNA-capped gold nanoparticles.

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