Influence of Intense Pulsed Laser Irradiation on Optical and Morphological Properties of Gold Nanoparticle Aggregates Produced by Surface Acid−Base Reactions

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Influence of Intense Pulsed Laser Irradiation on Optical and Morphological Properties of Gold Nanoparticle Aggregates Produced by Surface Acid−Base Reactions

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Gold nanoparticles were surface modified with an ionizable and pH-sensitive monolayer of thiobarbituric acid (TBA). By variation of the pH value of the solution, nanoparticle aggregates can be produced in a controlled way. The aggregates thus prepared were irradiated with an intense pulsed laser at 532 nm. The products in solution were examined by transmission electron microscopy (TEM) and optical absorption spectroscopy. The TEM images of the products revealed that the nanoparticle aggregates dissociate upon laser irradiation and form much smaller gold nanoparticles. The optical absorption spectra measured simultaneously show the gradual disappearance of the absorbance band of the aggregates at around 680 nm. Additionally, a blue shift (from 534 to 524 nm) of the resonance absorbance corresponding to isolated nanoparticles has been observed. All the observations suggest that the colloidal solution becomes more stable after laser irradiation. Both the reduced nanoparticle size and the stabilizing TBA ligands present on the particle surface contribute to the acquired stability of the colloidal solutions.

Introduction

Extensive research effort has been directed toward metal nanoparticles for fundamental and application reasons.[1] Among the numerous works about metal nanoparticles, gold has attracted much attention because both the synthesis and the surface modification of gold nanoparticles are relatively easy.[2] One important observation about gold nanoparticles is that small particles often exhibit strong plasmon resonance absorbance in the visible region of the electromagnetic spectrum.[3] Furthermore, while the size distribution of gold nanoparticles was held constant, their plasmon resonance absorbance maximum could be shifted hundreds of nanometers by changing their shape, orientation in the incident light field and in an electric field, or the arrangement of the particles in a matrix.[4] Recently, assembling individual nanoparticles into ensembles of specific shape and structure has become a widely pursued objective.[5]

It is interesting to generate and study the interparticle interactions while the particles are held by weak forces in an aggregate. Some strategies have been developed to

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control the aggregation process of nanoparticles in bulk solution and at solid/liquid or liquid/air interfaces. Controlled aggregation of nanoparticles on solid supports has been achieved by nanoparticle crystallization,[6] the Langmuir–Blodgett technique,[7] chemical cross-linkage,[8] self-assembly,[9] electrophoretic[10] and electrostatic[11] interaction, DNA hybridization,[12] and surface hydrophobic interaction.[13] In bulk colloidal solution, there was only limited success to control the aggregation process via "cross-linking" reagents,[14] chemical modification of the surfaces of nanoparticles with an ionizable protecting layer,[15] coating the nanoparticles with complementary single DNA strands,[16] and strong electrostatic interaction between negatively charged particles and multiple-charged cationic/oligocationic species.[17]

In this communication we report controlled aggregation of gold nanoparticles in water and their interaction with an intense pulsed laser beam. We achieve this goal by modifying gold nanoparticles with pH-sensitive and ionizable thiols, namely, thiobarbituric acid (TBA). At higher pH (completely deprotonated TBA) these colloids are stable due to the electrostatic repulsion of the oxyanion groups. Lowering of the pH leads to protonation of the anion group and the formation of the uncharged hydroxy functions, allowing hydrogen bond interactions between the particles and, thus, aggregation. We will focus our attention on the change in optical and morphological properties of these aggregates upon laser irradiation.

Experimental Section

Gold(III) chloride trihydrate (HAuCl$_4$·3H$_2$O, 99.9%), thiobarbituric acid (TBA, 98%), and sodium citrate dihydrate (99%) were purchased from Aldrich and used as received. Gold colloids[18] were prepared by adding HAuCl$_4$·3H$_2$O (20 mg) to a vigorously stirred solution of sodium citrate (60 mg) in boiling water

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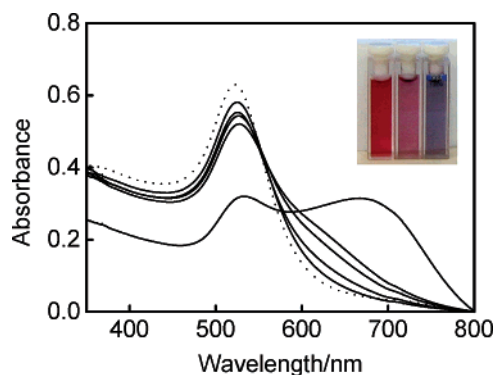
Figure 1. Optical absorbance spectra of Au colloidal solutions before (dotted curve) and after (solid curves) addition of small quantities of TBA as function of the pH of the solution (from top to bottom pH 12.0, 10.4, 8.6, 7.7, and 6.5). The inset shows samples at pH 12.0 (red), 8.7 (violet), and 6.5 (blue).

(250 mL). The solution was stirred under reflux for an additional 15 min before being allowed to cool. This colloidal solution had a pH of 5.3. The pH of the colloidal solution was adjusted from 2 to 12 using HCl and NaOH prior to capping with TBA. Capping of the gold nanoparticles was performed by mixing 30 mL of the colloidal solution with 1 mL of 0.1 mg of TBA/0.1 M NaOH. Assuming an area of 34 Å^2 per TBA molecule and total reduction of HAuCl$_4$, this concentration of TBA would lead to complete surface coverage of 21 nm gold nanoparticles.
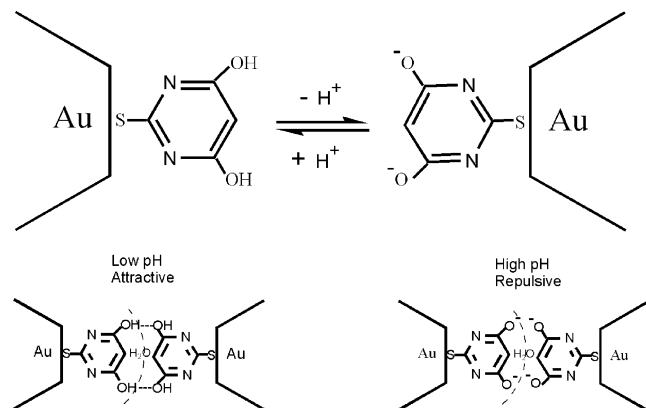
A pulsed Nd:YAG laser (Quanta Ray INDI series, Spectra Physics, Mountain View, CA) was used to irradiate the colloidal solution at 532 nm (frequency doubling of the 1.06 μm fundamental with a KH$_2$PO$_4$ crystal). The energy fluence per pulse is 130 mJ/cm^2 at a pulse length of 6 ns, 8 mm beam diameter, and a repetition rate of 10 Hz. Optical absorption spectra of the colloidal solution were recorded by using a Cary 300 UV/VIS spectrophotometer. Size and shape of the gold colloids were investigated with a LEO 922A transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. The samples were prepared by mounting a droplet of the colloidal solution of interest on a carbon-coated copper grid (Cu-400CK, Pacific Grid-Tech, USA) and allowing it to dry in air. Bright field images were recorded at a nominal magnification of 80000×, which was calibrated to 2% precision. The particle sizes were determined using successive gray level thresholding of the images, noise removal by image filtering, and particle erosion within the AnalySIS 3.2 software package. Overlapping particles that could not be separated were excluded manually from the statistical analysis. The average particle diameters calculated that way were checked to agree with similarly calibrated annular dark-field images recorded in the scanning mode to within 0.41 nm (for the 21 nm large particles in Figure 2) and 0.18 nm (for the 5 nm small particles in Figure 4), respectively. Finally, the individual size measurements were sorted into histograms using channels 1 nm wide.

Results and Discussion

The optical absorption spectra of the gold colloidal solution capped with TBA are shown in Figure 1 at various pH values. For comparison the spectrum for the uncapped gold colloidal solution is also presented (dotted curve). A successive shift in the surface plasmon resonance from 522 to 531 nm along with a successive reduction in intensity of the resonance absorbance is observed after addition of TBA molecules and adjusting the solution pH from 12.0 to 7.7, indicating capping of the gold nanoparticles.[3] One notable feature of Figure 1 is that a new absorbance band at around 680 nm evolved gradually, which is more clearly observed when the pH of the solution is decreased to 6.5. The colloidal solution at pH 6.5 is stable within the duration of our measurements. No deposits except a slight decrease in absorbance intensity and red shift of the absorbance of the colloidal solution at

Scheme 1. Possible Mechanism for the Formation of Nanoparticle Aggregates Based on a Surface Acid−Base Reaction[a]

[a] Note: diagram is not to scale.

around 700 nm have been observed overnight. Further lowering of the pH < 6.5 leads to fast aggregation. Deposits can be found at the bottom of the reaction cell, and the solution loses its colloidal properties within several minutes.

DLVO theory[19] indicates that the sum of the electrostatic repulsion and van der Waals attraction energies determines the stability of nanoparticles. Therefore in colloidal solutions several factors such as particle size, surface potential, and electric double layer influence the stability of nanoparticles and their aggregation. In our case an additional factor is the TBA molecules present on the particle surface, which provide a steric barrier against aggregation.[19] It has been demonstrated that for particles less than 10 nm diameter, a steric layer of 2 nm (about a C_{18} chain) is sufficient to offset the attractive van der Waals interactions.[2a] However, the surface potential should still be large to prevent formation of aggregates especially in the case where the steric stabilizer has poor solubility in the surrounding medium. Since the electrolyte concentration (c) of the colloidal solution studied here is kept at millimolar level, the thickness of the electric double layer (characterized by the Debye length $k^{-1} \sim (\epsilon\epsilon_o kT/2cz^2e^2)^{1/2}$) surrounding the colloidal particles is large enough to be treated as a constant. So the surface potential becomes the determining factor for the stability of the nanoparticles. By changing the pH of the solution the TBA molecules on the nanoparticle surface can be ionic or neutral; cf. Scheme 1. Thus, the density of the surface charge and the surface potential of the particles can be varied in a wide range. When the surface potential is far away from the potential of zero charge (pzc), the particles are highly dispersed and very stable; when the surface potential is near or equal to the pzc and the electrostatic repulsion cannot overcome the van der Waals attraction and hydrogen bridge bonding[15b] any more, the nanoparticles will aggregate.

The optical properties of nanoparticles are mainly determined by two contributions: (i) absorbance by isolated particles, and (ii) the coupled plasmon absorbance, which comes from the close contact of optically absorbing nanoparticles.[20] The more particles that are in contact, the larger is the range of the plasmon coupling. Very long range coupling can lead to absorbance that is red shifted several hundred nanometers from that of the individual

particles. These shifts are the basis for optical/color sensors based on metal nanoparticles.[21] The color of a solution of such aggregates depends on nanoparticle spacing. Nanoparticle aggregates of gold with interparticle distances substantially greater than the average particle diameter appear red with an absorbance maximum at around 520 nm; cf. the dotted curve in Figure 1. When the interparticle distances in the aggregates decrease to less than approximately the average particle diameter, the color of the solution becomes blue.[22] This change occurs in our case at pH 6.5 (see the inset of Figure 1), which indicates that the interparticle distances in the aggregates are less than the average particle diameter at pH ∼ 6.5, which is also evident from the TEM studies of the solution at pH 6.5. Figure 2 shows the TEM images of a sample from the colloidal solution at pH 6.5, where most of the nanoparticles are in close contact and form spongelike aggregates. This morphology of the aggregates can be tentatively correlated with the observation of a red-shifted band around 680 nm at pH 6.5 in Figure 1. However, we have a distribution of aggregates of different size in our sample (cf. Figure 2c), and we therefore cannot correlate the red-shifted band to aggregates of a specific size.

Intense pulsed lasers with various pulse widths, energies, and wavelengths have been used to prepare gold nanostructures[23] (sphere, wire and network) and to reshape gold nanorods into nanospheres.[24] When the plasmon band of well-dispersed gold nanoparticles is excited by an intense pulsed laser, the photon energy absorbed by electrons of the conduction band transfers into the lattice of the nanoparticles as heat (electron−phonon relaxation) in a few picoseconds.[24a,25] During a single laser pulse, one parent gold nanoparticle is considered to absorb consecutively more than a thousand photons, and its temperature reaches its boiling point.[24] The hot gold nanoparticle releases photofragments and part of the stabilizer molecules which cover the parent nanoparticles. After the laser pulse the heat diffuses into the solution and the temperature of the heated nanoparticle and the photofragments returns to room temperature before the next laser pulse heats the ensemble again. The precise time scale for heat dissipation to the embedding medium depends on the host's heat capacity and thermal conductivity, but in general it is on the order of

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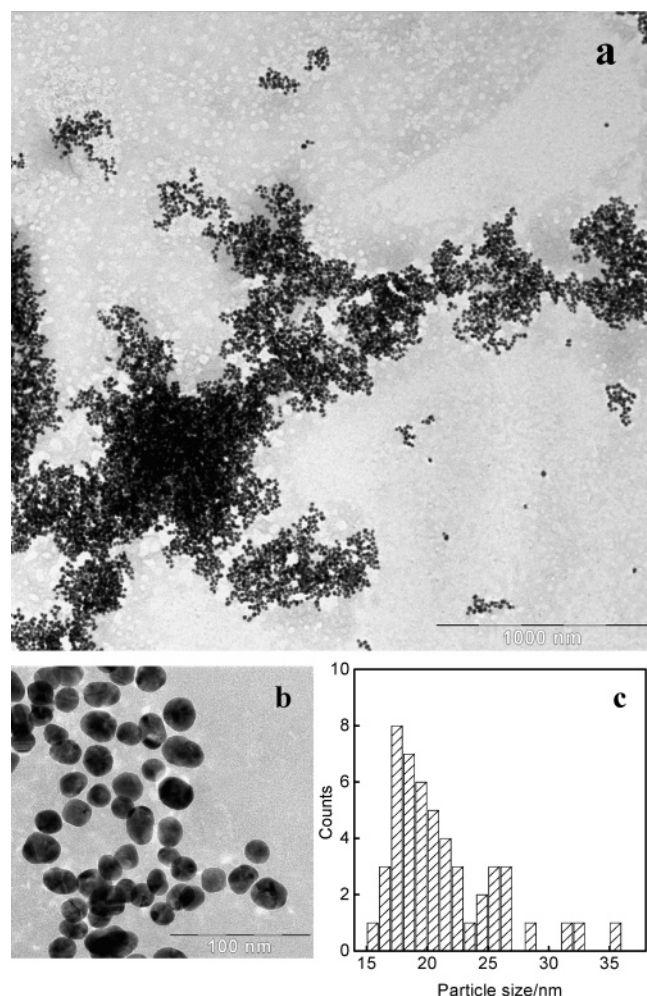(20) Quinten, M.; Kreibig, U. *Surf. Sci.* **1986**, *172*, 557.

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Figure 2. (a) TEM image of the gold nanoparticle aggregates at pH 6.5. (b) A magnified image, where individual nanoparticles can be observed. (c) The size distribution (21.3 ± 4.4 nm) of the gold nanoparticles as obtained from a computer evaluation of the TEM data is shown.

Figure 3. Optical absorption spectra of gold nanoparticle aggregates at different laser irradiation times (from bottom to top: 0, 1, 3, 5, 10, 20, and 30 min).

hundreds of picoseconds.[24d] Beside heating, multiple ionization followed by Coulombic explosion similar to an electrospray process may also contribute to fragmentation.[26] Although many achievements have been made to understand the interaction of laser light with isolated nanosystems (sphere and rod), less attention has been paid to the interaction between a pulsed laser and aggregated nanoparticles where the interparticle electronic coupling becomes dominant.[27]

Figure 3, bottom curve, shows the optical absorption spectrum of the solution a day after it was prepared by adjusting the pH value of the colloidal solution to 6.5. The other spectra were obtained at different laser irradiation times by using 130 mJ/pulse cm^2 laser energy flux and 532 nm excitation wavelength. There are two notable features in Figure 3. One is the disappearance of the absorbance band near 710 nm corresponding to the coupled resonance absorbance when the irradiation time exceeds 5 min. The intensity of this band is already reduced after a few laser pulses. This observation suggests that the electronic coupling between the nanoparticles becomes
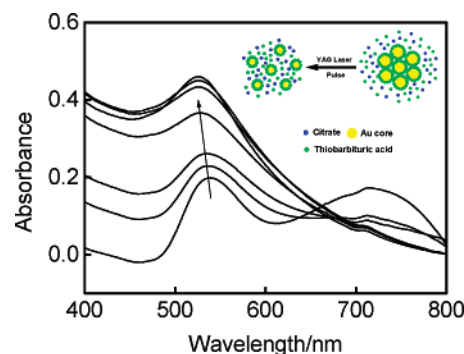
very weak after laser irradiation because the mean distance between particles became too large. The second one is the increase in intensity of the absorbance around 530 nm together with a gradual blue shift of the absorbance maximum from 534 to 524 nm after 5 min of irradiation. For isolated nanoparticles, the absorbance maximum is mainly dependent on particle size,[3,4] dielectric properties of the solvent,[28] the charge state of the particles,[29] and the surface modification.[4] In our case the main cause for the blue shift of the absorbance maximum indicated by an arrow in Figure 3 can be attributed to the decrease of particle size and the change in the complexation of the gold nanoparticles,[30] as they become progressively smaller during fragmentation. This is supported by the results of TEM investigations (see Figure 4), where tiny nanoparticles (4.9 ± 2.7 nm) together with very few large particles (from their size range of 15−23 nm considered as parent nanoparticles) have been observed. Generally in certain size ranges (2−50 nm) larger nanoparticles display more intense resonance absorbance than smaller ones. The observed increase in absorbance after laser irradiation can be explained by the increased number of the smaller nanoparticles. Assuming total reduction of 20 mg of HAuCl$_4$, the number of gold nanoparticles with diameter 21 nm in our system is 1.3×10^{10}; for 4.9 nm diameter nanoparticles, the number will be 1.0×10^{12} in our reaction cell.

It is intriguing why the smaller particles obtained from laser irradiation of the nanoparticle aggregates do not form aggregates again, since the pH value of the solution is the same before and after irradiation. We think that the excess TBA molecules present in the solution stabilize the newly formed fragments and prohibit the fragments from forming large aggregates by steric stabilization which is more effective for small particles.[31] It has been demonstrated that only rather small molecules are necessary to prevent coalescence and coagulation of small nanoparticles.[10] Furthermore, the first minimum in the plot of the interaction energy between two nanoparticles as function of nanoparticle separation is not as deep for small nanoparticles as for larger ones.[19] As a consequence coagulation can be reversible for small nanoparticles even if only small steric stabilizers are present on the particle

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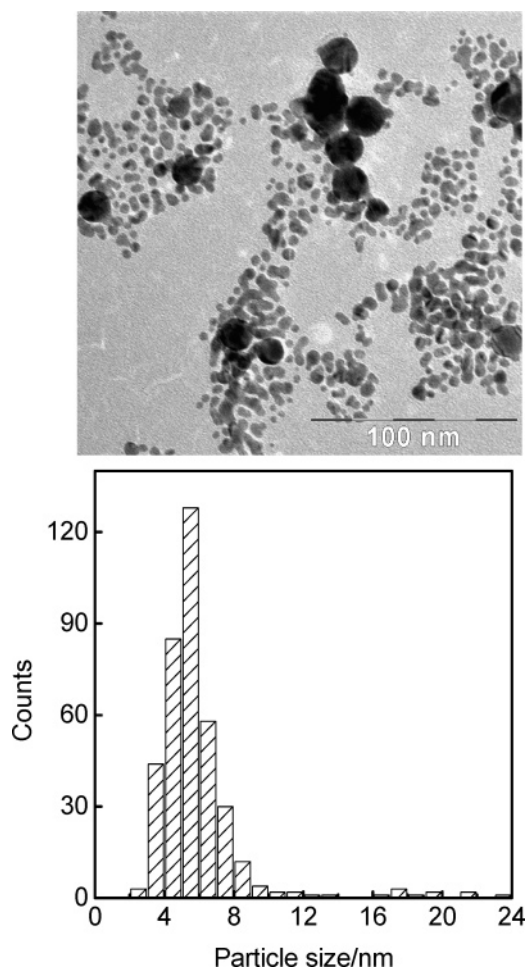
Figure 4. TEM images and size distribution (4.9 ± 2.7 nm) of nanoparticles produced after 532 nm pulsed laser irradiation for 30 min. This corresponds to the top curve of Figure 3. For evaluation of the size distribution, see text.

surface.[31] A previous demonstration of this steric effect is the enhanced stability of gold particles after addition of mercaptopropionic acid.[10] The surface-capped gold nanoparticles can coalesce reversibly on addition of acid to colloids. If the resulting colloid is centrifuged and the supernatant fluid is removed, addition of a drop of base will restore the red nanoparticle solution at once. This shows that even a small chain length combined with a noticeable surface charge density is sufficient for the particles to escape the interaction energy minimum.

Concerning the mechanism of the interaction between the intense pulsed laser and gold nanoparticles, Kondow et al.[23i] reported that formation of photofragment aggregates depends on the concentration of the stabilizer (in his case sodium dodecyl sulfate, "SDS"). In dilute SDS solution, parent gold nanoparticles and photofragments are not well stabilized by SDS molecules. As long as they are melted by a laser beam, they grow into network structures by encounter and coagulation. At high concentration of SDS, no aggregate structure but smaller spherical nanoparticles have been observed. So, the aggregation of a gold nanoparticle after each laser pulse is determined by the coverage of the photoproducts by ligand molecules and by the probability of encounters of heated gold nanoparticles or photofragments. In our case the ligand molecules are TBA with a −SH moiety which has strong affinity to the gold surface and their number in our solution (4.15×10^{17}) is large enough to cap all of the photofragments. So in the presence of TBA, the mechanism of the interaction between gold nanoparticle aggregates and the laser beam can be expressed as (i) the nanoparticles excited by the laser dissociate into photofragments, which leads to the dissociation of the aggregates, and (ii) the resulting photoframents being quickly surface capped by TBA molecules. It is the decreased size of the nanoparticles combined with a steric stabilizer of small size present on the particle surface that results in the stability of the products of the laser irradiation.

Conclusions

The treatment of citrate-stabilized gold nanoparticles with thiobarbituric acid molecules causes their aggregation. This aggregation has been monitored directly by TEM and indirectly by UV−vis absorbance spectroscopy. Upon aggregation, the solutions show additional absorbance around 700 nm, which is attributed to interparticle plasmon coupling. The degree of coupling, and thus the strength of this band, is influenced by the pH values of the colloidal solution. Intense pulsed laser irradiation of the aggregates leads to their dissociation and to the formation of smaller nonaggregate nanoparticles. Both the smaller particle size and the steric stabilizer present on the particle surface contribute to the acquired stabilization of the colloidal solution after laser irradiation.