Suppression of surface plasmon resonance in Au nanoparticles upon transition to the liquid state

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Abstract: Significant suppression of resonant properties of single gold nanoparticles at the surface plasmon frequency during heating and subsequent transition to the liquid state has been demonstrated experimentally and explained for the first time. The results for plasmonic absorption of the nanoparticles have been analyzed by means of Mie theory using experimental values of the optical constants for the liquid and solid metal. The good qualitative agreement between calculated and experimental spectra support the idea that the process of melting is accompanied by an abrupt increase of the relaxation constants, which depends, beside electron-phonon coupling, on electron scattering at a rising number of lattice defects in a particle upon growth of its temperature, and subsequent melting as a major cause for the observed plasmonic suppression. It is emphasized that observed effect is fully reversible and may underlie nonlinear optical responses of nanocolloids and composite materials containing plasmonic nanoparticles and their aggregates in conditions of local heating and in general, manifest itself in a wide range of plasmonics phenomena associated with strong heating of nanoparticles.

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The physics of interaction of metal nanoparticles with laser radiation constitutes a major direction in plasmonic research. Plasmonic nanoparticles producing strongly localized and enhanced electromagnetic fields are widely used in numerous applications and has become of topical interest in areas like nanosensorics, biomedicine, biotechnology, in laser excitation of plasmon-polaritons in waveguiding chains of plasmonic nanoparticles, photochromic reactions induced by laser excitation of resonant domains in disordered colloidal nanoparticle aggregates, and for various nonlinear optical processes, to mention a few out of many examples [1–5]. There is special interest how all these applications can be maintained in the case when nanoparticles are heated up to the melting point by radiation or in high-temperature conditions in general. The importance of thermal effects is connected with the influence of radiation on metal atomic vapors produced, for example, in heat pipes which are employed for nonlinear optical frequency conversion of laser radiation [6]. In such pipes the formation of aerosol components consisting of nanodrops in metal vapor is possible at high temperature. Such nanodrops result in enhanced scattering and attenuation of the laser radiation. In papers [7–9] we studied theoretically the impact of pulsed laser radiation on plasmonic nanoparticle aggregates.

In paper [9] we have first taken into account the heating factor of nanoparticles and their aggregates at a temperature above the melting point during interaction with pulsed laser radiation and suppression of resonant properties of liquid particles. We have shown that the results obtained with and without taking into account the melting factor differ dramatically. However, in mentioned study we did not have experimental evidence of suppression of surface plasmon resonance (SPR) in nanoparticles, and we used only calculated data based on the spectral dependences of the permittivity of the metal at temperatures above and below the melting point.

The features of melting of metal nanoparticles and associated processes are mentioned in a large number of papers. In particular, we can mention the papers [10, 11] devoted to models of interaction between plasmonic nanoparticles and radiation as well as to nonlinear optical properties, the paper [12] on measuring of optical constants for gold in thin films, the paper [13], describing reshaping and fragmentation of particles in laser fields, as well as the papers [14, 15] devoted to peculiarities of nanoparticle layer-by-layer melting at higher temperatures. The model presented in paper [15] allows one to estimate the thickness of liquid layer of metal in nanoparticle around a solid core for the given nanoparticle size at different temperature and the kinetics of a melting process.

It was found that the change of resonant properties of strongly heated and melted nanoparticles can significantly deteriorate their interaction with radiation and induce optical nonlinearity of nanocolloids and composite materials containing metal nanoparticles and their aggregates in

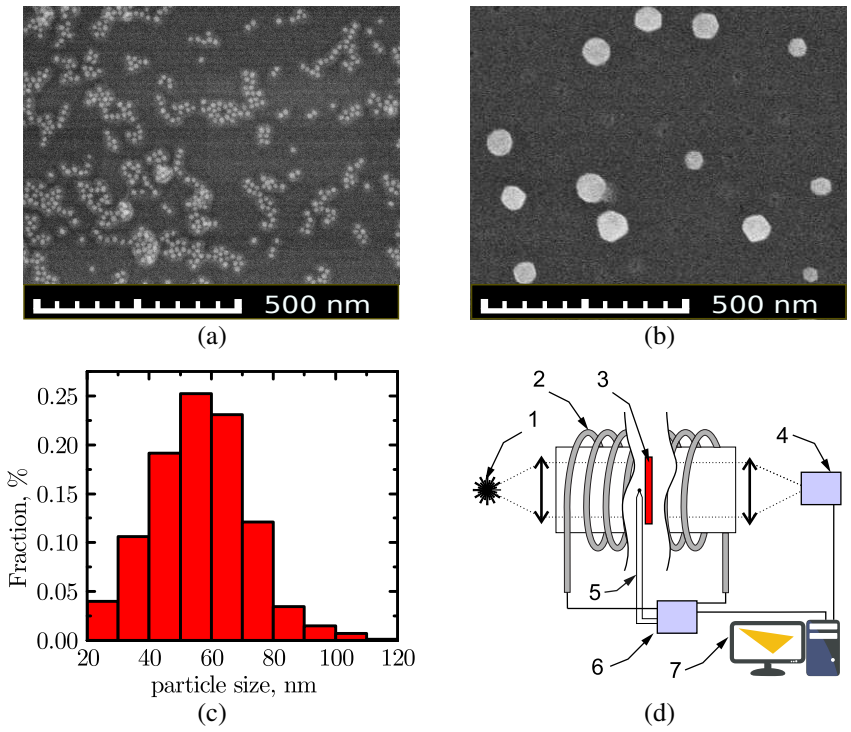

Fig. 1. SEM image of gold nanoparticles on the quartz substrate before (a) and after (b) first heating and cooling cycle in the furnace; (c) particle diameter distribution function after first heating and cooling cycle (averaged over several images); (d) experimental setup 1 — light source (250 W halogen lamp), 2 — heating element, 3 — sample, 4 — highspeed-spectrometer, 5 — K-type thermocouple, 6 — temperature controller, 7 — PC.

high intensity laser fields.

The goal of our work is to study experimentally the change of resonant properties of plasmonic gold nanoparticles in conditions of extreme heating and melting. Typical conditions for manifestation of such processes occur, particularly during interaction between nanoparticles and high intensity pulsed laser radiation.

We performed the experiment with a sample containing gold nanoparticles owing to their oxidation resistance compared to silver, copper and other plasmonic nanoparticles. Particles of 11 nm diameter were firstly deposited from Au hydrosol onto a quartz substrate in random positions with disordered and small fraction of highly ordered particle aggregates Fig. 1(a) shows Au nanoparticles on quartz substrate assembled during evaporation of water under the action of capillary and the van der Waals forces. Nanoparticles had the thiol adsorption layer as retarding agent to control coagulation rate. This adsorption layer provided minimum interparticle friction and contributed to formation of self-ordering structures. The choice of Au colloids with such particle size was arbitrary and the initial size was not critical: the particles could be larger or smaller than the value mentioned above to ensure the formation of particles of larger size ($\geq$ 50 nm) in the process of heating. At the second step the sample was slowly heated in the range from room (20 °C) to Au melting temperature ($\approx$ 1064 °C) for two hours in air. After the sample was heated up to 1100 °C and then slowly cooled for two hours, scanning electron microscopy (SEM) was applied to observe the sample structure, see Fig. 1(b). These observations indicate that closely spaced gold nanoparticles in small aggregates are merged, forming larger polydisperse particles with average diameter 56 nm (Fig. 1(c)) and in random positions. These

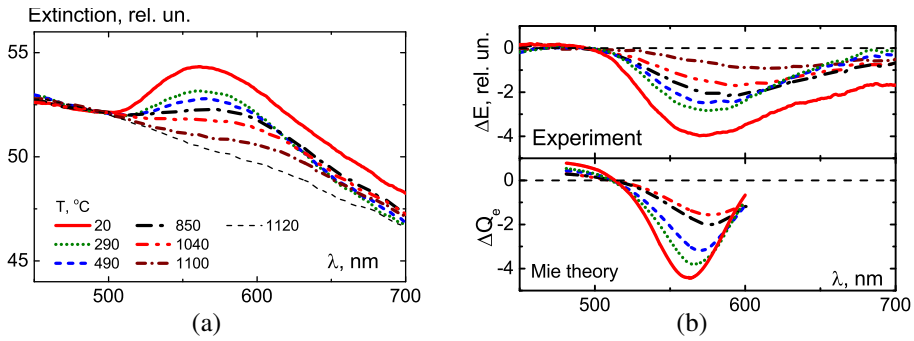

Fig. 2. (a) — experimental evolution of Au nanoparticle extinction spectrum and reduction of the amplitude of SPR from room to melting temperatures 20–1120 °C (see the legend); (b) — the same evolution of differential spectra and comparison with calculations based on the Mie theory using dielectric constants for gold at same temperature values. $\Delta E = E(1120°\mathrm{C}) - E(T)$ and $\Delta Q_e = Q_e(1064\ °\mathrm{C}) - Q_e(T)$.

nanoparticles did not undergo further changes during several heating cycles and did not merge into larger particles because large interparticle distance (see Fig. 1(b)) weakened the van der Waals attraction. It is confirmed by similar extinction spectra for different heating cycles after annealing. At the final stage the extinction spectrum of 2D sample was studied at different temperatures in the range 20–1120 °C. It is notable that in our case, the absorption factor in the extinction is dominant.

Figure 1(d) shows the experimental setup with the furnace to heat the sample. The furnace is made from 40 mm quartz pipe with a nichrome wire around it. We used a mullite wool for heat insulation that filled the space between the pipe and steel shell. The substrate was placed freely in the center of the cell without mechanical clamping.

A pulse width modulation (PWM) power controller was used to control the temperature of the sample with custom software. Actuating signals were generated by a National Instruments USB-6210 multi-function DAQ. The K-type thermocouple was installed in the vicinity of the sample surface. The collimated light beam from a halogen lamp was passed through the input and output apertures at the ends of the quartz pipe, and through the sample between them. The light was analyzed by a high-speed spectrometer Ocean Optics HR4000 UV-NIR.

Figure 2(a) shows the main result of our work — the evolution of the extinction spectrum near the band of SPR of the Au nanoparticles upon temperature growth of the sample — from room temperature (20 °C) and beyond the melting point (1064 °C) to 1120 °C. Figure 2(b) demonstrates the evolution in the differential extinction spectra at intermediate stages of the heating process (see the caption to Fig. 2(b)). This figure shows that when the temperature of the sample grows, the amplitude of the plasmon absorption peak gradually decreases towards complete suppression of SPR (Fig. 2(a)). Figure 2(b) shows a comparison of the difference between spectra at high temperature beyond the melting value and the ones at lower temperatures down to 20 °C obtained in experiments and calculations.

With the increase of a particle temperature, the amplitude of phonon oscillations grows. As a result, the rate of scattering of electrons by phonons grows too, which leads to an increase of the electron relaxation constant (above the Debye temperature the electron relaxation grows in proportion to the first power of temperature) [16]. The absence of periodic structure in a lattice of melting nanoparticles leads to additional scattering of the conduction electrons on the lattice defects. The process of melting is thus accompanied by an abrupt increase of the relaxation constants (Γ), which depends, beside electron-phonon and electron-electron coupling, on electron scattering at defects of crystal lattice — vacancies, dislocations, grain boundaries [17]. The

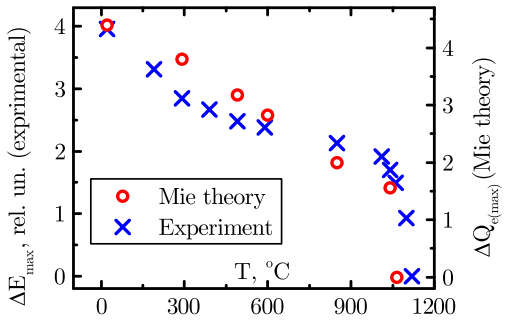

Fig. 3. Temperature dependence of SPR amplitude of Au nanoparticles in experiment ΔE_{max} and in calculations $\Delta Q_{e(max)}$.

dependence of dielectric constant (ε) on temperature (T) qualitatively follows from the Drude formula where ε is the function of $\Gamma(T)$.

The calculations were performed using standard Mie theory [18] with the dependence of scattered and inner fields on the radius of an ideal spherical particle and relative dielectric constants of its material. The experimentally obtained dielectric constants for gold [19, 20] has been modified taking into account the finite size effect in nanoparticles according to the conventional approach [1, 21].

Note that in calculations, we employed experimental values of dielectric constants for liquid gold [19]. The long wavelength (600 nm) and the temperature (1064 °C) limits in the calculated spectra Fig. 2(b) correspond to available experimental data of the dielectric constants for gold at high temperatures [19]. The effect of reshaping of liquid nanoparticles on their optical properties [13] in these conditions is not observed in the extinction spectrum which is recovered after each cooling. Averaging of spectral dependences was carried out according to the size histogram in Fig. 1(c) and the following expression:

$$Q_e(\lambda, T) = \left[\sum\nolimits_i Q_{e,i}(\lambda, T, R_i)\mu_i R_i^2\right] / \left[\sum\nolimits_i \mu_i R_i^2\right],$$

where μ_i is the fraction of particles whose radius R_i falls within the range $R_i \pm \Delta R$ (see Fig. 1(c)), $Q_{e,i}$ is the extinction efficiency $Q_{e,i}(\lambda, T, R_i) = \sigma_e(\lambda, T, R_i)/(\pi R_i^2)$, $\sigma_e(\lambda, T, R_i)$ is the dimensionless extinction cross-section of one particle with radius R_i [21], and T is the temperature of the particles.

The tendencies in variations of the amplitude of surface plasmon resonance (or in alternative terminology the Mie resonance) in experimental and calculated spectra are similar, see Fig. 2(b). FWHM of SPR in experimental curves is wider than in calculated ones that can be related to imperfections of the nanoparticle surface, its nonsphericity with the presence of crystallographic facets (Fig. 1(c)) and adsorbate on the surface, which result in broadening of the SPR when averaging over the ensemble.

Figure 3 shows the dependence of the amplitude of SPR (its changes) in extinction spectrum on the particle temperature. We can see that the amplitude decreases slowly up to a temperature of 850 °C. A further increase of the temperature leads to a significant and rapid downturn of this curve at temperatures higher than 1010 °C which can be explained by approaching to the melting temperature of nanoparticles (≈ 1064 °C). The observed effect was reproduced in several heating cycles.

Temperature reduction of the resonance amplitude was demonstrated in paper [22], but in the temperature range below the onset of melting of Au nanoparticles or slightly above for particles in nanocomposite films with Au nanoparticle radii 2, 8 and 15 nm [23]. We should note that for

these radii a considerable contribution of finite size effect to extinction spectra can obscure the contribution of heating and melting.

In comparison to [22] and [23] in our case, an employment of larger particle size allows one to provide the conditions with dominant influence of heating and phase transition in nanoparticles on their plasmonic spectra. Note that in [22] and [23], the finite size effect significantly changes both the spectra and melting point temperature [24]. An important distinction between our results and paper [23] is the maximum heating temperature in our case was slightly above the melting point (by 50 °C higher than in [23]). Only in these conditions we observed full suppression of SPR.

Thus, we can see that changes in optical properties of the particle material due to melting is an important factor in the process of interaction between nanoparticles, their aggregates, and laser radiation.

To conclude, we have presented experimental evidence for strong suppression of SPR in gold nanoparticles during heating and subsequent transition to the liquid state. The gold nanoparticles were chosen for demonstration of these experiments due to their high chemical resistance in contrast to silver, copper and other plasmonic metals. Obviously, the same pattern can be expected to occur during heating and melting of the other plasmonic nanoparticles as well.

Taking into account the experimentally observed effect, theoretical models earlier described in papers [1, 4, 7, 8, 18] for interaction between optical radiation and plasmonic nanoparticles require corrections for high temperature conditions. Thus, the factor of particle melting is critically important in a wide range of phenomena concerning interaction between nanoparticles and high intensity pulsed laser radiation. This factor, was first taken into account in our paper [9], however we had no experimental evidence of its real manifestation which may occur when using optical radiation of pulsed lasers or when nanoparticles are placed in a heated environment, for example in high temperature metal aerosols. In such cases, there is a sharp deterioration of the resonant properties of metal nanoparticles at the frequency of SPR when their aggregation state is changed. In high temperature metal vapors containing aerosol component the detection of nanoparticles by spectral methods may be difficult because of suppressed SPR, despite light transmission is accompanied by scattering.

We believe that the presented results have a general bearing on interpretation and use of plasmonic spectroscopy in applications where local heating effects can be anticipated. For instance the observed effect may underlie nonlinear optical responses of nanocolloids and composite materials containing plasmonic nanoparticles and their aggregates, it can affect optical limiting systems etc. The detailed analysis of the impact of the relaxation processes in the electronic subsystem of nanoparticles on their resonance properties will be published elsewhere.

Acknowledgment

This work was performed within the State contract of the RF Ministry of Education and Science for Siberian Federal University for scientific research in 2014–2016 (Reference number 1792) and SB RAS Program No II.2P (0358-2015-0010). The numerical calculations were performed using the MVS-1000 M cluster at the Institute of Computational Modeling, Siberian Branch, Russian Academy of Sciences.