Shaping nanoparticles with laser light: a multi-step approach to produce nanoparticle ensembles with narrow shape and size distributions

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Abstract. In this paper we present a multi-step laser tailoring process in order to narrow the size distribution of self-assembled supported metal nanoparticles. The method exploits the shape and size dependent optical absorption coefficients of metal particles. Silver nanoparticles were prepared by deposition of atoms on dielectric substrates followed by diffusion and nucleation. This results in ensembles of oblate nanoparticles with broad size and shape distributions. Post-growth irradiation allows tailoring the average size of the nanoparticles by laser-induced surface diffusion and evaporation of surface atoms of the nanoparticles. This makes it possible to shrink large particles to the desired size and remove all nanoparticles that are too small. We demonstrate here that the size distribution of silver nanoparticles can be narrowed significantly by subsequently applying different laser wavelengths.

1. Introduction

Due to their potential technological applications, metal nanoparticles (NPs) have been the subject of a great variety of experimental and theoretical investigations [1-3]. Especially the optical properties of noble metal NPs are of general interest because the optical spectra are dominated by excitations of collective oscillations of the conduction band electrons, i.e. surface plasmon polaritons. This resonance plays an important role in many future applications such as optical waveguides [4], surface-enhanced Raman scattering [5] or biosensors [6]. NPs of a certain size and/or shape are needed for optimum performance in these applications. Therefore, post-growth treatment of NPs with laser light in order to tailor the NPs size and shape has found great interest [7-12]. In this paper, we describe recent experiments using tunable laser light to narrow the size distribution of supported silver NPs in a multi-step process with different wavelengths.

In brief, the method works as follows: The NPs are prepared by deposition of atoms with subsequent surface diffusion and nucleation on dielectric substrates, i.e. Volmer-Weber growth. In general, the fabricated NP ensembles exhibit broad size and shape distributions with standard deviations around 30% [13]. Using absorption of laser light with subsequent release of thermal energy provides the possibility of heating metallic NPs selectively, due to the shape dependent absorption cross section dominated by the surface plasmon resonance (SPR). In the size regime studied here, i.e. between 2 nm and 20 nm, the resonance frequencies are determined only by the shape of the NPs [3]. During the decay of the SPR the absorbed photon energy rapidly heats the excited NPs selectively which causes evaporation of atoms from their surfaces [14,15]. Thus, the excited NPs shrink in size [10,16-18], and the shape of the NPs is altered due to diffusion of surface atoms. Taking into account the pronounced dependence of the shape on the size of the NPs [14], irradiation with laser pulses of a given photon en-
energy makes it possible to excite NPs of undesired sizes selectively, in order to shrink them in size or to remove them completely from the substrate surface. These processes proceed until the NPs do not interact anymore with the laser light. As presented in a previous publication [8], the size distribution narrows significantly if two appropriate laser frequencies are applied. In contrast to these earlier experiments, we demonstrate here that irradiation of NP ensembles with six different laser frequencies results in optimized tailoring and enables us to narrow the size distribution of the NPs very selectively.

2. Experimental

All experiments are conducted at room temperature in an ultrahigh vacuum (UHV) system with a base pressure of $p = 2 \times 10^{-8}$ mbar. The NPs are prepared on quartz substrates and have the shape of rotational ellipsoids [19]. Therefore, they are characterized by two parameters: the axial ratio $a/b$, $a$ being the short and $b$ the long axis, and the equivalent radius $R_{eq}$ which is the radius of a sphere with the same volume as the actual NP. For example, deposition of $1.0 \times 10^{16}$ atoms/cm$^2$ leads to Ag NPs with a number density of $1.8 \times 10^{11}$ cm$^{-2}$, fig. 1(a), a mean equivalent radius of $<R_{eq}> = 6$ nm and a standard derivation of the size distribution of about 30%, fig. 1(b). The mean shape of the NPs is determined by optical extinction spectroscopy and the comparison to theoretical spectra, calculated with electrodynamic theory in the quasistatic approximation [20]. In the size range studied here the extinction is identical to the absorption, scattering being negligible [3]. The optical spectra are measured with the light of a Xe-arc lamp (Osram, XBO 450 W/1) combined with a monochromator (AMKO, 1200 lines/mm, blaze: 220 nm). The angle of incidence is $45^\circ$ with respect to the substrate surface normal.

3. Results and Discussions

Due to the growth process, larger NPs have a pronounced oblate shape. Hence, two plasmon modes can be excited in the NPs if p-polarized light is used [3]; a high-energetic (1,0)-mode corresponding to an electron oscillation along the short axis and a low-energetic (1,1)-mode corresponding to an electron oscillation along the long axis of the NPs. Due to the growth kinetics, the axial ratio of the NPs drops off if they increases in size. The change of the axial ratio results in a shift of the (1,0)- and (1,1)-mode to higher and lower photon energies respectively. If s-polarized light is used only the (1,1)-mode can be excited. Furthermore, the optical spectra are inhomogeneously broadened because of the
size and shape distribution of the NPs on the substrate. This inhomogeneous broadening is exploited in our experiments for selective excitation.

For the laser treatment, the NPs are irradiated with nanosecond laser pulses generated by an optical parametric oscillator (Spectra Physics, Quanta-Ray MOPO-730) and a sum frequency generation unit (Sirah Auto-FCU) which are pumped with a Nd:YAG-laser (Spectra Physics, Quanta-Ray Pro-230). The pulse duration is about 5 ns and the repetition rate 10 Hz. The laser frequency is tunable in the range between 0.7 eV and 4 eV. The angle of incidence is perpendicular to the substrate surface.

![Figure 3](image_url)

**Figure 3.** Extinction/absorption spectra of Ag nanoparticles ensembles before and after irradiation by two-step (a) and multi-step laser tailoring (b), recorded with s-polarized (a) and p-polarized light (b), respectively. See text for details. The spectra are typical examples of our measurements. We also find that the polarization does not affect the narrowing.

With the objective to optimize the narrowing process, the absorption coefficients have been calculated (fig. 2) for the NP ensemble presented in fig. 1(a). We computed the absorption cross section for six different photon energies (i.e. for six different NP sizes) used in the tailoring experiments (fig. 3(b)), considering the abundance for the different sizes. As can be seen in fig. 2, tailoring is ideal for large oblate NPs because of the narrow absorption cross sections. For small NPs tailoring is more difficult since spherical NPs do not exhibit a sharp plasmon resonance. However, tailoring is possible as we will show in the following.

In order to demonstrate the improvement of the tailoring by using a multi-step laser process, two identical samples of Ag NPs with $<R_{eq}> = 6$ nm have been prepared. Sample A was treated with only two different laser frequencies at high fluence while sample B has been irradiated subsequently with six different laser frequencies at low fluence. Fig. 3(a) depicts the extinction/absorption spectra of sample A, before and after laser irradiation with 1000 pulses of $\nu = 3.3$ eV and 2.8 eV, at a fluence of $\phi = 150$ mJ/cm$^2$. A clear narrowing of the line width of the SPR from 0.83 eV to 0.52 eV (FWHM) as well as a significant reduction of the extinction amplitude from 37% to 23% (fig. 3(a)) is observed. To relate these results to the morphological changes we have performed atomic force microscopy measurements (Thermo-Microscopes, Autoprobe CP, AP-0100) before and after laser irradiation (fig. 1(a) and (c)). The analysis of the microscope images reveals a drastically improved size uniformity and a reduction of the width of the size distribution from 27% to 14% which is associated with the reduced line width. Additionally, the mean size of the NP ensemble decreases from $<R_{eq}> = 6$ nm to 5 nm which explains the drastic decrease in the extinction amplitude due to the evaporation of a significant amount of Ag. The reason for such high evaporation rate is that for high fluences NPs not fully in
resonance with the laser frequency still absorb enough energy to induce evaporation of atoms. This leads to a significant overall decrease of the extinction.

In order to obtain nearly the same reduction of the line width for sample B as for sample A, sample B has been irradiated subsequently with 1000 pulses of six different laser frequencies of $h\nu = 3.5, 3.4, 3.3, 2.6, 2.5$ and $2.4 \text{ eV}$ at a low fluence of $\phi = 60 \text{ mJ/cm}^2$ (fig. 3(b)). Again, we observe a clear reduction of the line width from 0.83 eV to 0.57 eV (FWHM). More importantly, almost no reduction of the extinction amplitude is seen. This is in contrast to the results obtained with only two laser frequencies at high fluence. The reason therefore is that for low fluences only NPs fully in resonance with the laser light absorb enough energy to be efficiently tailored. Thus, by using low fluences and applying different laser frequencies in subsequent steps only those NPs fully in resonance with the laser light are effectively heated, making the tailoring process more selective.

Although the morphological characterization is still in progress, the optical spectra of fig. 3(b) can be used to extract information about the narrowing process. In general, the line width of a single resonance is caused by the homogeneous line broadening arising from the finite decay time of the plasmon. Because of the broad size distribution of the initial NP ensemble an inhomogeneous broadening can be seen which dominates the optical spectra [3,12,21]. Therefore, a change of the line width of the resonance directly reflects modifications of the NP size and shape distributions. Thus, comparison of the optical spectra of sample A and B provides information about the narrowing of the size distribution. Since the reduction of the line width for both samples is very similar, we conclude that the size distribution of sample B has been decreased to a similar value as compared to sample A, i.e. to approximately 14%.

4. In Conclusion
We have shown that narrowing the size distribution of NP ensembles can be significantly improved by applying successively different laser frequencies at low fluences in a multi-step tailoring process. Using additional laser frequencies closer to the center frequency of the SPR, this holds the promise of narrowing the size distribution to approximately 5%.

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