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Self-influence of a femtosecond laser beam upon ablation of Ag in liquids

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ABSTRACT Formation of nanoparticles of either Au or Ag is reported under ablation of metallic targets exposed to radiation of a femtosecond Ti:sapphire laser (wavelength of 810 nm, pulse width of 120 fs) in either water or ethanol. Nanoparticles are characterized by UV-visible spectroscopy and transmission electron microscopy. Nanoparticles of Ag are several times smaller than those of Au at otherwise equal conditions. The effect is attributed to the self-influence of a laser beam via generation of the second harmonics of the laser radiation on Ag clusters and its good matching to the plasmon resonance of Ag.

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Formation of nanoparticles by laser ablation of solids in a liquid environment has attracted much attention during recent years [1–15]. This way of generation of various nanoparticles, either metallic [1–14] or semiconductor quantum dots of CdS or ZnSe [15], is an alternative to the well-known chemical way and is characterized by relative simplicity of the experimental setup. Moreover, nanoparticles produced by laser ablation of solid targets in a liquid environment are free of any counter-ions or surface-active substances. At sufficiently high peak power of laser radiation the generated nanoparticles can effectively interact with the laser radiation, which leads to a shift of their size distribution towards smaller size under laser exposure [3, 6, 14]. Fragmentation (splitting) of nanoparticles occurs due to their melting and further interaction with surrounding high-pressure vapor of the liquid. Splitting of nanoparticles occurs due to hydrodynamic instabilities, e.g. asymmetry of the vapor shell that surrounds them. The smaller the size of the particle, the higher the laser fluence required for its melting and subsequent fragmentation. At a given value of the laser fluence, the fragmentation of nanoclusters stops as soon as the majority of nanoparticles become too small to absorb the energy sufficient for their melting from the laser beam. The molten nanoparticle is stabilized by the surface tension, and in first approximation the stability condition can be expressed as follows: $2\sigma/R \sim p_{\text{liq}}$, where σ stands for the coefficient of surface tension of the melt, R is the particle radius, and p_{liq} is the pressure of vapor of the liquid surrounding the particle. For noble metals, e.g. Au or Ag, the melting temperature is about 1000 °C, and in the case of water as surrounding liquid $p_{\text{liq}} \sim 1$ kbar. The temperature of the nanoparticle is determined by the peak power of the laser beam, its geometrical cross section, and by the spectral dependence of the extinction coefficient $k = k(\omega)$. Far from resonance k is close to that of the bulk metal, while in the vicinity of the plasmon resonance $\omega \sim \omega_{\text{p}}$ the spectral dependence of $k(\omega)$ is described by the well-known Lorentzian profile [9]. Therefore, the closer the laser frequency to the plasmon resonance, the higher the temperature of nanoparticles at otherwise equal conditions.

The presence of nanoparticles in a liquid contributes to its dielectric function and may result in non-linear (intensity-dependent) behavior of the liquid due to a high value of the third-order non-linear susceptibility $\chi^{(3)}$ typical for metal nanoclusters, leading to non-linear lensing. Another type of self-influence may arise under non-linear transformation of the frequency of the laser beam in the colloidal solution of nanoparticles. The transformed laser beam may be closer to the plasmon resonance of the nanoparticles and therefore be absorbed by them more than the initial beam. For instance, formation of nanoparticles in the liquid under laser ablation of a metal target may alter the frequency of the laser beam due to second-harmonic generation (SHG). The efficiency of this process is high for pulses with high peak power, e.g. for femtosecond laser pulses. We report this effect for the first time for Ag nanoparticles produced by ablation of an Ag target in liquids (water, ethanol) using femtosecond laser pulses. Good matching of the SHG radiation to the plasmon resonance of Ag nanoclusters leads to a striking difference in their size distribution compared to nanoparticles of another metal, e.g. Au, produced in similar experimental conditions. Different experimental observations support this phenomenon.

The experimental setup used for generation of metal nanoparticles by laser ablation in liquids is described elsewhere [13–15]. Briefly, all the ex-

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periments were carried out using a 810-nm output of a Ti:sapphire laser. The repetition rate of the laser was 1 kHz. The average energy per pulse was 500 µJ on the sample at a pulse width of 120 fs. Laser radiation was focused onto the metallic target placed horizontally in a Pyrex cell to a spot size of ∼ 100 µm through a thin (several mm) layer of liquid. The total volume of liquid in the cell was about 2 ml, and a typical exposure time was about 10 min. The cell was displaced under the laser beam during exposure. Two kinds of liquid were used as the surrounding medium, either ethanol or de-ionized water. In some cases polyvinylenepyrrolidone (PVP), molecular mass of 10^{-4}, was added at a concentration up to 2 g/100 ml. Ablation of the Ag target is accompanied by intense eye-visible blue emission observed through the transparent bottom of the glass cell. The intensity of this emission increases with exposure time. In a few minutes of exposure the 810-nm laser radiation almost completely disappears, while the blue light reaches its maximum intensity. The blue emission is merely different from a white continuum radiation that is observed in liquids under exposure to femtosecond laser pulses. Express measurements with a simple spectrometer indicate that this blue emission corresponds to the second harmonic of the Ti:sapphire laser with a wavelength of 405 nm.

The generated nanoparticles were characterized by the UV-visible absorption spectrum of the liquid (Cary spectrometer) and with a transmission electron microscope (TEM). The absorption spectra of both Ag and Au nanoparticles in the solution are typical for these metals [1–15]. Both types of nanoparticles show the plasmon absorption bands in the visible spectrum at 520 and 400 nm for Au and Ag, respectively (Figs. 1, 2). Note the blue shift of the plasmon frequency of Ag nanoparticles with the increase of exposure time (Fig. 2), which is characteristic for decrease of their size. The shape of the metal nanoparticles is disk-like, as has been reported recently for ablation with a 20-ns laser pulse in water for both Ag and Au [13]. TEM images show a striking difference in the size distribution of nanoparticles of these two metals. The size distribution of Ag nanoparti-

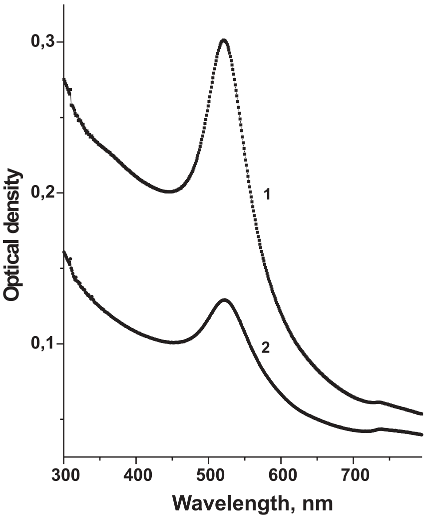

FIGURE 1 Absorption spectrum of colloidal solution of Au nanoparticles generated in water by ablation with a Ti: sapphire femtosecond laser. 1 – ablation of Au target in pure water, 2 – ablation in water with addition of PVP (0.1 g/l)

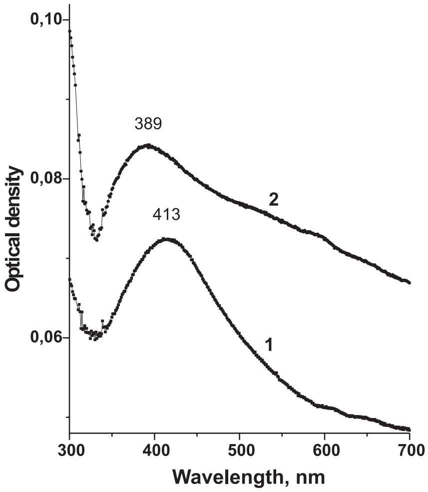

FIGURE 2 Absorption spectra of Ag nanoparticles generated by ablation of an Ag target in water. 1 – 5 minutes of exposure, 2 – 10 minutes of exposure

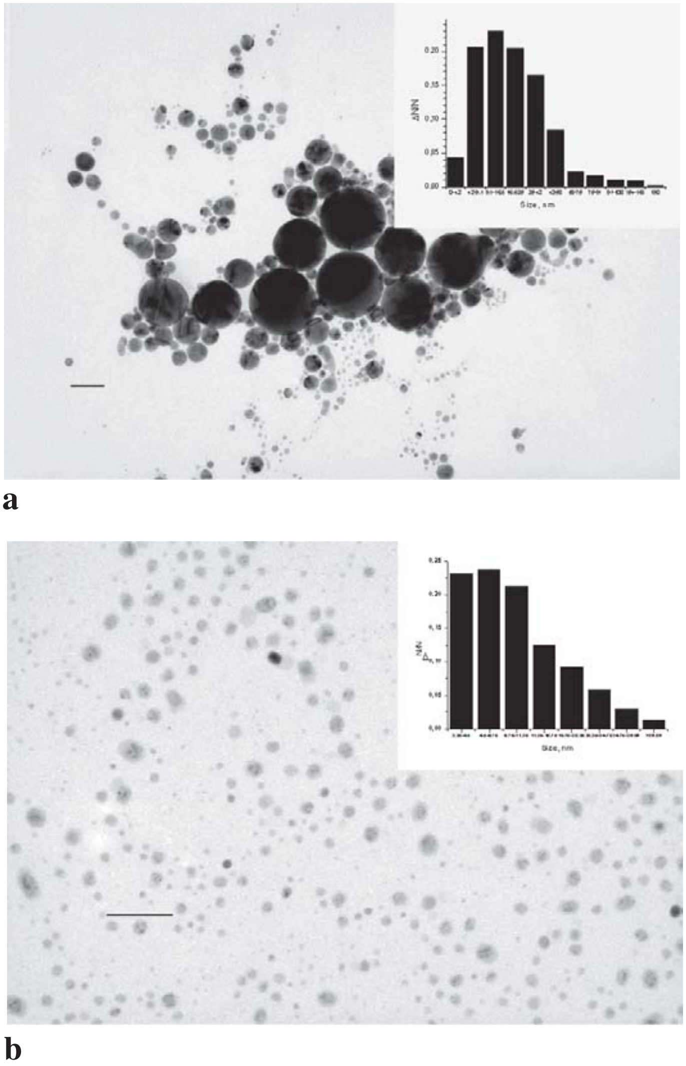

FIGURE 3 TEM view of Au (**a**) and Ag nanoparticles (**b**) obtained by ablation of corresponding metals in water. Scale bar denotes 100 nm. *Insets* show size distributions that are calculated over 550 (Au) and 760 (Ag) particles. Average size of Au nanoparticles is about 12 nm, while that of Ag is 5 nm

cles is merely shifted to smaller particle size compared to Au. The TEM views and distributions are shown in Fig. 3. Namely, the maximum of the size distribution function for Au particles lies between 9 and 16 nm, while for Ag nanoparticles it is centered between 4.6 and 6.4 nm. Moreover, there are quite a number of even smaller Ag particles, whose size is at the limit of the TEM resolution.

We suggest that the difference in size distribution is due to the self-influence of femtosecond laser radiation via frequency doubling on metal nanoclusters. First, the initial 810-nm laser radiation produces metal nanoclusters by ablation of a solid target immersed in liquid. Second, a highly efficient second-harmonic generation transforms the initial laser wavelength of 810 nm to 405-nm radiation. The latter fits well to the plasmon resonance of Ag nanoparticles. Therefore a good coupling of the second harmonics to the plasmon frequency of Ag nanoparticles leads to better energy transfer of the laser pulse to the nanoparticles. This results in the increase of temperature of smaller Ag nanoparticles and therefore leads to their splitting and to the increase of their density. Note that for Au nanoparticles the second harmonics are not so effectively coupled, and thus positive feedback is not realized.

The effect of SHG on small metal clusters is well documented in the literature [16–19]. Despite the small size of metal clusters compared to the laser wavelength, SHG can be very effective due to their high density, so that the conditions of spatial synchronism are are easily fulfilled. The peculiar feature of SHG with a femtosecond laser in a liquid is a relatively small length of coherence for SHG that cannot exceed the length of the light pulse in the medium, which is about 30 μm. Several models that account for the high value of the second-order non-linear susceptibility $\chi^{(2)}$ and for efficient generation of the second harmonics are proposed. This is assigned to the quantum size effect for wave functions of electrons in a small sphere, which gives rise to quadruple oscillations and, consequently, to non-zero $\chi^{(2)}$ even for nanoparticles with a center of symmetry. The exact mechanism of SHG remains to be elucidated. The present communication points out the fact that this generation can be responsible for self-influence of a laser beam with high peak intensity upon initiation of ablation in liquids. The scenario we propose to explain the phenomenon is as follows. The initial laser radiation of 810 nm produces metal clusters upon exposure of the metal target immersed in a liquid. A significant portion of the laser radiation is frequency doubled on these clusters. In the case of Ag clusters the second harmonic (405 nm) perfectly fits their plasmon resonance (see Fig. 2). This causes the further fragmentation of the Ag nanoclusters and increases their concentration. The latter, in turn, leads to an increase of the second-harmonic intensity, and so on. The absorption of laser radiation increases thus in an avalanche-like way. As soon as the nanoparticles become very small, their melting and possible fragmentation are facilitated by a decrease of melting temperature with decrease of size [20–23]. The cascade generation of higher harmonics as well as frequency summing on Ag nanoparticles is not excluded and requires further studies.

It is worthwhile mentioning that the situation with a Ti:sapphire laser and Ag clusters is not unique. Indeed, SHG on Au clusters of a Nd:YAG laser (wavelength of 1060 nm) would result in a very good coupling to the plasmon frequency of these nanoparticles (520–530 nm depending on the surrounding liquid). Therefore, one should expect a similar difference in size distribution between Au and Ag nanoparticles upon ablation of metals by sufficiently powerful 1.06-μm laser radiation of picosecond or femtosecond range, but this time Au nanoparticles should be much smaller than Ag ones.

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