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Production of copper and brass nanoparticles upon laser ablation in liquids

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Abstract. The production of nanoparticles upon ablation of copper and brass by pulsed radiation from Nd: YAG and copper lasers in water, ethanol, and acetone is studied. The nanoparticles were investigated by the methods of X-ray diffractometry, optical spectroscopy, and transmission electron microscopy. The produced copper and brass nanoparticles were shown to exhibit a plasmon resonance lying in the visible spectral range near 580 and 510 nm. The brass nanoparticles produced by ablation in ethanol have a shell approximately 10-nm thick for an average dimension of 20–30 nm. A chemical modification of ethanol was observed, which manifested itself in the appearance of intense UV absorption bands. Upon laser irradiation of brass nanoparticles in a liquid their absorption spectrum gradually transformed into the spectrum of copper nanoparticles.

Keywords: laser ablation, nanoparticles, plasmon resonance.

1. Introduction

Laser ablation of solids embedded in a liquid is an alternative technique of producing diverse nanoparticles [1-10]. Chemical methods for producing nanoparticles, metallic in particular, are well known. However, apart from the nanoparticles resulting from reducing reactions or ion exchange, the liquid always contains other ions and reaction products, which are impossible to separate from the liquid. The laser ablation of solids in liquids is basically free from this limitation, because nanoparticles in this case are produced owing to the mechanical interaction of dense vapour of the liquid with the molten layer on the target surface. Of course, this does not eliminate the chemical interaction of the nanoparticles with the ambient vapour of the liquid, which is especially efficient for an elevated target temperature during the laser pulse. On the other hand, in nearly all practical cases it is possible to select the liquid which minimises the above chemical interaction.

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Received 7 July 2004 *Kvantovaya Elektronika* **34** (10) 951–956 (2004) Translated by E.N. Ragozin The nanoparticles produced in the course of laser ablation may heat up in the laser beam during the pulse. The nanoparticle temperature is proportional to the peak power of laser radiation and its effective absorption cross section decreases as the laser radiation frequency is detuned from the free-carrier plasmon resonance frequency of the metallic nanoparticle [11].

In some cases, the chemical nanoparticle-liquid interaction in laser ablation may lead to a modification of their physicochemical properties. The rate of this interaction varies strongly in the course of laser ablation. The hot nanoparticles ejected from the target during the laser pulse may efficiently interact with the vapour of the surrounding liquid, but this interaction terminates abruptly with a temperature decrease upon completion of the laser pulse. The newly formed colloidal solution continues to interact with gases dissolved in the liquid, for instance with atmospheric oxygen. The rate of such oxidation at room temperature is low, but the oxidation effect may be quite significant because the specific nanoparticle surface is large. Somehow or other, the products produced as a result of the chemical interaction may significantly change the morphology and optical properties of the colloidal solution. The majority of papers known to date are concerned with noblemetal nanoparticle production by laser ablation in a liquid. In this case, the interaction of resultant nanoparticles with the liquid as well as with the gases dissolved in the liquid is minimised. A greater diversity of nanoparticles may be generated in the ablation of targets made of chemically more active metals. For instance, in the laser ablation of titanium in a liquid it is possible to obtain the nanoparticles of titanium itself, titanium carbide, or titanium oxide by selecting the liquid in which the ablation takes place [8].

Copper nanoparticles possess, like gold and silver nanoparticles, a plasmon resonance in the visible spectral range [12]. Unlike the nanoparticles of these noble metals, the chemically synthesised copper nanoparticles are easily oxidised by atmospheric oxygen dissolved in the liquid, and the pronounced peak of plasma absorption vanishes [13, 14].

The diversity of reaction products and hence the different composition of nanoparticles produced by laser ablation may also be related to the specific catalysis of one or other reaction. The information on such catalytic processes is hardly available, because they can occur at temperatures close to the melting temperature of the target material, i.e. for 800–1000 °C. By and large, the problem has been poorly studied, and the aim of our work is to partly fill this gap. We investigate the production of the nano-

particles of copper and its alloy (brass) in the laser ablation in different liquids. Two laser sources are employed for this purpose: a copper vapour laser and an Nd: YAG laser. The wavelengths of these lasers are located at different distances from the plasmon resonance of copper nanoparticles, and therefore the properties of nanoparticles (such as size and morphology) are likely to depend on the wavelength of initiating radiation.

2. Experimental

The experimental technique for generating nanoparticles by laser ablation of solids immersed in a liquid was described in detail earlier [8–10]. Electrolytic copper and brass were employed as the targets. The composition of brass was determined with the aid of characteristic X-ray radiation occurring under exposure to the beam of a scanning electron microscope. The target consisted primarily of copper and zinc, the content of zinc amounting to 40 %, with insignificant iron and lead dopants.

Two laser sources were employed to obtain metallic nanoparticles. The first was a repetitively-pulsed Nd: YAG laser emitting 1.06- μ m, 130-ns pulses. The pulse repetition rate could be varied from 1 to 5 kHz; the average output power depended on the repetition rate and pump current and amounted to \sim 5 W. The radiation was focused on the surface of a metal target to a spot 60 or 90 μ m in diameter; the at-target fluence was 20–50 J cm⁻², depending on the lens selected.

The second source was a 0.511-µm copper vapour laser emitting 20-ns pulses with a pulse repetition rate of 7.5 kHz, and an average power up to 3 W. In this case, the average energy density at the target surface was about 30 J cm⁻². The laser radiation was focused on a 1–2 mm thick metal target covered with a layer of the selected liquid. The cell with the liquid was placed on a computer-controlled translation stage, which moved the target under the laser beam in order to avoid the formation of a deep crater in the target. In several cases, the ablation was carried out in a thin liquid layer flowing above the target to reduce the optical thickness of the resultant colloidal solution; the flow velocity was typically equal to several centimetres per second.

The following technique was used to investigate the effect of laser radiation on the colloids obtained upon ablation of the corresponding targets. The laser radiation was focused with an objective onto the interface between the colloid and the horizontal glass substrate, which was the bottom of the cell; the focal spot was approximately 60 µm in diameter. The glass cell with the colloid and the substrate was placed on a computer-controlled translation stage, which moved the cell to achieve uniform irradiation. As a rule, the laser beam energy density used in this case was higher than in the target ablation (up to 50 J cm⁻²).

For a liquid in which the ablation of targets was carried out, use was made of distilled water, ethanol (95%), and ultra-pure acetone. Several experiments were made employing diethyleneglycol as the ablation medium; however, a high nanoparticle density was hard to achieve in this case owing to its high viscosity. The spectra of colloidal solutions produced by ablation in the above liquids were recorded with the aid of a fibre-optic spectrometer in the 200–850 nm range. X-ray diffraction patterns of the nanoparticles were recorded after evaporating the colloidal solution on a glass substrate. The crystallographic forms were identified

employing the JCPDS-ICDD database. The nanoparticle morphology was investigated using a transmission electron microscope with an electron energy of 100 keV. For this purpose, the colloidal solution was diluted with ethanol to the requisite nanoparticle density and evaporated on a copper mesh covered with a carbon membrane. In several cases, the nanoparticle composition was investigated by Raman spectroscopy (for an excitation wavelength of 514 nm).

3. Results

3.1 Copper nanoparticles

The ablation of a copper target in ethanol and acetone by the radiation of both the visible and IR laser sources had the effect that the liquid acquired a reddish colour. To this colour there corresponds an absorption peak near 590 nm and a broad absorption band in the blue region (Fig. 1). This shape of absorption spectrum is typical of copper nanoparticles synthesised both by chemical methods and by laser ablation under anaerobic conditions [13, 14]. The absorption spectrum of the water in which the ablation of a copper target was carried out has a different appearance. The peak near 590 nm is absent, and only a broad absorption band is observed between 600 and 700 nm. This absorption band is typical for the aquaion of univalent copper. Indeed, the resultant absorption spectrum of the aqueous solution of CuCl is characterised by the same

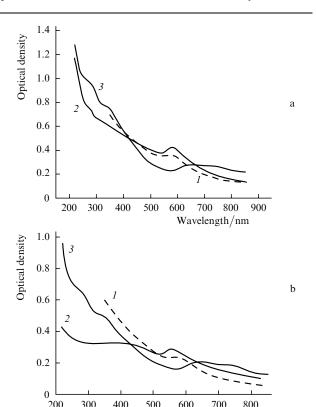


Figure 1. Absorption spectra of the colloidal solution of nanoparticles produced by the ablation of a copper target with the radiation of a copper vapour laser for a laser beam fluence at the target of 30 J cm⁻² (a) and with the radiation of an Nd:YAG laser for a fluence of 20 J cm^{-2} (b) [(1) - acetone, (2) - ethanol, (3) - water].

Wavelength/nm

absorption band. Copper nanoparticles are therefore not produced in the ablation of a copper target in water, and copper itself reacts with water to form compounds of univalent copper. By and large, the spectra of liquids in which the ablation of copper was carried out with an Nd:YAG laser are similar. In particular, the plasmon resonance peak of copper nanoparticles is also observed in the ablation in ethanol and acetone (Fig. 1b). Like in the initiation of ablation by the radiation of a copper vapour laser in water, only the peak of univalent copper is present. On the other hand, distinctions are seen in the UV absorption spectrum of copper nanoparticles in ethanol: the optical density of the solution in the UV region is significantly lower than in the case of ablation initiation by the radiation of the copper vapour laser, although the intensities of plasmon resonance peaks in the visible region are comparable. Identification of the compounds produced in the course of laser ablation in ethanol relying on absorption spectra presents difficulties and calls for special investigation, for instance with the aid of chromatography.

In the course of time there occurs an appreciable variation of the spectrum of the colloidal solution of copper obtained by ablation in ethanol. Figure 2 shows the spectra of an as-prepared colloidal solution of copper produced by ablation in ethanol and the solution obtained six months ago. One can see that the plasmon resonance peak nearly vanishes and the solution absorption increases smoothly towards shorter wavelengths. Interestingly, the ageing of colloidal copper solution in ethanol, which is accompanied with the above changes of absorption spectrum, is reversible. Indeed, the irradiation of an aged solution by the focused beam of a copper vapour laser leads to the restoration of the plasmon resonance peak near 590 nm.

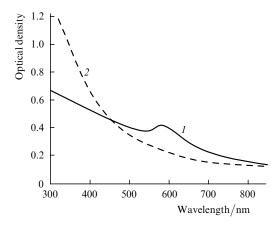
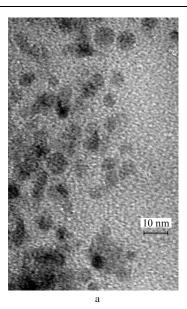


Figure 2. Absorption spectrum of the colloidal solution of nanoparticles produced by the ablation of a copper target in ethanol using the radiation of a copper vapour laser. As-prepared solution (1) and solution six months later (2).

A prolonged (up to 3 h) exposure of the colloidal copper solution itself to the Nd:YAG-laser radiation with an energy density of about 50 J cm⁻² leads to a variation of its spectrum. On further prolonged irradiation of the colloidal solution in the absence of the metal target we observed further changes in the UV spectral region.

The colloidal solution of copper nanoparticles obtained by the ablation of a copper target in acetone exhibits a higher temporal stability of the spectrum. This may be due to the difference of the chemical interaction of copper nanoparticles with the aforementioned liquids at the stage of laser ablation of the copper target. Figure 3 shows the photographs of copper nanoparticles obtained by the target ablation in ethanol and acetone. One can see that the nanoparticles in ethanol exhibit a low contrast and supposedly consist of the copper oxide. Their average dimension is 5–10 nm. By contrast, the nanoparticles of copper in acetone are represented by a high-contrast image and are enclosed in some diffuse cloud. This cloud consists of glassy carbon. Interestingly, this cloud is not observed in the ablation of silver in acetone.



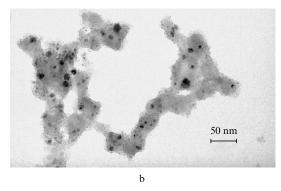
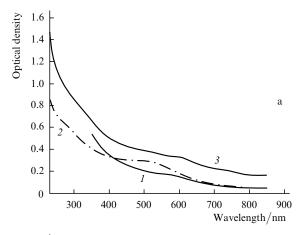


Figure 3. Image of copper nanoparticles produced by ablation of a copper target in ethanol (a) [see the corresponding spectrum (2) in Fig. 1a] and acetone (b) by the radiation of a copper vapour laser. Use was made of a transmission electron microscope.

3.2 Brass nanoparticles

The ablation of a brass target in ethanol and acetone by the radiation of both laser sources also leads to the emergence of liquid colouring. However, the ablation in ethanol is characterised with a reddish tint and that in acetone with a yellowish tint (the peaks near 515 and 564 nm, respectively). The absorption spectra of the three liquids under study after the ablation of a brass target in them are plotted in Fig. 4. The absorption spectra of the water in which the brass target was subjected to ablation are different from the spectra of the water in the case of copper target ablation in it (see Fig. 1).



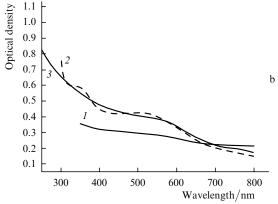


Figure 4. Absorption spectra of the colloidal solution of brass nanoparticles obtained in the ablation of a brass target by the radiation of a copper vapour laser for an energy density of 30 J cm^{-2} (a) and the radiation of an Nd:YAG laser (b) in different liquids [(1) – acetone, (2) – ethanol, (3) – water].

The absorption peak in the visible spectral region is hardly dependent on the laser type employed and is located near 515 nm in the case of ablation in ethanol. In the ablation of a brass target by the radiation of a copper vapour laser using diethyleneglycol as the liquid, we observed a plasmon resonance peak with the absorption maximum also at about 510 nm.

One can see from Fig. 1a that the UV absorption of the liquid increases upon ablating in it the brass target by the radiation of a copper vapour laser, which is supposedly due to a chemical modification of ethanol. The increase of the optical density in the UV range is also observed when the ablation is initiated by the Nd:YAG-laser radiation, although the absorption spectrum has a different appearance in this case. By centrifuging the resultant solution at 18000g for 10 min we found that the UV absorption is related to the modification of the liquid itself rather than the metal nanoparticles produced. As a result of centrifuging, the majority of particles precipitates but the remaining liquid is characterised by strong UV absorption as before, which is absent in the initial ethanol. It may be assumed that the possible composition of ethanol pyrolysis products is very broad and may comprise both elementary carbon and high-molecular compounds. The latter assumption is attested by the fact of formation of a stable light-scattering emulsion on addition of water to the ethanol with brass nanoparticles produced by the ablation of a brass target using the Nd:YAG laser. Moreover, the product composition also depends on the wavelength of the laser source used.

The spectrum of nanoparticles produced by the ablation of a brass target in ethanol remains stable for at least several months. Interestingly, on further laser irradiation, the spectrum of the colloidal solution of brass nanoparticles begins to approach the spectrum of pure copper nanoparticles obtained by the ablation of a copper target in the same liquid. One may draw a conclusion that the brass nanoparticles under irradiation lose zinc, which supposedly passes into the solution in the form of an oxide or hydroxide.

In the case of brass target ablation in water, the plasmon resonance peak is observed, though it is feebly defined. The plasmon resonance peaks lie at 605 and 560 nm when the ablation is initiated by the radiation of copper vapour and Nd:YAG lasers, respectively (Figs 4a and 4b). For the ablation of a brass target in water by both laser types there occurs a chemical interaction of water with the target material at a high temperature, and the solution contains copper oxide Cu₂O and zinc hydroxide Zn(OH)₂ apart from nanoparticles (see the X-ray diffraction pattern in Fig. 5). The Zn(OH)₂ peak is almost coincident with the zinc oxide (ZnO) peak, and therefore the diffraction pattern does not allow judging the density ratio of these compounds. The absorption peak near 360 nm, which corresponds to the width of the ZnO bandgap, counts in favour of the occurrence of ZnO.

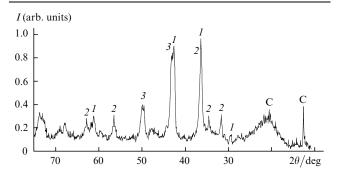


Figure 5. X-ray diffraction pattern of brass nanoparticles produced in the ablation of a brass target in water by Nd: YAG-laser radiation for an energy density of 50 J cm⁻². The highest intensity value corresponds to 2000 counts per second. Identified reflexes: (1) Cu₂O; (2) Zn(OH)₂; (3) brass; (C) cell.

One can see from the X-ray diffraction pattern that there is a large fraction of brass particles (the X-ray diffraction peak for 42.4°) when the ablation is carried out in water. Interestingly, the same reflexes are also observed with brass nanoparticles obtained by the ablation of a brass target in ethanol, though with somewhat different relative intensities.

The location of the summit of nanoparticle X-ray diffraction peak corresponds to the location of the summit of the X-ray diffraction peak of the initial brass. We can therefore conclude that the nanoparticles obtained in the ablation of the brass target are brass nanoparticles.

Unlike copper, nanoparticles produced in the ablation of a brass target in ethanol have a shell. The typical appearance of these core-shell nanoparticles is given in Fig. 6. One can see that the shell surrounding the nanoparticle is closed. Its image is soft (has a lower contrast than

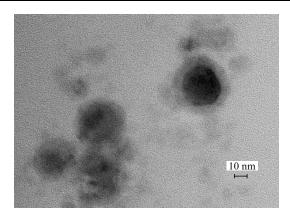


Figure 6. Typical appearance of core-shell nanoparticles produced in the ablation of a brass target in ethanol by the radiation of a copper vapour laser.

the nucleus) and the thickness is comparable to the nucleus dimensions. In some cases, crystallographic planes are resolvable in the shell. The planes are spaced at regular intervals of 7 Å in this case, several differently oriented blocks are distinguishable within one shell (Fig. 7). However, no combinations of the elements (copper, zinc, oxygen, and carbon) collected in the JCPDS-ICDD database possess an elementary cell with this value of the lattice parameter. Crystallographic planes with the same period are observed on nanoparticles of different dimension as well as on low-contrast fragments which supposedly belong to parts of shells without a nucleus, which emerge in the fragmentation of particles.

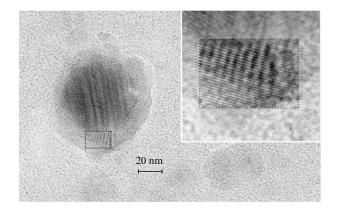


Figure 7. Appearance of a core-shell brass particle and magnified part of the shell, also seen are fragments of shells. Marked in the inset are the crystallographic shell planes with a period of $7\,\text{Å}$.

Decomposition into components of the absorption spectrum of colloidal particles (the Lorentz approximation) obtained by the ablation of a brass target in ethanol allows marking out the spectra of at least two types of particles (Fig. 8). The first of them corresponds to the nanoparticles of brass itself [about 500 nm, curve (3)] and the second to copper nanoparticles [about 570 nm, curve (2)]. These results agree well with the results of brass nanoparticle irradiation in the absence of a target. In this case, there occurs zinc depletion of the nanoparticles, and a long irradiation has the effect that only the peak corresponding

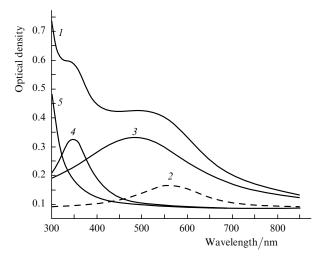


Figure 8. Decomposition of the absorption spectrum of brass nanoparticles in ethanol into components: (1) initial spectrum of brass nanoparticles; (2) peak corresponding to copper nanoparticles; (3) peak corresponding to brass nanoparticles; (4,5) peak corresponding to ZnO and modified ethanol.

to copper nanoparticles is observable in the spectrum of colloidal solution of brass nanoparticles.

4. Discussion

As noted above, the ablation of a solid in liquids involves a local melting of the solid and the sputtering of this layer into the surrounding liquid in the form of nanoparticles. Our results on the ablation of a copper target with the use of two types of laser sources are in good agreement with previously published data. Specifically, in Refs [13, 14], in which an investigation was made of copper nanoparticle production by exposing a CuO powder in 2-propanol to the pulsed radiation of the fundamental harmonic of a neodymium laser, a high air contact immunity of the absorption spectrum of a colloidal solution was also noted. The authors of Refs [13, 14] do not interpret this fact, although from the results of our work it may be inferred that the formation of protective shell around copper nanoparticles takes place both in the ablation in acetone and in the ablation in 2-propanol. Under the conditions of our work, in the ablation in ethanol this shell is not produced, and copper nanoparticles can be oxidised by atmospheric oxygen. This is indication of a high chemical selectivity of decomposition initiated at nanoparticles – two different alcohols exhibit different behaviour for comparable target temperatures.

The higher optical density of ethanol in the UV spectral region in the ablation of a copper target with the radiation of a copper vapour laser in comparison with the IR laser may be ascribed to a higher temperature of the copper nanoparticles in the laser beam of the visible range. Indeed, the resultant nanoparticle—liquid contact surface area is far greater than the laser spot on the target surface. That is why the major part of decomposition products is produced precisely at the nanoparticles heated in the laser beam during the pulse. However, the absorption of visible copper vapour laser radiation by nanoparticles is many times higher than the IR radiation absorption by these particles, because the laser line is virtually coincident with the nanoparticle plasmon resonance peak. Accordingly, the nanoparticle

temperature achieved during the pulse of the copper vapour laser is higher than in the IR laser beam, with the result that the chemical modification of ethanol is more significant.

The observation of plasmon resonance in the ablation of a brass target in water is an indirect indication that the nanoparticles are core-shell structures. Unlike the nanoparticles obtained in ethanol and acetone, these shells may consist of the products of a chemical reaction of zinc with water, for instance Zn(OH)₂. This compound is indeed present in the X-ray diffraction pattern of brass nanoparticles in water. The absence of the peaks of copper in the X-ray diffraction pattern is supposedly due to its oxidation in the course of preparation (evaporation) of the sample.

From the above results it is evident that by and large the spectra of colloidal solutions obtained by the ablation of both metals in liquids are more likely to depend on the nature of a liquid rather than the wavelength of laser radiation. This is testimony to the negligibility of photochemical processes which might make a contribution to the production of nanoparticles, for instance, by generating electron-hole pairs in the copper oxide Cu₂O by the photon of the copper vapour laser.

The stability of the absorption spectrum of copper nanoparticles obtained by ablation in acetone is supposedly due to the formation of (glassy) carbon clouds around the nanoparticles, which prevent the diffusion of oxygen towards the metal of the particles. As is evident from the photographs (see Fig. 3), the copper nanoparticles produced in the ablation of a copper target in ethanol are devoid of such a shell and are therefore oxidised by the atmospheric oxygen dissolved in the liquid. In the case of brass nanoparticles, the spectrum stability is ensured by the shell formed, which impedes the diffusion of oxygen.

Note that there is no way of producing brass nanoparticles chemically whatsoever, because its components are too different in chemical properties. In this sense the technique of producing brass nanoparticles by the laser ablation of a brass target is unique, and the plasmon resonance location to 4. of the brass nanoparticles (near 515 nm) was first measured in our work. It appears reasonable that this peak resides between the plasmon resonances of copper and zinc, as is usually the case with alloyed nanoparticles, for instance, the nanoparticles of a gold-silver alloy [15].

The laser irradiation of a colloidal solution in the absence of a metal target decreases the average particle 600 8. dimension [9, 16]. It is hypothesised that the process is related to the fragmentation of a molten nanoparticle owing to the development of hydrodynamic instabilities at its 100 10. boundary with the ambient vapour cloud. As a rule, the vapour pressure of the metal itself at the nanoparticle melting temperature is well below the vapour pressure of the surrounding liquid at the same temperature. For brass, however, its components differ greatly in vapour pressure. The melting temperature of the brass of the composition investigated in our work (60 % Cu, 40 % Zn) is about 900 °C [17]. At this temperature, the vapour pressure of zinc is far [17]. greater than the copper vapour pressure, with the consequence that it can escape from a molten nanoparticle. The 6015. small nanoparticle radius merely enhances this effect owing to the dependence of vapour pressure on the surface curvature. That is why the brass nanoparticles under irradiation lose zinc and are enriched with copper, which manifests itself in a gradual displacement of the initial peak of their plasmon resonance towards the copper peak.

As for now, the combination of analytical methods used in our work does not allow us to determine the composition of the shell surrounding brass nanoparticles. Its abnormally large period (7 Å) does not correspond to any of the compounds in the accessible JCPDS-ICDD database on X-ray diffraction. At the same time, so long a period may correspond, for instance, to some high-molecular compounds produced in the catalytic decomposition of ethanol molecules at hot nanoparticles. Determination of the shell composition invites further investigation.

5. Conclusions

We obtained for the first time brass nanoparticles and determined the position of their plasmon resonance peak (510-520 nm). In the ablation in ethanol, these nanoparticles are surrounded by a dense shell several nanometers in thickness. In the laser ablation of copper in ethanol this shell does not emerge, and the resulting nanoparticles are slowly oxidised by atmospheric oxygen. A prolonged laser irradiation of the colloidal solution of brass nanoparticles has the effect that the nanoparticles lose zinc and their plasmon resonance gradually shifts to the plasmon resonance of the copper nanoparticles.

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