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In-situ study of Ag nanoparticle hydrosol optical spectra evolution during laser ablation/fragmentation

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ABSTRACT The results of in-situ monitoring of a laser fragmentation process of a largely polydisperse and morphologically heterogeneous citrate-reduced Ag hydrosol containing a fraction of Ag nanowires are presented. The laser fragmentation was performed using several wavelengths of the incident laser pulses (1064, 532 and 355 nm). Surface plasmon extinction spectra monitoring the nanoparticle fragmentation process were acquired pulse by pulse and related to transmission electron microscopy (TEM) images and statistical TEM image analysis of Ag nanoparticles collected in selected stages of the fragmentation. It was found that, due to different interactions of the laser pulses of various wavelengths with a specific fraction of the Ag nanoparticles in the hydrosol, the course of the fragmentation process depends on the wavelength, leading to different size distributions of the nanoparticles in the resulting hydrosol. The laser pulses of 532 nm wavelength are the most effective for the fragmentation process of the citrate-reduced Ag hydrosol, yielding the narrowest size distribution and the smallest mean radius of the Ag nanoparticles.

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1 Introduction

Laser ablation of a metal target in liquid ambient was introduced by Fojtík and Henglein as a novel method of metal nanoparticle preparation [1]. The invention of two-wavelength laser fragmentation applicable to both the laser ablated as well as the chemically prepared Ag nanoparticle hydrosols offered new possibilities to control the properties of the resulting hydrosols [2]. The laser fragmentation can be visualized as a rather complex process which may involve the ablation of bigger particles, photodissociation of Ag nanoparticles as well as other subsequent photoinitiated chemical reactions, depending on the wavelength and energy of the laser pulses used for the fragmentation. However, the results of the investigation of the mechanisms of the laser ablation and nanoparticle fragmentation were, up to now, somewhat hindered by possible changes of the morphology and optical properties of the relatively unstable hydrosols during the sample transportation and handling for ex-situ measurements. In this paper, we report the results of measurements employing an original experimental set-up which enables us to monitor the ablation/nanoparticle fragmentation process directly in a sample cell as a function of a single-pulse excitation and acquire SP (surface plasmon) extinction spectra directly in situ. Furthermore, to probe the wavelength selectivity of the Ag nanoparticle fragmentation procedure, we perform the Ag nanoparticle fragmentation with three different wavelengths of laser pulses. Our effort is targeted to controlling the polydispersity of Ag nanoparticle hydrosols and the values of their mean nanoparticle sizes, allowing for preparations of Ag hydrosols tailored for a particular type of application. For example, monodispersed Ag hydrosols are required for molecule-mediated assembling of Ag nanoparticles into 2-D and 3-D arrays [3]. By contrast, our SERS and SERRS (surface-enhanced/resonance/Raman scattering) spectral testing of laser ablated and subsequently fragmented Ag hydrosols has shown that polydispersity of the hydrosol favorably affects the SERS and SERRS spectral detection limits of selected adsorbates [4].

2 Experimental

The experimental arrangement for the Ag hydrosol fragmentation and its investigation consists of a quartz cell (3×3 mm) filled with Ag hydrosol. An active Q-switched Nd:YAG laser system (Continuum Surelite I) with a repeti-

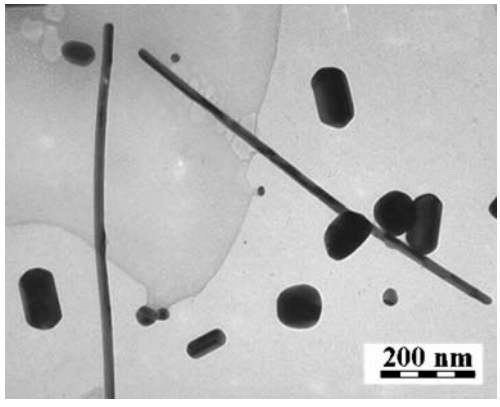

FIGURE 1 TEM image of parent (as-prepared) citrate-reduced Ag hydrosol containing Ag nanowires

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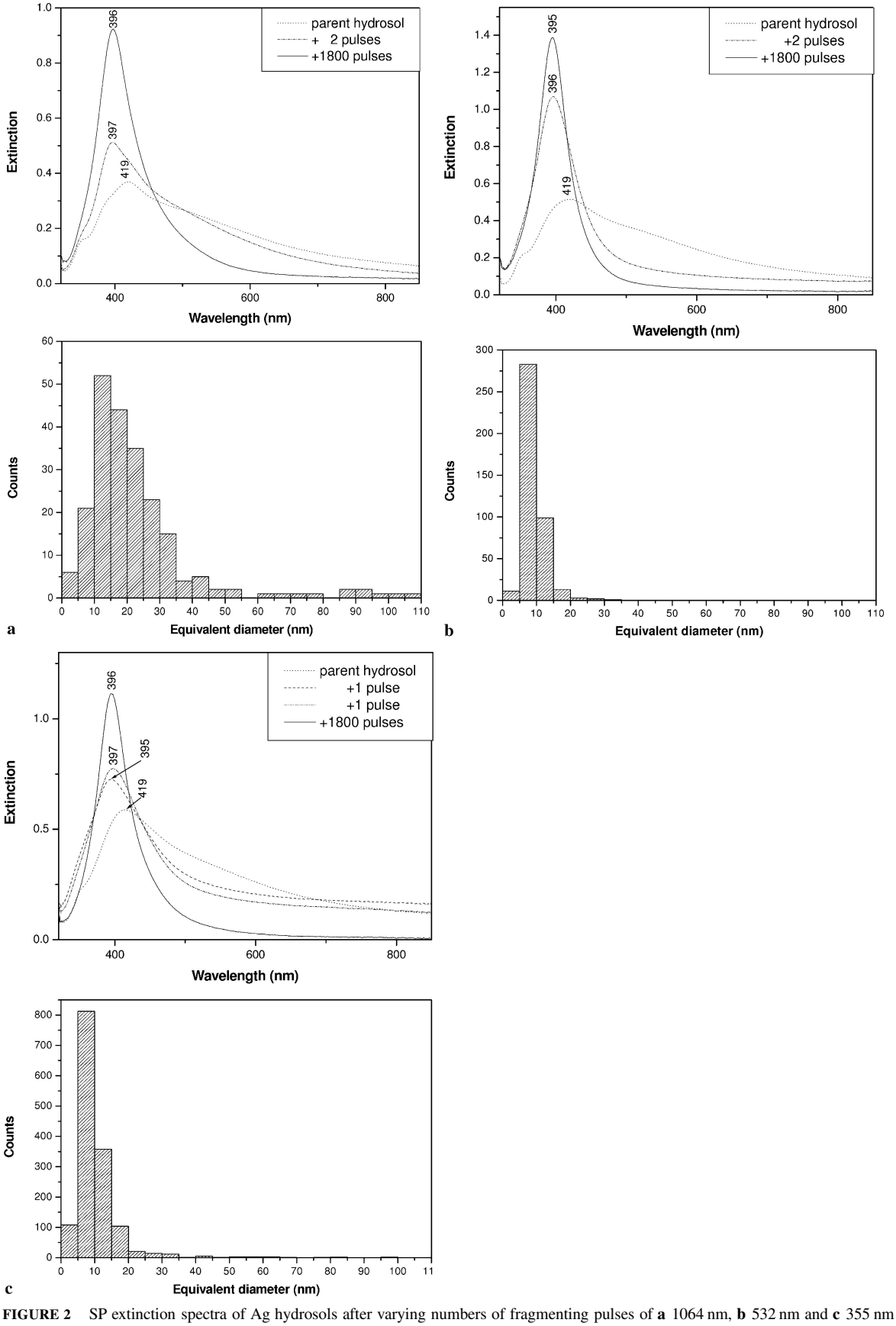

FIGURE 2 SP extinction spectra of Ag hydrosols after varying numbers of fragmenting pulses of **a** 1064 nm, **b** 532 nm and **c** 355 nm wavelengths. *Dotted curve* – original hydrosol, *dashed line* – after first fragmentation pulse, *dashed and dotted line* – after two fragmentation pulses, *straight line* – after 1800 pulses (3 min). Nanoparticle size distribution histograms of Ag hydrosols at the final stage of fragmentation at each of the above wavelengths are also presented

tion rate of 10 Hz, an effective diameter of a pseudo-Gaussian spot of 5 mm and a pulse width (FWHM) of 6 ns was used for fragmentation of Ag hydrosol. The output power was controlled by the laser lamp discharge voltage and measured using an optical power detector (Gentec PSV-103). The wavelengths used for Ag nanoparticle fragmentation were 355, 532 and 1064 nm with the energies of the laser pulses 310 mJ (1064 nm), 170 mJ (532 nm) and 85 mJ (355 nm), respectively.

The Ag hydrosol preparation was carried out by a chemical reduction of silver nitrate by sodium citrate. An aliquot of 3.0 or 4.5 mL of an aqueous solution of sodium citrate (10 mg/mL) was added drop-wise into 150 mL of a boiling and stirred aqueous solution of silver nitrate of 0.18 mg/mL concentration. After addition, the resulting hydrosol was further boiled for 10–15 min. The stirring of the boiling hydrosol was interrupted (7 min) and continued (12 min) after the beginning of the preparation procedure. The hydrosol was stirred for more than 15 min and, after that, diluted with water to get a total volume of 126 mL.

UV/VIS (SP extinction) spectra of the parent as well as the fragmented hydrosols were acquired in situ on a LASP2 UV/VIS CCD optical fiber spectrometer (manufactured by LAO, Czech Republic) in the transmission mode. A steady-state 250 W halogen lamp with properly selected band-pass filters was used as an illumination source. In the particular stages of the fragmentation process, a small drop of the hydrosol was also transferred onto a copper-mesh grid covered by a carbon foil and left to dry. These samples were used for transmission electron microscopy (TEM) imaging performed by a JEOL JEM200CX transmission electron microscope. The statistical evaluation of the nanoparticle size distribution was performed using the Laboratory Imaging Ltd. software LUCIA v. 4.6.

3 Results and discussion

Shown in Fig. 1 is a representative TEM image of the parent citrate-reduced Ag hydrosol prepared by a variation of the Lee–Meisel procedure [5] described in detail in Sect. 2. While the citrate-reduced hydrosol typically contains a fraction of ellipsoidal particles, our variation of the preparation procedure (i.e. the temporary absence of stirring) leads also to the formation of Ag nanowires of about 15 nm in diameter and more than 1 μm in length (Fig. 1). The polydispersity of the parent Ag hydrosol and the heterogeneity of the nanoparticle shapes (Fig. 1) result in a broad and asymmetric SP extinction band (Fig. 2a–c, parent hydrosol SP extinction curves).

The development of the SP extinction spectra of this Ag hydrosol during its irradiation by a given number of the laser pulses together with the corresponding nanoparticle size distribution histograms in the final stages of fragmentation are shown in Fig. 2. For fragmentation by pulses of the 1064 nm (Fig. 2a) and 532 nm (Fig. 2b) wavelengths, the maximum of SP extinction was shifted down to 395 nm after just the first fragmentation pulse; a stepwise decrease in absorption width was observed. Interestingly, fragmentation with 355 nm laser pulses caused an increase of the near-infrared absorption tail of the spectra after the initial two pulses. The subsequent pulses caused, similarly as before, a narrowing of the SP extinction band accompanied, somewhat surprisingly, by the shift of the SP maximum back towards the longer wavelengths. Comparing the final characteristics of the fragmented hydrosols after 1800 pulses, we observed that the most efficient for fragmentation of the nanoparticles at the given energies are the laser pulses of the 532 nm wavelength. They provide the narrowest SP plasmon band as well as the narrowest nanoparticle size distribution (Fig. 2b). In addition to that, the time required to accomplish the fragmentation process (determined by achievement of a constant value of the transmitted light intensity) was the shortest for this wavelength and pulse energy. The majority of large nanoparticles were fragmented to smaller ones during the process. Irradiation of Ag hydrosol by laser pulses of 355 nm wavelength led to hydrosols with a slightly broader SP extinction band and nanoparticle size distribution profile than in the case of 532 nm wavelength (Fig. 2c). Nevertheless, the mean size of the resulting Ag nanoparticles was similar (about 10 nm). Importantly, the nanoparticles with the mean size of about 50–65 nm remained unaffected during the fragmentation process by the pulses of 355 nm wavelength. In addition to that, the duration of the fragmentation was longer at 355 nm than at 532 nm. The SP extinction band of the Ag hydrosols prepared by fragmentation by the 1064 nm laser pulses (Fig. 2a) yielded the broadest SP extinction band of all the wavelengths used for the fragmentation as well as the broadest nanoparticle size distribution profile. Also, the mean size of the Ag nanoparticles was shifted to larger values, reaching about 19 nm.

4 Conclusions

1. Ag hydrosols containing Ag nanowires were prepared by a modification of the routine preparation procedure [5].
2. Monitoring of the Ag hydrosol nanoparticle fragmentation carried out with laser pulses of 1064, 532 and 355 nm wavelengths at 310, 170 and 85 mJ energies per pulse, respectively, has shown that the 532-nm pulses are the most efficient in the fragmentation of the largely polydisperse Ag hydrosols containing spherical and ellipsoidal Ag nanoparticles together with Ag nanowires. The wavelength of the laser pulses thus emerges as a key parameter affecting the efficiency and rate of the fragmentation process as well as optical and morphological characteristics of the resulting hydrosols.

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REFERENCES

1 A. Fojtík, A. Henglein: Ber. Buns. Gesellsch. Phys. Chem. Chem. Phys. **97**, 252 (1993)
2 J. Pfleger, P. Šmejkal, B. Vlčková, M. Šlouf: Proc. SPIE **5122**, 198 (2003)
3 A. Taleb, C. Petit, M.P. Pileni: Chem. Mater. **9**, 950 (1997)
4 P. Šmejkal, K. Šišková, B. Vlčková, J. Pfleger, I. Šloufová, M. Šlouf, P. Mojzeš: Spectrochim. Acta A **59**, 2321 (2003)
5 P.C. Lee, D. Meisel: J. Phys. Chem. **86**, 3391 (1982)