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A simple method to synthesize silver nanoparticles by photo-reduction

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Abstract

In this work, a photo-induced method for obtaining silver nanoparticles (SNPs) was investigated using UV LED, xenon lamp and sodium lamp excitation. Silver colloidal solutions were prepared using autopolymerizable resin and $AgNO_3$ in an ethanol solution. This study shows that the combination of pulsed laser ablation in liquids with previous UV–visible illumination provides a simple, applicable and flexible technique for the fabrication of nanoparticles of 5–8 nm in size.

Keywords: Nanoparticles; Polymers; Laser; Spectroscopy; Silver nanoparticle; Photo-reduction

1. Introduction

Silver nanoparticles (SNPs) show remarkable optical properties that depend on their size and shape [1,2]. Metal nanoparticles can be used as optical biomarkers because they exhibit significant advantages over alternative markers. One of their key advantages is that unlike fluorophores, fluorescent proteins or even quantum dots, silver nanoparticles do not photodecompose during extended illumination. These properties make SNPs ideal for the spectral interrogation of various biological interactions [3–5] and allow their use as tags to indicate the location and environment of the target of interest. Therefore, nanoparticles can be used as a probe to continuously monitor dynamic events in living cells for weeks or months. One exciting application of metal biomarkers is the development of tools for cancer diagnostics. When gold or silver nanoparticles are conjugated to cancer antibodies, cancer cells are marked with those particles and every cell can be detected under a simple microscope due to their enhanced scattering properties [6].

A challenge in colloid chemistry is to control not only metal nanoparticle size but also particle shape and morphology [7]. Many techniques have been exploited in the preparation of shape-controlled silver nanoparticles.

Polymers have been shown to be excellent hosts for trapping nanoparticles of metals and semiconductors [8] and also capable of acting as stabilizers or surface capping agents. When nanoparticles are embedded or encapsulated in a polymer, the polymer terminates the growth of the particles by controlling their nucleation.

The photolysis process with nanosecond laser excitation in a silver colloidal solution has recently been used for the synthesis of nanoparticles. Kamat et al. [9] proposed that the photolysis process causes silver nanoparticles to lose electrons by photoejection, producing a transient state which precedes the complete fragmentation of the larger particles used in their work. Takami et al. [10] proposed that the reduction in the size of gold particles observed after irradiation with nanoseconds Nd:YAG laser pulses is explained by particle heating, melting and vaporization. Mohanty et al. [11] proposed that laser irradiation causes silver nanoparticles to break down into smaller fragments which reassemble producing particles of new dimensions. Maillard

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et al. [12] reported that the shape of silver nanoparticles produced by photo-reduction of silver ions with citrates and seed silver nanoparticles strongly depend on the excitation wavelength. They proposed that the excitation of a specific plasmon determines growth direction. The aspect ratio is controlled by the irradiation wavelength (i.e., the longer the wavelength, the larger the aspect ratio) due to the shape dependence of the silver plasmon resonance.

In this work, photo-induced method [13] for converting silver nanoparticles was investigated using UV LED, xenon lamp and sodium lamp excitation prior to nanosecond laser irradiation. Silver colloidal solutions were prepared using autopolymerizable resin and $AgNO_3$ in an ethanol solution. The photo-process was characterized by ultraviolet–visible spectroscopy and electron transmission microscopy, which allowed the observation of characteristics of the conversion process.

2. Materials and methods

2.1. Chemicals

$AgNO_3$ (reagent grade) was purchased from Labsynth Produtos para Laboratório Ltda. Poly(methylmethacrylate)-based polymer for dental prostheses, autopolymerizable resin, powder and liquid were purchased from Classico Odontological Goods Ltda. All chemicals were used without further modification or purification. Ethanol (96%) was used in the reaction and in all cleaning procedures.

2.2. Synthetic method

Silver nanoparticles were synthesized according to the following method: 0.034 g of silver nitrate was dissolved in 10 mL of ethanol, then 0.011 g of acrylic powder (polymer of methylmethacrylate) was added to 1 mL of "acrylic" liquid and 10 mL of ethanol; the process was accompanied by vigorous stirring for 30 min. After this period both solutions were mixed, with additional stirring for 30 min.

2.3. Instrumentation

UV–vis spectra were taken on a Varian Cary 17D spectrophotometer. UV–vis spectra were measured with 1-cm quartz cells. Optical transmission micrographs were taken on a Leica DM2500 Optical Microscope. Transmission electron images (TEM) were obtained using a Carl Zeiss CEM 902 microscope equipped with a Castaing-Henry energy filter spectrometer within the column and a ProScan slow-scan coupled charged device (CCD) camera controlled by a microcomputer running the AnaluSis 3.0 system. A drop of Ag particles dispersed in ethanol was placed onto a carbon-coated copper grid. The excess liquid was removed using a paper wick and the deposit was dried in air prior to imaging.

A 70-W, inner igniter, high-pressure sodium lamp (which produces virtually monochromatic light in the 589 nm wavelength), a 150-W xenon lamp, and an ultraviolet LED (390 nm) were used to induce colloidal suspension of silver particles. Second harmonic Nd:YAG coherent laser pulses, at wavelength of 532 nm, 15–200-mJ pulse energy, 10 ns duration

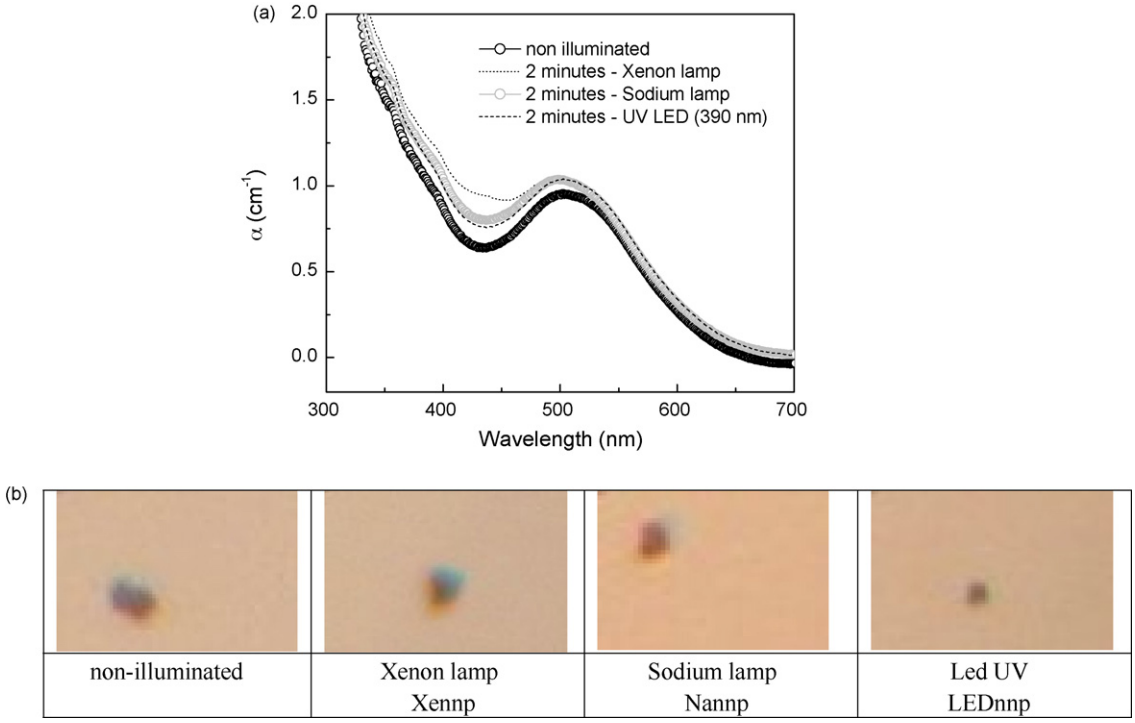

Fig. 1. (a) Changes in the absorption spectrum of a colloid solution caused by 2-min illumination with non-focused xenon light (XeNPs), sodium light (NaNPs) and UV LED (390 nm) (LEDNPs), compared to a non-illuminated solution. (b) Correspondent optical microscopic photography (∼2200× magnification) of a colloidal structure observed under white light illumination.

and a repetition rate of 10 Hz, were employed to synthesize nanoparticles.

3. Results and discussion

Surface plasmon resonance is a collective excitation of the electrons in the conduction band near the nanoparticle surface. Electrons are limited to specific vibration modes by particle size and shape. Therefore, metallic nanoparticles have characteristic optical absorption spectra in the UV–vis region. Dipole plasmon resonance position relates to particle size. Fig. 1a shows details of the evolution of colloid absorption spectra after spontaneous aggregation in the dark and after photo-induced aggregation. The characteristic peak of the Ag colloid, prepared by chemical reduction, is centered at 505 nm. Note a blue shift of the plasmon frequency of Ag nanoparticles after UV/visible illumination, and an increased absorption coefficient in the blue and ultraviolet region, mainly in the case of xenon lamp irradiation (XeNPs). Fig. 1b shows optical micrographs of agglomerated silver particles. Different sizes and different scattered light colors can be observed with each illumination process; the smallest cluster formations were obtained after LED (LEDSNPs) excitation. Clusters or micellar formations can be reduced to nanoparticles through photolysis with nanosecond laser pulses. Because the color of light scattered by nanoparticles depends upon their size [14], it is possible to estimate that these particles have sizes around 30 and 90 nm. Optical microscopy is a very easy and fast procedure and we propose that this method, combined with optical spectroscopy, can be useful in particle size characterization.

The optical absorption spectrum for a 15-min xenon lamp irradiation of colloidal silver nanoparticles (XeNPs), kept in the dark for 12 h, is shown in Fig. 2a. In this case, the altered plasmon band suggested a change in particle size. The optical micrograph (Fig. 2b) for this solution revealed two different colors of cluster formations, also observed in the absorption spectra. Some clusters contain larger particles (red color, particles ~70 nm in size) and others contain smaller particles (blue color, particles 40 nm in size). Fig. 3a displays the TEM image for this solution.

The XeNPs solution was irradiated for 5 min, by nanosecond pulses at 532 nm with 15, 45, and 200 mJ energies, and the results are shown in Fig. 4. In this case, a reduced absorption band, around 500 nm, and the presence of a band around 395 nm, in the case of 200 mJ irradiation, can be observed. The blue shift in maximum absorption was accompanied by a narrowed surface plasmon band and an increased absorption coefficient. A blue shift and an increase in the oscillator strength of the surface plasmon band are indicative of decreased particle diameter. With 45 mJ energy, an unexpected result was obtained: a decrease in the 395 nm band and an enhancement in the 460 nm band were observed, suggesting the formation of intermediate-size particles. Reduced absorptions in the UV range can also be observed, showing that this energy is sufficient to promote a multiphoton process but not sufficient to produce an effective charge accumulation to break the particles into smaller ones. In this case, irradiation with 200 mJ was better than with 45 and 15 mJ. Fig. 3b displays the TEM image for the solution irradiated with 200 mJ. The TEM images shown in Fig. 3 demonstrate

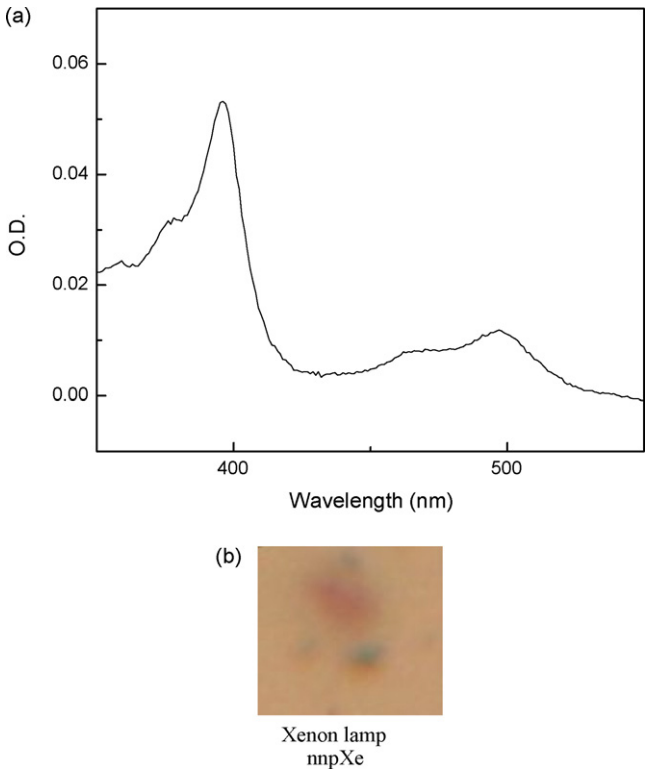

Fig. 2. (a) Optical absorption obtained from a sample exposed to xenon lamp irradiation for 15 min after being kept in the dark for 12 h (XeNPs). (b) Correspondent optical microscopic photography (~2200× magnification) of a colloidal structure observed under white light illumination.

the role of photolysis in silver nanoparticle size control. Fig. 3a shows that without photolysis big and small particles exist, but after photolysis there is a predominance of small particles.

Size reduction can be explained considering that a multiphoton process promotes the photoexcitation of the surface plasmon band. The particles become charged on laser irradia-

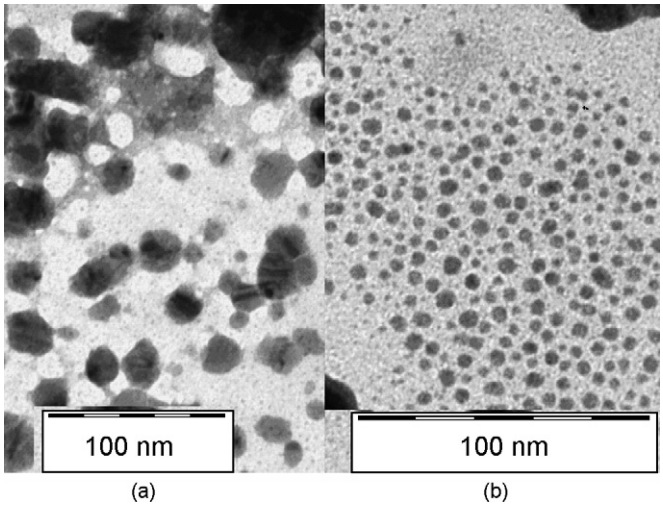

Fig. 3. TEM images of silver colloid particles produced with: (a) Ag colloids prepared with autopolymerizable resin and $AgNO_3$ into an ethanol solution kept in the dark for 12 h and then illuminated with xenon lamp for 15 min; (b) same colloidal suspension after photolysis with 532 nm (200 mJ, 10 Hz) laser excitation for 5 min.

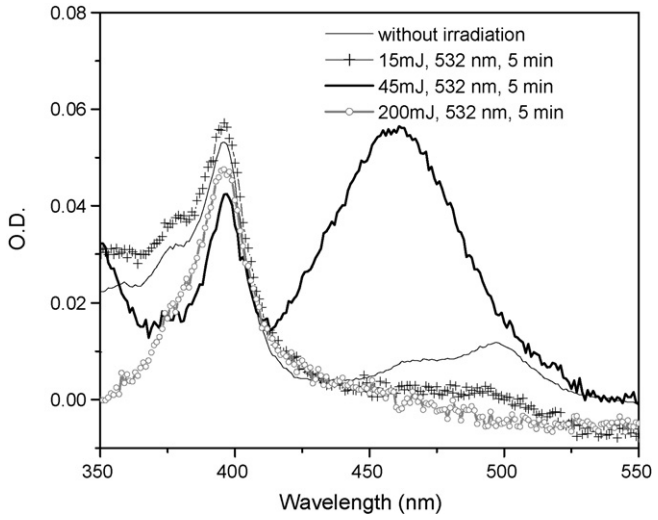

Fig. 4. Optical absorption obtained from XeNPs solution before and after 5 min exposure to 532 nm Nd:YAG irradiation with 15, 45 and 200 mJ energies.

tion and, with sufficient charge accumulation, a rupture of the particles occurs resulting in size reduction. An energy threshold to break down nanoparticles was observed: energy must produce sufficient charge accumulation to break the nanoparticles and, simultaneously, reach the gap energy to induce a multiphoton process.

4. Conclusions

This article has presented a novel and easy method for the preparation of silver nanoparticles with well-defined size and shape which exploits an autopolymerizable resin, visible illumination and laser irradiation. No additives, such as solvents, surfactants or reducing agents, are needed in the procedure. Optical measurements of colloidal silver nanoparticles in ethanol exhibit single maximum optical extinction at 395 nm, which is related to surface plasmon resonance. This study demonstrates that the combination of pulsed laser ablation with UV–visible illumination produces spherical silver nanoparticles 5–8 nm in size. An energy threshold to break down nanoparticles was observed: energy must produce sufficient charge accumulation to break the nanoparticles and, simultaneously, reach the gap energy to induce a multiphoton process.

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References

[1] J. Zheng, R.M. Dickson, J. Am. Chem. Soc. 124 (2002) 13982.
[2] L.A. Peyser, A.E. Vinson, A.P. Bartko, R.M. Dickson, Science 291 (2001) 103.
[3] C. Sonnichsen, B. Reinhard, J. Liphard, A. Alivisatos, Nat. Biotechnol. 23 (2005) 741–745.
[4] A. Haes, W. Hall, L. Chang, W. Klein, R. Van Duyne, Nano Lett. 4 (2004) 1029–1034.
[5] N. Nath, A. Chilkoti, J. Fluoresc. 14 (2004) 377–389.
[6] K. Sokolov, M. Follen, J. Aaron, I. Pavlova, A. Malpica, R. Lotan, R. Richards-Kortum, Cancer Res. 63 (2003) 1999–2004.
[7] C.J. Murphy, N.R. Jana, Adv. Mater. 14 (2002) 80.
[8] Z. Zhang, M. Han, J. Mater. Chem. Commun. 13 (2003) 641.
[9] P.V. Kamat, M. Flumiani, G.V. Hartland, J. Phys. Chem. B 102 (1998) 3123.
[10] A. Takami, H. Kurita, S. Koda, J. Phys. Chem. B 103 (1999) 1226.
[11] J. Mohanty, D.K. Palit, L.V. Shastri, A.V. Sapre, Proc. Indian Acad. Sci. (Chem. Sci.) 112 (1) (2000) 63–72.
[12] M. Maillard, P. Hung, L. Brus, Nano Lett. 3 (2003) 1611.
[13] H. Jia, J. Zeng, W. Song, J. An, B. Zhao, Thin Solid Films 496 (2) (2006) 281–287.
[14] NCI Alliance for Nanotechnology in Cancer, "Mission to the inside of a living Cell", National Cancer Institute, Monthly Feature, May 2006, 1–3.