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THE INTERACTION OF SILVER NANOPARTICLES WITH LIPOIC ACID

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ABSTRACT. Silver nanoparticles of about 6 nm average size were prepared by reduction of an aqueous silver nitrate solution with sodium citrate and characterized by UV-Vis spectroscopy and transmission electron microscopy (TEM). The interaction of this aqueous colloidal silver solution with the α-lipoic acid solution in ethanol was investigated. The changes in the optical spectra and the TEM images suggest the adsorption of lipoic acid molecules onto the silver nanoparticles and the self assembly of the particles in three dimensional aggregates.

Keywords: *silver nanoparticles, α-lipoic acid, UV-Vis spectra, TEM, self aggregation*

INTRODUCTION

Silver is well known for its special optical properties, conferring him its role in photography, and for its bactericidal properties. Silver nanoparticles are of great interest for their various applications in surface enhanced Raman scattering (SERS) [1, 2], photonics [3] and photocatalysis [4], microelectronics [5-6], optics [7] and as antibacterial and antimicrobial agent [8, 9].

Thus it is not surprising that a great number of methods were devised for the synthesis of silver nanoparticles, both in aqueous and in biphasic systems. The silver source was mostly silver nitrate and the reducing agents were sodium citrate [10-12], sodium borohydride [13, 14], ethanol or methanol [15], polyols such as ethylene glycol, in the presence of poly(vinylpyrrolidone) as a polymeric capping reagent [16,17], or glycerol in the presence of o-phenylenediamine [18], formamide [13] and *N,N*-dimethylformamide [19-21], *N*-hexadecylethylenediamine [22], sodium acrylate [23] and even a cell filtrate from a fungus [24].

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Since colloidal silver presents a high sensitivity toward oxygen, at times synthesis was achieved in an inert atmosphere [23]. The formation of silver nanoparticles was also favored by γ radiation [12], laser irradiation [25] or UV illumination [26].

Bioconjugates of the hemoproteins, myoglobin, and hemoglobin have been synthesized by their adsorption on spherical silver nanoparticles [27]. Silver nanoparticle-oligonucleotide conjugates were prepared, based upon DNA with cyclic disulfide-anchoring groups [28]. When silver nanoparticles functionalized with complementary DNA sequences are combined, they assemble to form DNA-linked nanoparticles networks. The interaction between silver nanoparticles and various DNA bases (adenine, guanine, cytosine, and thymine) was described [13]. Silver nanoparticles were adsorbed on the surface of natural wool, as a result of the interaction of silver with sulfur moieties related to the cysteine group [29]. The adsorption of aliphatic-nonpolar amino acids represented by L-methionine on silver nanoparticles was studied by the FT-SERS method [30] and a physical and chemical adsorption by $-NH_3^+$, COO^-, S, was identified

In previous works, we synthesized gold nanoparticles in aqueous solutions and investigated their functionalization and self aggregation with various biomolecules, such as proteins [31] and amino acids [32-35].

The goal of the present investigation is to obtain silver nanoparticles in colloidal aqueous solution and to study their interaction with α-lipoic acid.

RESULTS AND DISCUSSION

The colloidal aqueous solution containing silver nanoparticles is yellow. The UV-visible absorption spectrum of this solution presents a well-defined absorption band with a maximum at the wavelength λ_{max} = 399 nm (Fig. 1). This value is characteristic for plasmon absorbance for nanometric Ag particles. The colloidal solution is rather stable; after one month, only slight modifications in the spectrum were observed.

As reported in literature, the position of λ_{max} for silver nanoparticles is highly dependent on particle shape and can range from around 400 nm for spherical particles to near 800 nm for sharp-edged triangles. For aggregated particles, a red shift is observed [36]. Wavelength and shape of this band are also affected by various adsorbed solutes [27].

The size of the colloidal silver particles has been measured by TEM imaging (for example, Fig. 2). The particles present mostly spherical or ovoid shape. From the sizes of a great number of particles, measured on the TEM images, the following characteristics were calculated: average size (diameter): 5.9 nm; standard deviation: 2.7 nm (extreme values 1.4 and 13.7 nm); average mass of a particle (considered spherical): $1.1 \cdot 10^{-18}$ g; average number of silver atoms in a particle: $6 \cdot 10^3$.

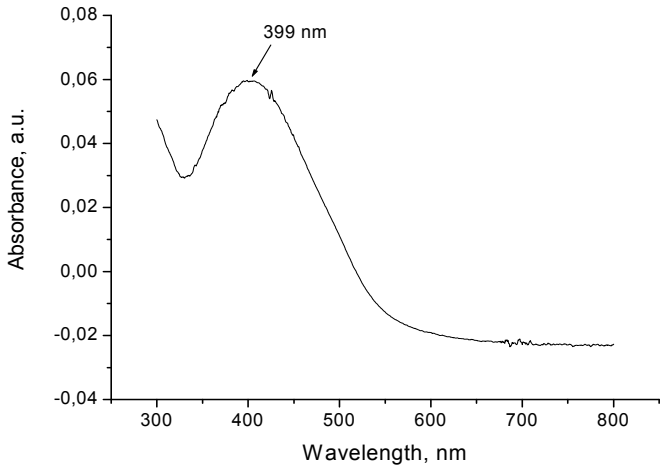


Figure 1. Optical spectrum of the colloidal silver solution

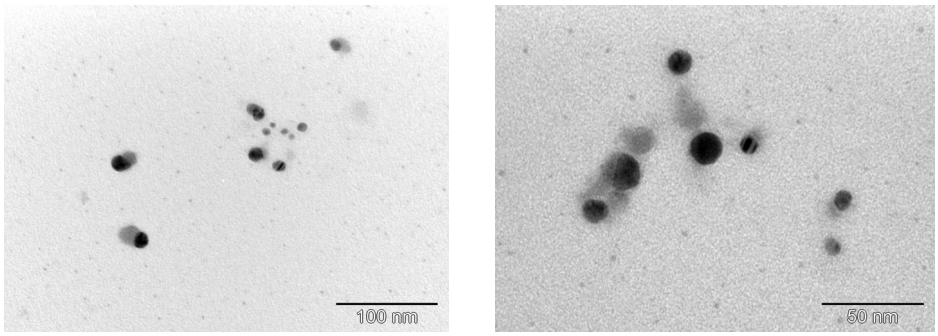


Figure 2. TEM images for silver nanoparticles

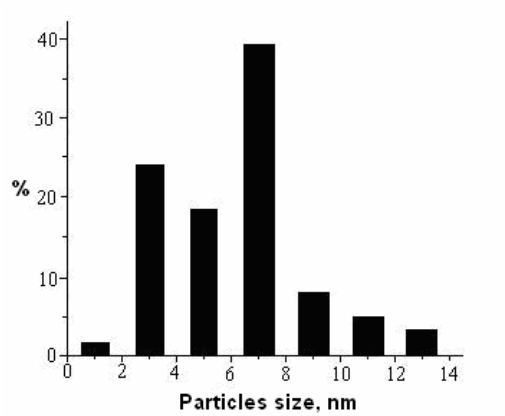
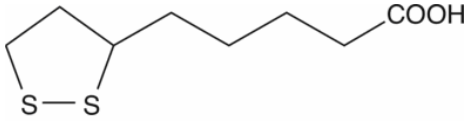


Figure 3. Histogram of size distribution for Ag particles

A histogram providing the size distribution of silver nanoparticles, obtained from TEM pictures, is given in Fig. 3. The predominant fraction is that of particles with about 7 nm diameter, but there are also important contributions from the particles of about 3 and 5 nm size.

The α-lipoic acid or thioctic acid, IUPAC name: 5-(dithiolan-3-yl)pentanoic acid (Scheme 1) is an important biomolecule, known for its antioxidant properties, and is used in the treatment of various diseases [37-39]. The presence of the disulfide group (the ditholane ring) suggests a potential strong interaction with silver nanoparticles. Lipoic acid is practically insoluble in water, so its ethanol solution had to be used to investigate its interaction with the colloidal silver solution.



Scheme 1.

In the UV-Vis spectrum of α-lipoic acid, an absorption band with the maximum at 336 nm is observed (Fig. 4). Adding a small amount of the α-lipoic acid 0.01 M solution in ethanol to the aqueous silver colloidal solution (volume ratio 1/7.5) strongly modifies the spectra of both solutions. The absorption peak of α-lipoic acid disappears, being replaced by a shoulder at low wavelength, and the absorption peak of the silver nanoparticles vanishes

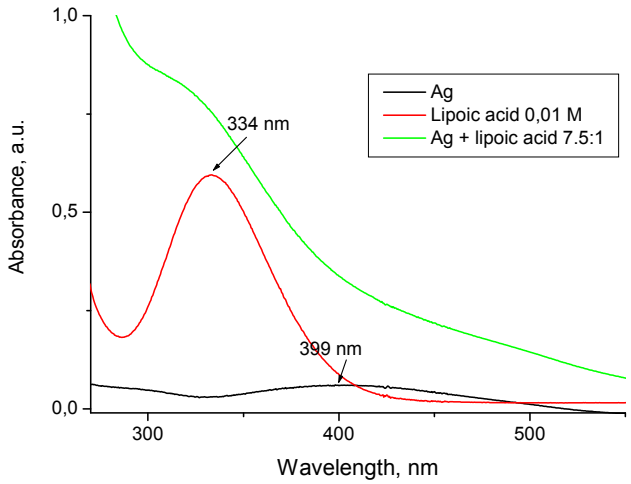


Figure 4. Optical spectra of the aqueous colloidal silver solution, of the α-lipoic acid solution in ethanol and of the mixture of the two solutions in the volume ratio 7.5/1

also (Fig. 4). The yellow color of the solutions fades away. These changes in the spectra suggest a strong interaction between silver nanoparticles and α-lipoic acid.

The TEM images of the mixtures of silver nanoparticles and α-lipoic acid, given in Fig. 5 for different magnifications, confirm this interaction. Large aggregates of silver nanoparticles are seen, resulted by their self assembly mediated by the α-lipoic acid molecules. The adsorption of the biomolecules proceeds probably by means of the sulfur containing groups. The process should be analogous to the adsorption of *n*-octadecyl disulfide onto colloidal silver nanoparticles [40], where the formation of three-dimensional self-assembled monolayers was observed.

On the other part, by introducing the lipoic acid solution in ethanol in the aqueous colloidal solution, an emulsion of lipoic acid is generated, and the silver nanoparticles seem to be trapped in the nanodrops of the organic phase (Fig. 5d).

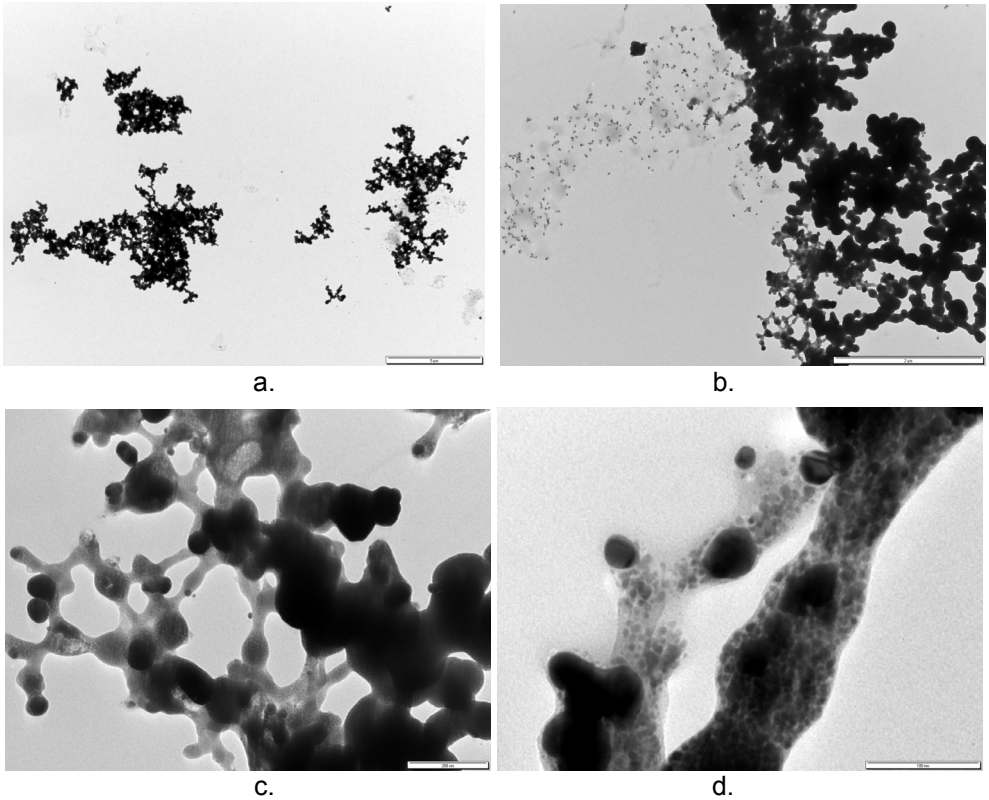


Figure 5. TEM images of silver nanoparticles with α-lipoic acid. The images bars correspond respectively to 5 μm (a), 2 μm (b), 200 nm (c), and 100 nm (d)

CONCLUSIONS

A stable silver colloidal solution was prepared and characterized by UV-Vis spectroscopy and TEM imaging. By means of these techniques the self-aggregation of silver nanoparticles is evidenced, the process being induced by α-lipoic acid. Functionalization of silver nanoparticles through biomolecules is important for the development of new biomaterials with implications in nanoscience and nanotechnology.

EXPERIMENTAL SECTION

The colloidal silver solution was prepared by a method adapted from [11]. 125 mL of 0.001 M solution of silver nitrate in water was heated until boiling under continuous magnetic stirring. Then 5 mL of 1% sodium citrate solution was added and the heating continued until the color was pale yellow. The solution was then rapidly cooled on ice to room temperature. The solution of colloidal silver particles was stored in brown bottles and kept at 4 ^{o}C. The silver content of the solution is 104 mg/L.

$AgNO_3$ was purchased from Merck (high purity above 99.5 %). The trisodium citrate dihydrate was obtained from Sigma Aldrich (high purity above 99%). α-Lipoic acid (extrapure) was purchased from Jiangsu Chemical Company – China, and its 0.01 M solution in ethanol was prepared. All aqueous solutions were prepared using deionized water with resistivity of 18 MΩ·cm, obtained from an Elgastat water purification system.

The UV/Vis absorption spectrum of the solutions was studied using a Jasco UV/Vis V-530 spectrophotometer, with 10 mm path length quartz cuvettes in the 190 – 900 nm wavelengths range.

The silver nanoparticles suspension (7 µL), in the absence and in the presence of lipoic acid, was deposited for 30 s on the carbon coated specimen grid and observed with a transmission electron microscope (TEM: JEOL – JEM 1010). TEM images have been recorded with a JEOL standard software

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