PRODUCTION OF GOLD AND SILVER NANOPARTICLES IN CLEAN LIQUID AMBIENCE BY LASER ABLATION

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Abstract. We present experimental results related to laser ablation-based nanofabrication in clean aqueous solution. This method makes possible the production of pure nanoparticles in biologically-friendly environment. Gold and silver nanoparticles were produced in distilled water, deionized water and ethanol. The TEM and spectral measurements were carried out to determine average size and size distribution. The plasmon resonance absorption spectra Au and Ag nanoparticle colloids and their coalescence were studied. The average size of produced Au nanoparticles was reduced to 3-4nm in ethanol by plasmon resonance absorption using second harmonics 532 nm of Nd:YAG laser.

Keywords: Plasmon resonance, laser ablation,laser-induced fragmentation.

I. INTRODUCTION

At present, noble metal nanoparticles in liquid environment have become a promising material for variety of applications such as nonlinear optical devices, optical recording media, biosensing and bioimaging appliacations Several physical and chemical or electrochemical methods have been developed to produce metal nanoparticles such as, ultrasonic reduction, radiolytic reduction, chemical reduction, etc . In recent years, pulsed laser ablation method was employed for preparation of several metal and semiconductor materials in different media. One of the advantages of laser ablation method in comparison with the other conventional methods is the synthesis of nanoparticles in arbitary liquids including organic liquids and biologically-friendly environments with ease and without contamination by a reducing agent [1]. In contrast to chemical nanofabrication methods laser ablation can be performed in a clean, well-controlled environment such as deionized water, distilled water, giving rise to the production of ultrapure nanomaterials. In addition, laser ablation provides techniques to control size of nanoparticles by laser-induced fragmentation or changing nature of liquid carrier medium [2].

We studied to develop pulsed laser ablation method in our laboratory for noble metal nanoparticle fabrication. Silver and gold nanoparticles were prepared successfully by pulsed laser ablation in our laboratories. The role of liquid environment, laser fluence, laser irradiation time were studied to determine laser ablation procedures.

II. EXPERIMENTS

We used a Quanta Ray Pro 230 Nd: YAG laser to ablate silver (or gold) plate in liquid environment. The laser was set in Q-switch mode to give the fundamental wavelength (1064 nm) in pulses with energy of about 80-100mJ, duration of 8 ns and repetition rate of 10Hz. The laser beam was focused by a lens having the focal length of 150mm on the silver (or gold) plate (99.9 % in purity) which was placed in a glass cuvette filled with 10 ml liquid. The cuvette was placed on a horizontal platform, which executed repetitive circular motions at a constant speed to

prevent agglomeration of particles. Silver and gold nanoparticles were produced by laser ablation in different liquid environments. A small amount of the metal nanoparticles colloids was extracted for absorption measurement and TEM observation. The absorption spectrum was measured by a Shimadzu UV-2450 spectrometer. The TEM micrograph was taken by a JEM 1010-JEOL. The size of nanoparticles was determined by ImagieJ 1.37v software of Wayne Rasband (National institutes of Health, USA). The size distribution was obtained by measuring the diameter of more than 500 particles and using Origin 7.5 software.

III. RESULTS AND DISCUSSION

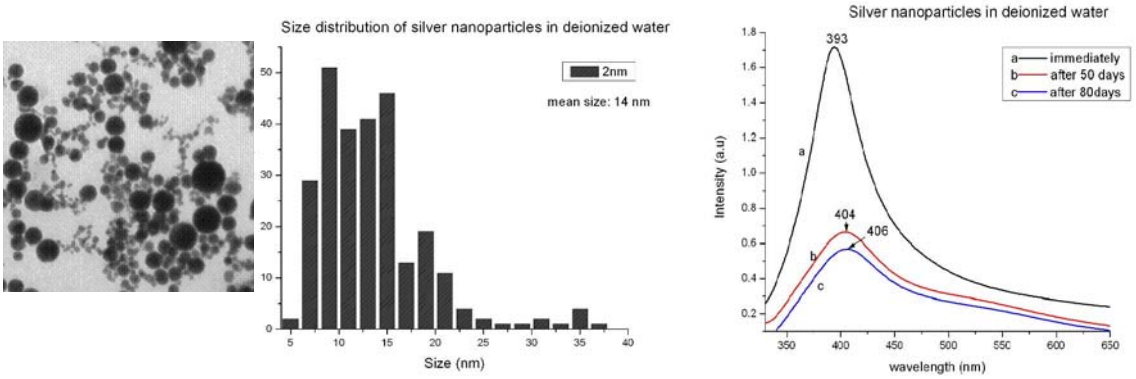

Fig. 1. *TEM image and size distribution of silver nanparticles preparedin deionized water by average laser power of 400mW, laser irradiation time of 7 minutes.(a) and the absorption spectra of the sample right after preparation and after a certain times(b)*

Using fundamental wavelength 1064nm of Nd:YAG laser with average power of 400mW irradiation time of 7 minutes we prepared silver nanoparticles in deionized water. TEM image and corresponding size distribution of silver nanoparticles in deionized water are presented in Fig.1.a. The silver nanoparticles are rather spherical in shape with mean diameter of 14nm.

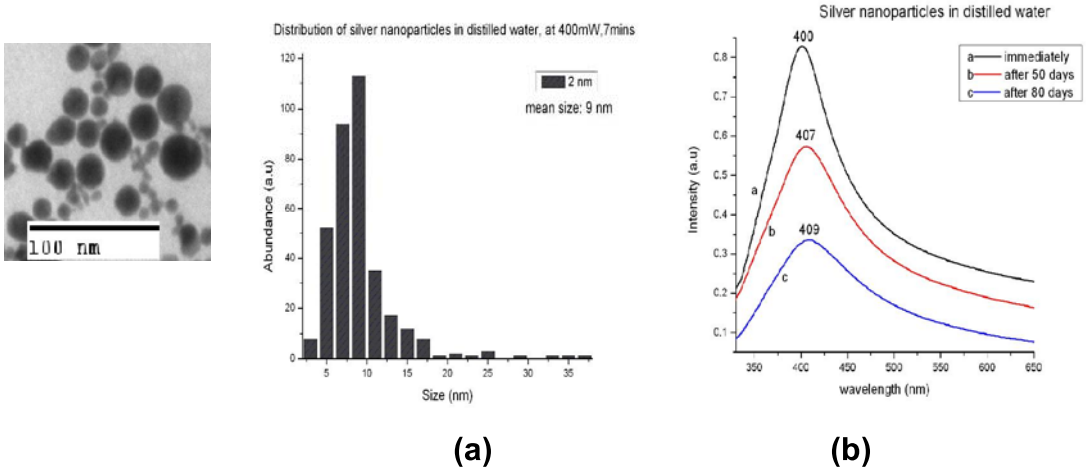

Fig. 2. *TEM image and size distribution of silver nanparticles prepared in distilled water by average laser power of 400mW, laser irradiation time of 7 minutes (a) and the absorption spectra of the sample right afterpreparation and after a certain times*

The characteristic Plasmon resonance absorption peak of silver nanoparticles around 400nm appeared in the absorption spectra of the prepared nanoparticle colloids (Fig.1.b). In order to determine stability of silver nanoparticles in deionized water we measured absorption spectrum

of the sample after a certain period of time . Fig.1.b shows that the Plasmon resonance peak in the absorption spectra of the sample after 50 days and then 80 day are shifted to longer wavelength and broaden. That means there was a strong aggregation of silver nanoparticles in deionized. In fact, the silver nanoparticle sample remain stable about 7 days.

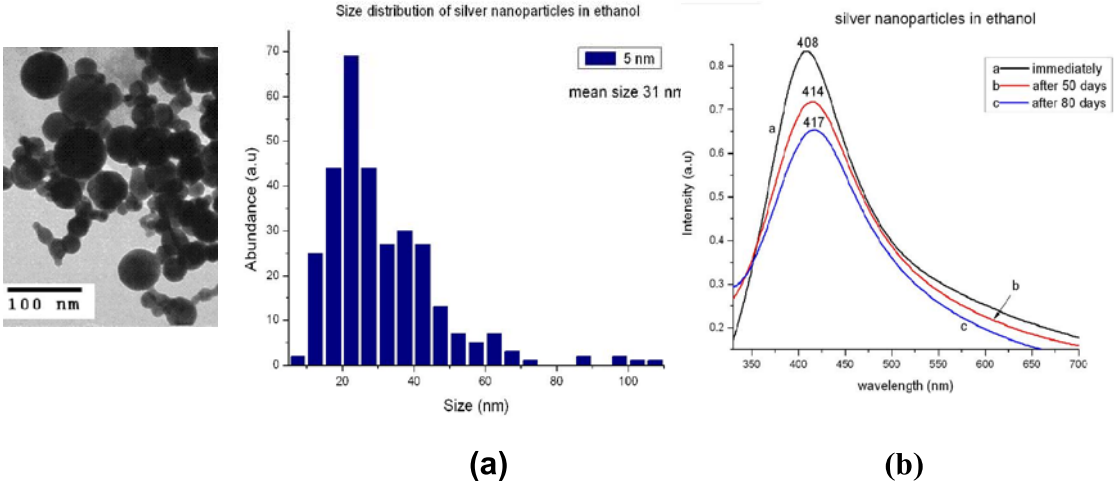

Fig. 3. *TEM image and size distribution of silver nanparticles prepared in ethanol by average laser power of 400mW, laser irradiation time of 7 minutes (a) and the absorption spectra of the sample right afterpreparation and after a certain times*

Keeping the same average power of 400mW and irradiation time of 7 minutes we prepared silver nanoparticles in distilled water. The results in Fig.2 show silver nanoparticles are rather spherical in shape with mean diameter of 9nm and size distribution become narrower in comparison with silver nanoparticles in deionized water. Fig 2.b shows the aggregation of silver nanoparticles in distilled water was rather slow. The silver nanoparticles remain stable in distilled water around one month. These results confirm the role of ions in liquids environment during laser ablation process [4].

By the same procedure we prepared silver nanoparticles in ethanol. The TEM and spectral measurements are given in Fig.3. The silver nanoparticles in ethanol has larger mean diameter (31nm) than those in water (9nm) and remain more stable (Fig 3.b). Infact, the silver nanoparticles remained stable in ethanol about at 2 months.

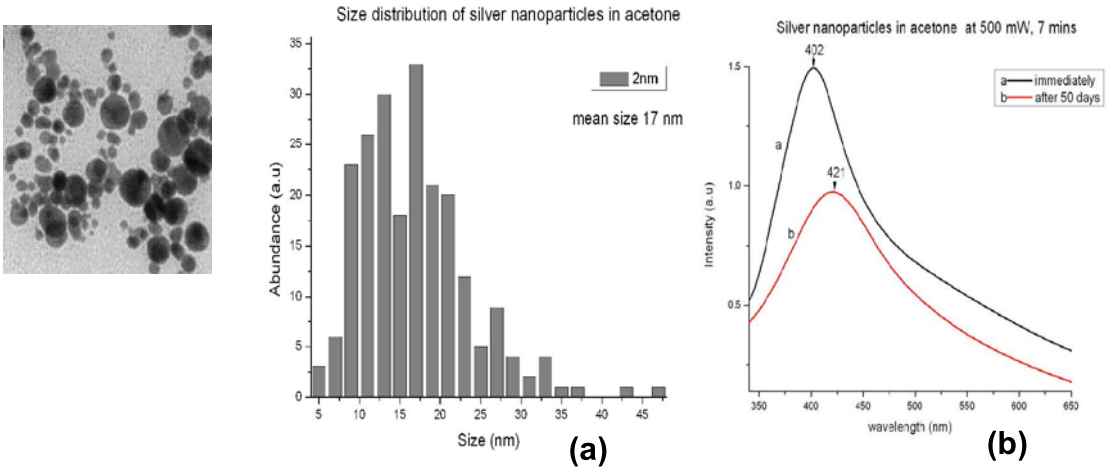

Fig. 4. *TEM image and size distribution of silver nanparticles prepared in acetone by average laser power of 400mW, laser irradiation time of 7 minutes (a) and the absorption spectra of the sample right afterpreparation and after 50 days(b)*

Growth rate of nanoparticles depends on the number of particles formed in the first stage and molecular polarity of liquid environment. Molecules with high dipole moment cause more packed and stronger bonds to the surface of the particles. It was demonstrated that in liquids surface of metal nanoparticles such as Au and Ag is charged negatively because of interaction with medium and different affinity of electron to the surface [6,7]. In water and ethanol the dissociation of OH group on metal nanoparticles results in surface charge and electrical double layer forms. Since the molecule of water has higher dipole moment than pure ethanol, the electrostatic repulsive force restricts more effectively the growth mechanism. As a result smaller Ag and Au nanoparticles and narrower size distribution were observed in water than those in pure ethanol.

We also prepared silver nanoparticles in acetone. The TEM and spectral measurements are given in Fig.4. The silver nanoparticles in acetone has mean diameter of 17nm and remain stable about one month.

After preparing successfully silver nanoparticles we studied to prepare gold nanoparticles with the same method. Using fundamental wavelength 1064nm of Nd:YAG laser with average power of 400mW and irradiation time of 15 minutes we prepared gold nanoparticles in deionized water, distilled water, ethanol and acetone. The absorption spectra of the samples are shown in Fig.5.

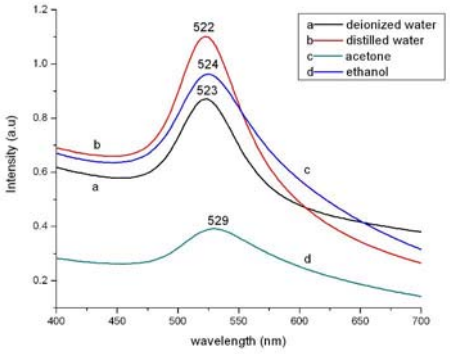

Fig. 5. *The absorption spectra of silver nanoparticles prepared in deionized (a) distilled water (b) acetone (c) and ethanol (d)*

Among these absorption spectra, the plasmon resonance peak of silver nanoparticles prepared in distilled water is the narrowest and shifted to the shorter wavelength. Fig. 6 shows TEM images and corresponding size distribution of silver nanoparticles prepared in deionized water, distilled water and ethanol respectively.

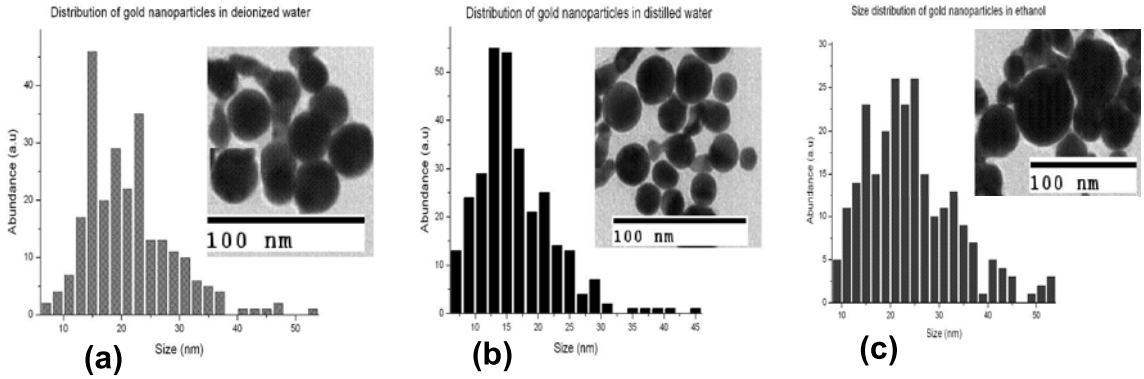

Fig. 6. *TEM image and size distribution of silver nanparticles prepared in deionized (a) distilled water (b) and ethanol (c) by average laser power of 400mW, laser irradiation time of 15 minutes.*

Gold nanoparticles are rather spherical in shape and have mean diameter of 21nm, 16nm and 24nm in deionized water, distilled water and pure ethanol respectively.

In order to verify the role of molecular polarity of liquid environment in the growth mechanism of nanoparticles, we carried out laser ablation of Au in solution of ethanol in water with different concentrations. Fig.7 shows the absolution spectra of gold nanoparticles colloid prepared in distilled water, solution of 30% ethanol and solution of 60% ethanol . As obviously seen, when the ethanol concentration increases the absorption spectrum is broaden and absorption peak is shifted to longer wavelengths. The weak electrical double layer due to low polarity of ethanol molecules cause growth and results in the size broadening.

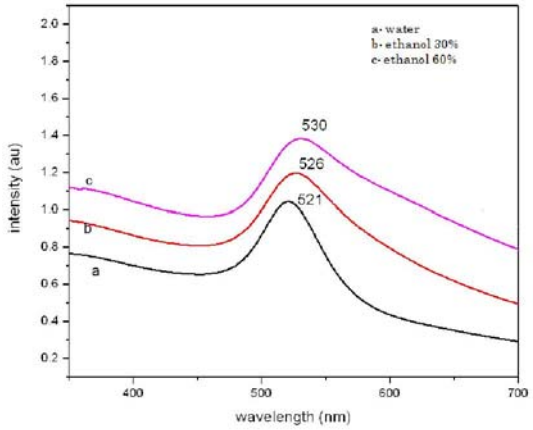

***Fig.7** .The absolution spectra of gold nanoparticles colloid prepared in distilled water (a) solution of 30% ethanol (b) and solution of 60% ethanol (c)*

This results suggested that we can control average size and size distribution of gold nanoparticles by changing the concentration of ethanol in water. We can also decrease mean size of gold nanoparticles in ethanol solution by laser-induced fragmentation . Using second harmonic 532nm wavelength of Nd:YAG laser corresponding to plasmon resonance absorption wavelength (~520nm) of gold nanoparticles we could decrease average diameter of gold nanoparticles to few nanometers . Fig 8 shows TEM images and corresponding size distribution of gold nanoparticles prepared in ethanol 60% before and after 532nm irradiation. The average size of gold nanoparticles is 9nm and 3nm before and after 532nm irradiation respectively.

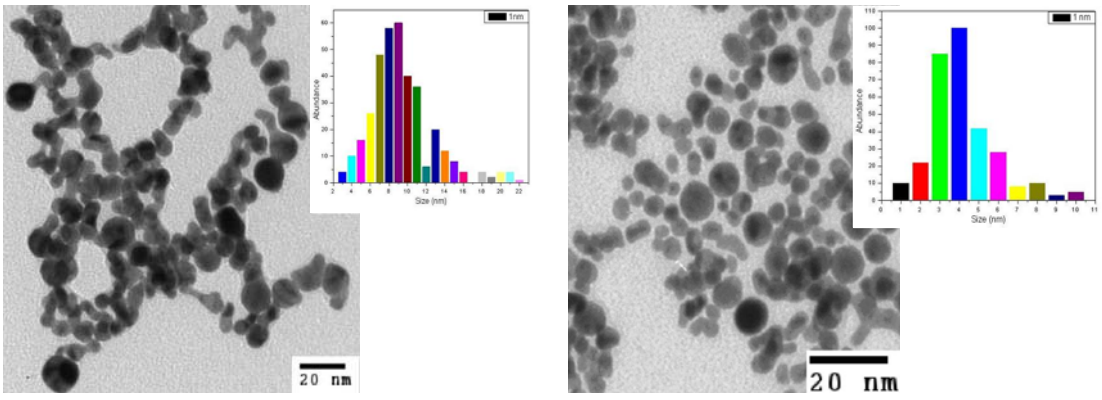

Fig. 8. *TEM images and corresponding size distribution of gold nanoparticles prepared in ethanol 60% before and after 532nm irradiation*

IV. CONCLUSION

Silver and gold nanoparticles were prepared successfully in several clean liquids such as deionized water, distilled water and ethanol soltions by pulsed laser ablation . The mean size and size distribution of gold nanoparticles in ethanol solutions could be controlled by changing concentration of ethanol in water or irradiation of 532nm second harmonic wavelength of Nd:YAG laser. The results support a technique to control mean size and size distribution of metal nanoparticles by changing nature of liquid environment and by laser-induced fragmentation.

V. ACKNOWLEDGMENTS

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