

Fabrication and Nonlinear Refractive Index Measurement of Colloidal Silver Nanoparticles

Adeleh Granmayeh Rad, Hamed Abbasi, and Keyhan Golyari

Abstract—In this paper we report the measurement of nonlinear refractive index of colloidal Ag nanoparticles and fabrication of Ag nanoparticles. In order to fabricate the colloidal silver nanoparticles laser ablation method has been used. A silver coin as a target (purity 99.9 %) was ablated by a Q-Switched Nd: YAG laser with a fluence of about 91 mJ/cm^2 at a repetition rate of 10 Hz at room temperature. In order to characterize these particles transmission electron microscopy (TEM) and spectrophotometry (from UV to NIR) have been used. The average size of fabricated nanoparticles is $\sim 20 \text{ nm}$. The importance of morphology of nanoparticles has been investigated. We used the Z-scan technique to investigate the nonlinear refractive index of Ag nanoparticles. The excitation source was a CW 532nm Second harmonic Nd:YAG laser with a beam power of 55 mW. Mostly used applications of silver nanoparticles have been studied; silver nanoparticles are considered as biocompatible and low in toxicity and have good potential for biological applications. Lately silver nanoparticles have found a novel approach in different fields of medicine, biology and industry. In this paper n_2 refers to nonlinear refractive index, ΔT_{p-v} is the difference between the normalized peak and the valley transmittance. s is the aperture linear transmittance. L_{eff} is the effective thickness of the sample. EIS, SPR, TEM and SEM refer to: electrical impedance spectroscopy, surface plasmon resonance, transmission electron microscope and scanning electron microscope, respectively.

Index Terms—Ag nanoparticles, laser ablation, nonlinear refractive index, z-scan.

I. INTRODUCTION

Nowadays, silver nanoparticles have received attention due to their antimicrobial activity which offers the possibility of their use for medical and hygiene purposes. Actually, silver nanoparticles in different formulations and with different shapes and sizes show variable antimicrobial activity. Silver nanoparticles are fabricated by various methods including physical, chemical and biological methods [1]-[6]. One of these methods that widely used is laser ablation [7]. Evaluation nanoparticles after fabricating them is an essential section of this science. Scientist all over world with various methods can fabricate nanoparticles in controlled shapes and sizes. One of the controlled shapes and sizes silver nanoparticles is reported in [8]. Metal nanoparticles have many potential technological applications.

Manuscript received February 23, 2012; revised March 25, 2012.

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Silver is well known for possessing an inhibitory effect against many bacteria and microorganisms commonly present in medical and industrial processes. In medicines, silver and silver nanoparticles have extended applications including skin ointments and creams containing silver to prevent infection of burns and open wounds [9]-[25]. Although the most common applications of silver nanoparticles are because of its anti-bacterial properties, these nanoparticles are used in various filed in medicine and industry [26]-[31]. Reference [32] shows how to measure nonlinear refractive index. The authors have previously investigated fabricating and characterizing of gold and silver nanoparticles, and studied developed applications of these nanoparticles [32]-[34].

II. MATERIAL PROCESSING

Nanoparticles can be synthesized using various approaches including chemical, physical, and biological. Laser ablation method has been used to produce colloidal silver nanoparticles. In this work, Q-Switched Nd:YAG laser with a wavelength of 1064 (6 ns, 10 Hz) has been used. In this method, a silver coin (99.9 % purity) with diameter of 1 cm and 2 mm thickness has been placed, in a clean can containing 6 ml distilled water. Then laser beam after being passed from a lens ($f=75 \text{ mm}$) is focused and radiated for 15 min (with 91 mJ/cm^2 fluence).

Fig. 1 shows fabricated colloidal silver nanoparticles.



Fig. 1. Colloidal silver nanoparticles.

Metallic particles are separated and inter the water as a result of hitting the laser beam to mentioned plate. The average size of fabricated nanoparticles is $\sim 20 \text{ nm}$. In this way metallic colloidal solution has been fabricated.

III. CHARACTERIZATION

After the fabrication of the nanoparticles, the next stage is the Evaluation. The Evaluation will give information about the size and shape of the nanoparticles and spectrum of the plasmon band. Some important ways to characterize nanoparticles are: electrical impedance spectroscopy (EIS), surface plasmon resonance (SPR), cyclic voltammetry and conductive measurement. Commonly, scientists all over the worlds use transmission and scanning electron microscope (TEM and SEM) in order to observe size, shape and distribution of nanoparticles. One more method to characterize nanoparticles is use of spectrophotometry. Spectrophotometer determines the absorption spectra of nanoparticles solution. For silver nanoparticles under 40 nm in diameter, absorption peak is located at near 400 nm. Leading to a characteristic yellow color for colloidal silver nanoparticles as primarily blue light is absorbed.

Metallic nanoparticles have been extensively studied in because their properties differ markedly from those of the corresponding bulk substances. Metal nanoparticles have high surface energies because they have very small diameters. Hence, they have been used as guest materials encapsulated in host matrices such as glass, polymers, fibers or carbon. Metal nanoparticles have a high specific surface area and a high fraction of surface atoms. Nanotechnology has been developed owing to the unique physicochemical characteristics of nanoparticles, including catalytic activity, optical properties, electronic properties, antibacterial properties, and magnetic properties. Therefore geometry of nanoparticles is so important. The size of nanoparticles is also important for different applications such as medicine. For example, the size of nanoparticles has an important function to develop anticancer drugs. Distribution of nanoparticles is also an important issue to utilize nanoparticles for medicine.

Fig. 2 shows the TEM image of colloidal silver nanoparticles produced during laser ablation method

Fig. 3 shows the absorption spectrum of the colloidal silver nanoparticles.

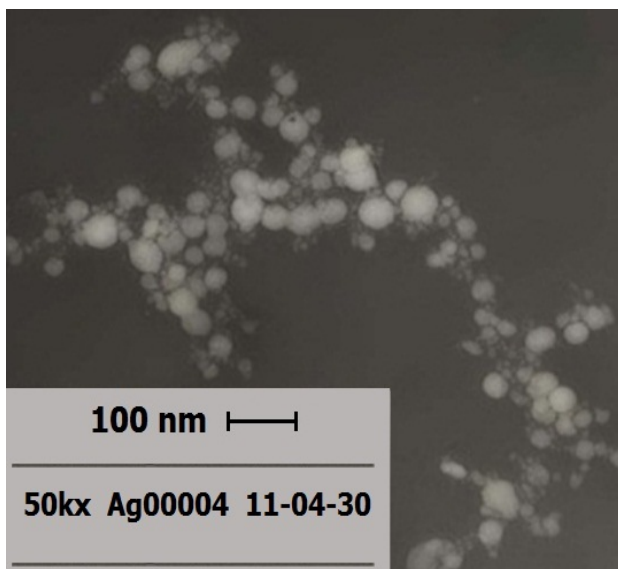


Fig. 2. Image of silver nanoparticles fabricated during laser ablation technique by method of transmission electron microscopy. The scale bar is 100 nm.

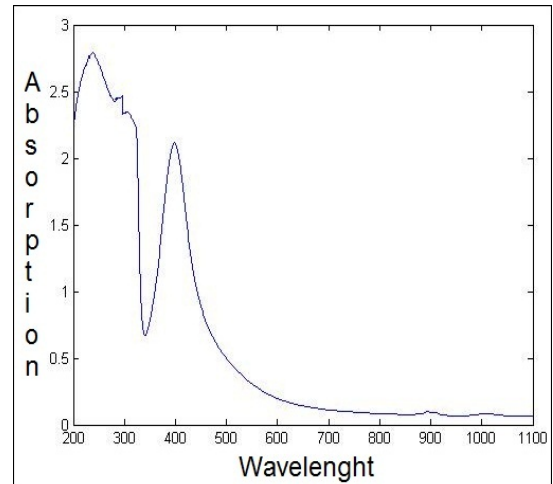


Fig. 3. Absorption spectrum of silver nanoparticles (From UV to NIR), with a peak near 400 nm.

IV. NONLINEAR REFRACTIVE INDEX MEASUREMENT

We used the Z-scan technique [32] to investigate nonlinear optical (NLO) properties of silver nanoparticles. Z-scan technique is a simple and high sensitive method to determine both n_2 (nonlinear refractive index) and β (nonlinear absorption coefficient). The Z-scan technique is based on the intensity-dependent refractive index and measures the variation of the refractive index as a function of intensity of incident beam. The induced lens inside the sample holds different focal lengths for each position of the sample and the focal length depends on the on the intensity of the laser beam.

To measure the nonlinear refractive index the laser beam was focused and the sample was scanned along a focused Gaussian-beam (TEM_{00}) through its focal plane. The intensity of the laser beam for each position as a function focus position was measured using finite aperture at far field. To measure the total beam intensity of the laser, the input beam is divided by a beam splitter, and was detected by a suitable detection system.

The closed aperture allowed measurements of both sign and value of nonlinear refraction coefficient. Since the light intensity irradiated on the sample is different at each position, therefore a typical peak-valley transmittance curve is obtained when the nonlinear refractive index of the medium is negative.

A negative refraction index for the sample means that the sample acts as a concave lens in the vicinity of the focal. As the sample moves closer to the negative position of the z towards the focal, the focal position shifts to positive z direction. This suppresses the beam at the aperture plane and the intensity at the detector becomes larger. As the sample becomes near to the positive position of z to the focal position, the beam spreads at aperture and the intensity becomes larger at positive side.

The excitation source was a CW 532nm second harmonic Nd:YAG laser with a beam power of 55 mW. The excitation light was focused onto the sample by a lens with 30cm focal length, and the beam waist radius (w_0) was measured to be 22.8 μ m. The thickness of a quartz cell containing the sample is 1mm.

Fig. 4 shows the block diagram of Z-scan experimental set-up.

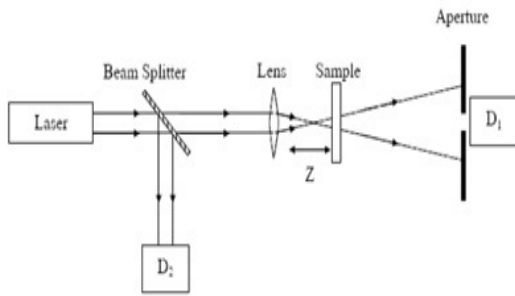


Fig. 4. The optical geometry for measuring nonlinear optical refractive index of Ag nanoparticles. D_1 and D_2 are detectors for beam intensity detection.

V. RESULT AND DISCUSSION

The z-scan data was analyzed with the procedures described in [32]. The nonlinear refractive index n_2 of the silver nanoparticles is given according to the following equation:

$$n_2 = \frac{\Delta\phi_0\lambda}{2\pi L_{eff}I_0} \quad (1)$$

The $\Delta\phi_0$ was calculated from the experimental data of the normalized peak to valley transmittance, ΔT_{p-v} given as:

$$\Delta T_{p-v} \approx 0.406(1-s)^{0.25} |\Delta\phi_0| \quad (2)$$

Therefore:

$$n_2 = \frac{\Delta T_{p-v}\lambda}{0.406(1-s)^{0.25} 2\pi L_{eff}I_0} \quad (3)$$

That s is the aperture linear transmittance and taken to be 0.7 for present experiment, I_0 is the intensity of the laser beam at focus $z=0$, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, $\alpha = -\frac{1}{L} \ln\left(\frac{I}{I_0}\right)$ is the linear absorption

coefficient and L is the thickness of the sample. In the case of $I_0 = 3.47 \times 10^3 \text{ W cm}^{-2}$, n_2 is obtained as $-7.52 \times 10^{-7} \text{ cm}^2 \text{ W}^{-1}$. The solid line in fig .5 is the calculated value using analytical equation proposed by Liao et al.(1997);(1998):

$$T(z, \Delta\phi) = 1 - \frac{4\Delta\phi_0 x}{(x^2+1)(x^2+9)} \quad (4)$$

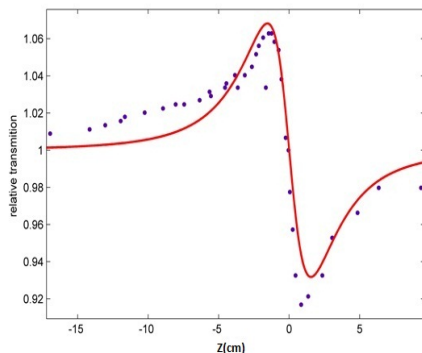


Fig. 5. Closed aperture z-scan experimental data for Ag nanoparticles at 532 nm laser. The solid line is the theoretical curve calculated using Eq.4.

Fig. 5 shows the closed aperture z-scan experimental data for Ag nanoparticles at 532 nm laser. The solid line is the theoretical curve calculated using Eq.3

VI. STUDY ON APPLICATION OF SILVER NANOPARTICLES

Nowadays, Nano-materials are expected to be used for medical applications such as research on pharmacokinetics and novel therapeutic agents. Silver is the most used antibacterial agent with a number of advantages. The increasing fight toward infections caused by bacteria poses new challenges for development of materials and medical devices with antimicrobial properties.

Silver and some other nanoparticles have a antimicrobial activities against an environmental soil microbe, *Pseudomonas Putida* KT2440. Some of other microbes and bacteria which silver has powerfully challenged are: *Staphylococcus aureus* (S. aureus), *Escherichia coli* (E. coli), *Pseudomonas aeruginosa*, *Streptococcus pyogenes* and *Valeriana officinalis* L. Coating cadaveric bone grafts using silver nanoparticles is another applications of these particles. The novel chitin/nanosilver composite scaffolds have been produced using chitin hydrogel with silver nanoparticles.

These scaffolds were also found to have great blood clotting power, which will be useful for wound healing applications. Nanotechnology has found a novel approach to the visualization of fatty acids in mouse liver and retinal samples has been developed using silver nanoparticles.

Silver has been found to enhance photothermal conversion for photothermal ablation therapy (PTA), PTA is directly connected to the promise of new nanotechnology for cancer diagnosis and therapy. We can mention Tumor Imaging, Target Delivery, and Interaction with HIV-1 as three important and interesting applications of silver nanoparticles. Antifungal Effect of Silver Nanoparticles have been investigated by scientists, antifungal activity of silver nanoparticles against the oak wilt pathogen *Raffaelea* sp., and *Candida albicans* is one of the examples.

Compare with antibacterial applications of silver nanoparticles, its industrial applications are less developed. However composite of these nanoparticles are widely used in various fields of industry. Textile is one these fields that broadly uses silver nanoparticles to improve itself. Nanoparticles change properties of materials by means of their different properties such as its high area to volume ratio. Providing the cotton fabric with antibacterial properties is one of these applications.

Silver nanoparticles can help making anti-reflective coatings for CRTs by sol-gel Process. Cleaning drinking water using nano silver-coated polypropylene filters, making UV-protective nano suspension, silver nanoparticles sensor and plasmonic solar cells are some of the other developed applications. Moreover, unique properties of these particles provide the opportunity for developing novel functional paper products for antimicrobial packaging, medical dressings, and clothing.

VII. CONCLUSION

We fabricated colloidal silver nanoparticles by pulsed Nd:

YAG laser. We used the Z-scan method to investigate nonlinear optic properties of silver nanoparticles. Z-scan method is a simple and high sensitive technique to obtain both n_2 (nonlinear refractive index) and β (nonlinear absorption coefficient). The Z-scan method is based on the intensity-dependent refractive index and measures the variation of the refractive index as a function of intensity of incident beam.

We used spectrophotometry and transmission electron microscopy (TEM) to characterize the fabricated nanoparticles. Shape, size and distribution of nanoparticles are some of the very important factors of them. Lately nanomaterials are widely applied to medical diagnoses and treatments such as researches on pharmacokinetics and novel therapeutic agents.

The function of these materials depends on their composition and structure. In the past several years, the investigations of silver nanomaterials have drawn considerable attention because of their excellent biocompatibility and low toxicity. Silver nanoparticles also have important applications in the fields of biology, such as antibacterial, antiviral, antifungal effects, and biosensor. Some of the most important applications of silver nanoparticles in medicine and biology are Tumor Imaging, Target Delivery, and Interaction with HIV-1.

Colloidal silver nanoparticles and composite of silver nanoparticles are used in different fields of industry such as textile, cleaning drinking water, sensors and solar cells. Nanostructures particularly metallic nanoparticles exhibit very practical, interesting and growing applications. Beside gold, silver is one of the most applicable metallic nanoparticles which play an important role in nanotechnology.

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