International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 10 Issue 3 ǁ 2022 ǁ PP. 32-37

Preparation of Silver Nanoparticlesusing Pulsed Laser Technique

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Abstract
Silver nanoparticles have attracted much attention nowadays in textile industry, in biological sensors and in biomedical devices because of their size dependent properties. Pulsed laser ablationin liquids known as Liquid Phase Pulsed Laser Ablation LP-PLA technique, confine the movement of the resultant plasma plume which can greatly influence the kinetic properties. This causes distinctly different environments of the condensing phase formation from that of laser ablation of solids in vacuum or diluted gas. In this study, silver nanoparticles were prepared by two different techniques namely liquid phase pulsed laser ablation using IR or UV laser types were used to ablate silver rods in distilled water.
For the different methods, the different shape and size of silver nanoparticles were carried outfor samples prepared by IR Nd:YAG laser (Coherent 206)of λ = 1064 nm, pulse duration = 6 ns and 110 m J laser energy. The UV Nitrogen laser (Donation by Bochum Univ.) has wave length of λ = 337 nm, pulse duration = 15ns and 375 m J energy per pulse.The measured average size, shape and crystallinity were determined using High Resolution Transmission Electron Microscope HRTEM (JEOL, JEM-2100) and electron diffraction ED microscopy.Samples prepared by UV laser showed different properties. The results confirmed thatthe silver nanoparticles prepared by IR laser have average size of 9.9 nm and those prepared by UV laser showed average size of 13.9nm. Crystalline structure was noticed for the two cases. These silver nanoparticles will be applied to cotton fabrics to study the dying behavior of the treated fabrics, such as color fastness and antibacterial strength.

Date of Submission: 09-03-2022 Date of acceptance: 25-03-2022

I. Introduction

Nowadays, nanotechnology has attracted scientists from many different areas. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometer range, due to their high surface-to-volume ratio. Metallic nanoparticles exhibit size and shape-dependent properties[1-3] that are of interest for applications ranging from catalysts and sensing to optics, antibacterial activity and data storage. For instance, the antibacterial activity of different metal nanoparticles such as silver colloids are closely related to their size; that is, the smaller the silver nuclei, the higher the antibacterial activity.

Metal nanoparticles can be prepared by two routes; the first one is a physical approach that utilizes several methods such as evaporation/condensation and laser ablation[4-8]. The second one is a chemical approach in which the metal ions in solution are reduced in conditions favoring the subsequent formation of small metal clusters or aggregates9,10.

The introduction of pulsed laser ablation at the solid-liquid interface was first reported by Patil and co-workers in 1987, who used a pulsed laser to ablate a pure iron target in water11 to form iron oxides with metastable phases. This method is known as Liquid Phase Pulsed Laser Ablation (LP-PLA), in which a solid target is immersed in a liquid medium and the laser beam is focused through the liquid onto the target surface12-16. Compared to the conventional physical methods (including chemical vapor deposition, vapor phase transport, and pulsed laser ablation in vacuum), and chemical methods (including hydrothermal methods, soft-template and use of various surfactants), the technique of LP-PLA has many distinct advantages17-21. These include (i) a chemically simple and clean synthesis, the final product is usually obtained without byproducts and no need for further purification; (ii) low cost of experimental setup and easily controlled parameters; (iii) the extreme confined conditions and induced high temperature, high pressure region favor the formation of unusual metastable phases. These advantages allow the designer to combine selected solid targets and liquid to fabricate compound nanostructures with desired functions

II. Methods

In this study, silver nanoparticles were prepared by two different techniques; LP-PLA and chemical reduction.

1- In liquid phase pulsed laser ablation (LP-PLA); as shown in Figure 1, Two nanosecond pulsed lasers were employed each at a time:

1.1- The IR laser was Nd:YAG with λ = 1064 nm, pulse duration = 6 ns, and 110 mJ laser energy per pulse

1.2- The UV type was nitrogen laser with λ = 337 nm, pulse duration = 15 ns, and 375 mJ laser energy per pulse

Highly pure silver rod (~99.99%) was placed in the quartz cell, which was filled with double distilled water at room temperature. The silver rods were fragmented by the focused pulsed laser irradiation. The solutionlooks transparent post irradiation, but when Ultrasonically treated for one hour,the liquid turned grey due to the deposition of suspended silver nanoparticles.

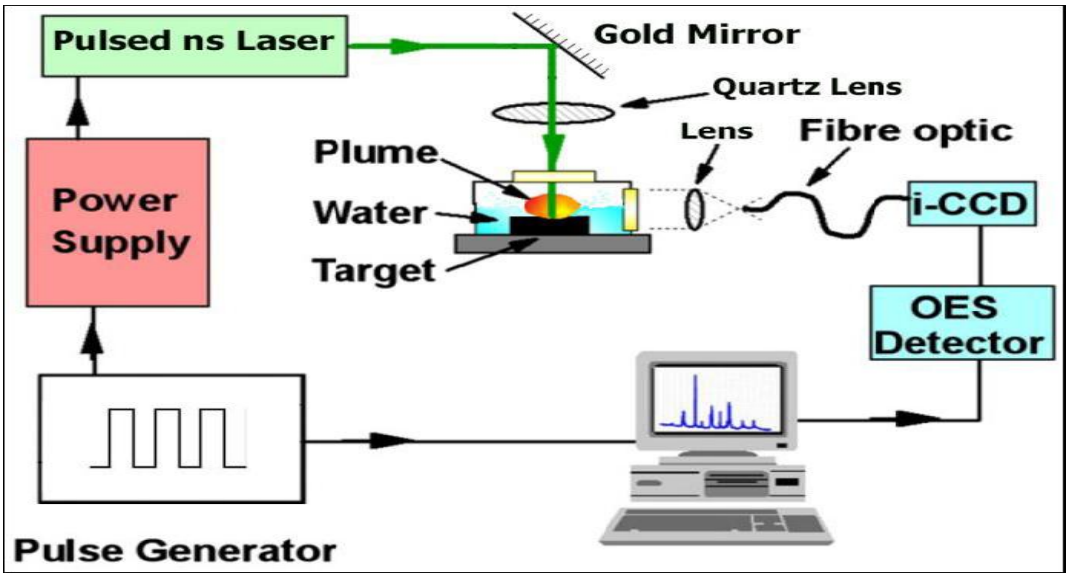

Fig.1 Schematic representation of the experimental set up of LP-PLA Technique and the used equipment.

2- In the chemical reduction a silver sulphate, sodium boron hydride and tri-sodium citrate are used. The 100 mL solution of 1×10^{3} M $AgSO_4$, kept in a specially designed reaction chamber, was slowly reduced by dropped-wise addition of very dilute chilled solution of sodium borohydride in nitrogen atmosphere. During the reaction the mixture was stirred vigorously. When the color of solution is changed to light yellow, 5 mL of 1% trisodium citrate was added drop by drop with vigorous stirring. Fig. 2 represent the formation of the silver free particles.

Fig. 2. Images taken during the chemical reductionprocedure.

III. Results

The structural properties were studied using High Resolution Transmission Electron Microscopy (HRTEM) (JEOL JEM-2100) with facility for selected area transmission electron diffraction. Samples were irradiated by systematic increase in the number of laser shots, up to 880 shots from the Nd: YAG laser are shown in figure 3a. Those for nano silver prepared by chemical reduction are shownin figure 3b. HRTEMof the nano silver prepared by800 shots from the Nitrogen Laser reveals needle and triangle crystal shape structures as shown in figure 4 and figure 5.

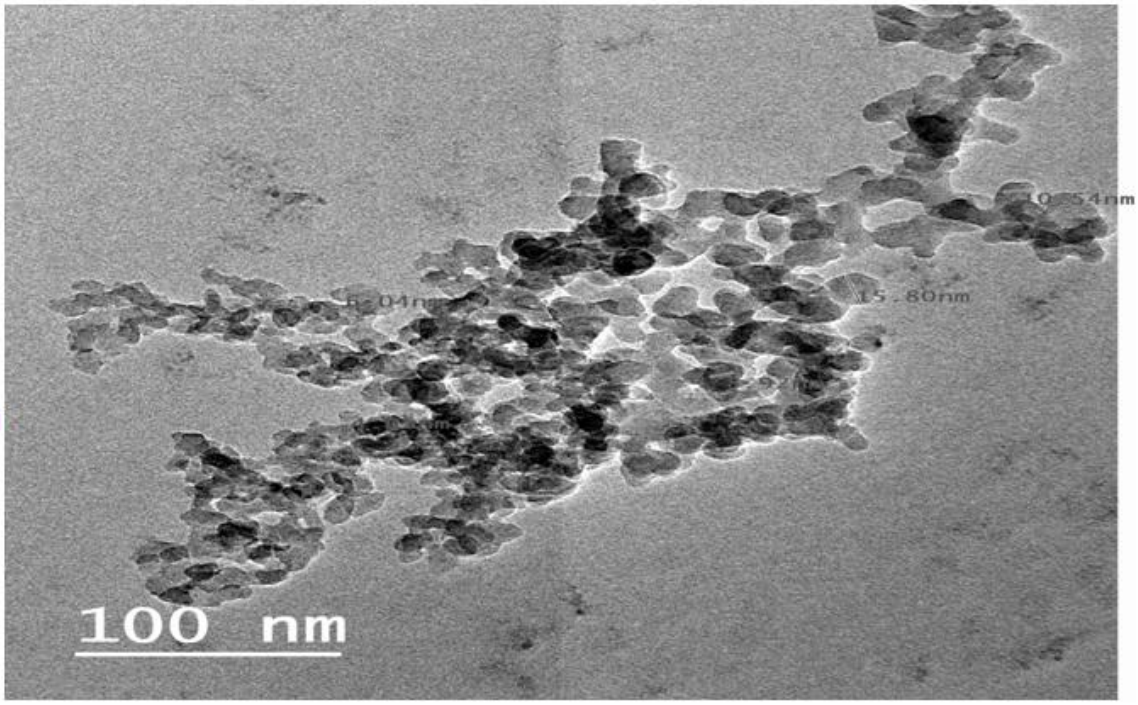

Fig.3 HRTEM images of Ag nanoparticles produced by (a) PL-LPA with λ= 1064 nm in distilled water. Show about spherical shape crystallite of average size ~ 9.9 nm. The inserted electron diffraction ED fig. indicate crystal structure of Ag {111}.

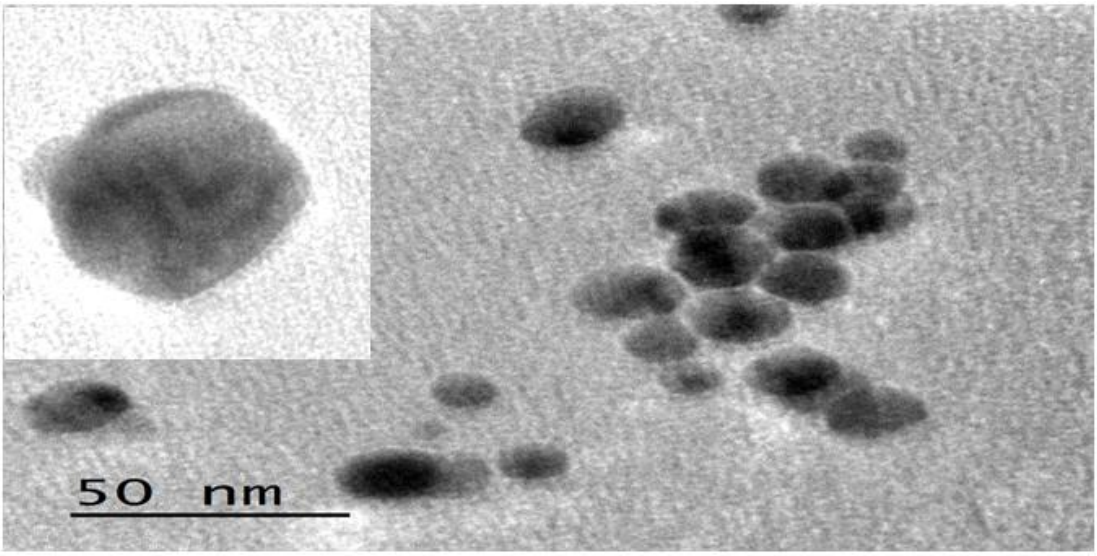

Fig. 3b The nano silver prepared by chemical reduction produced crystalline nano silver of average size ~ 13.9 nm. The inserted figure is a magnified image showing Ag nanoparticle with crystallite faces.

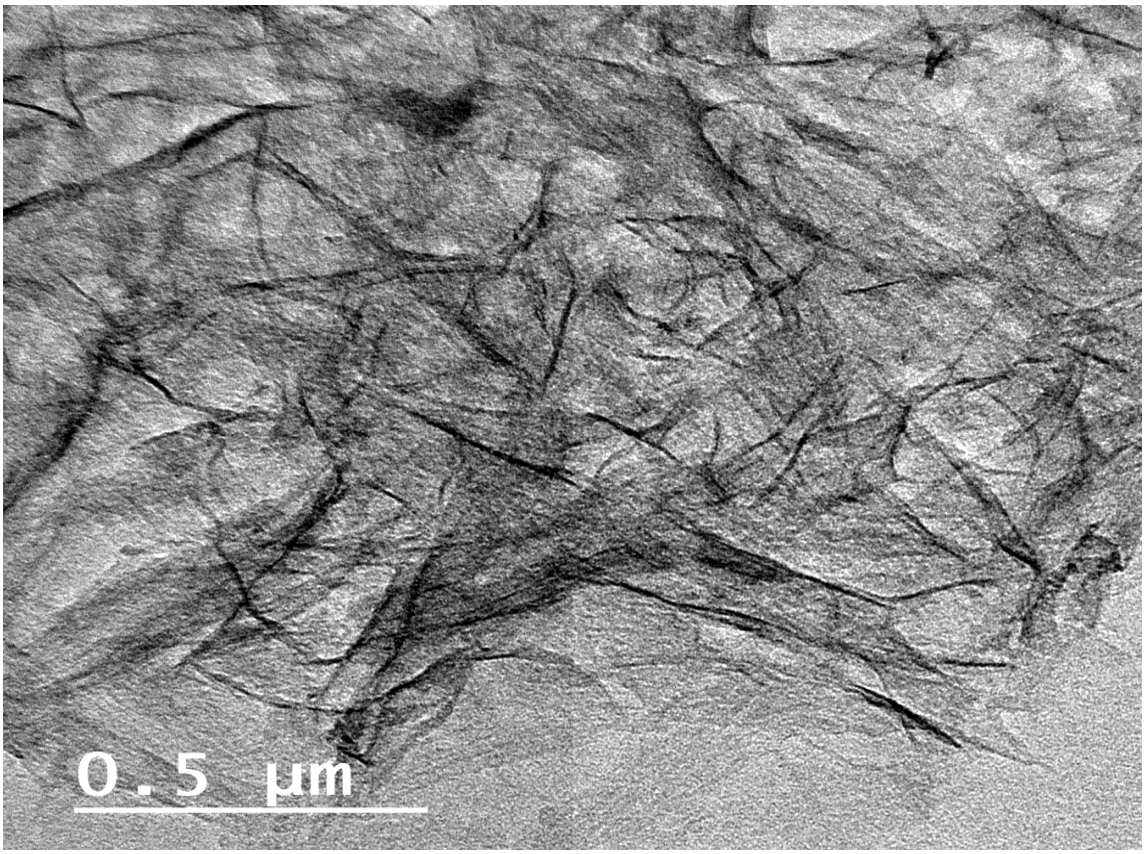

Fig. 4. HRTEM image of Ag nanoparticles shows needle shape produced by laser ablation in distilled waterwith λ= 337 nm. The average width is10.19 nm and average length 193.3 nm.

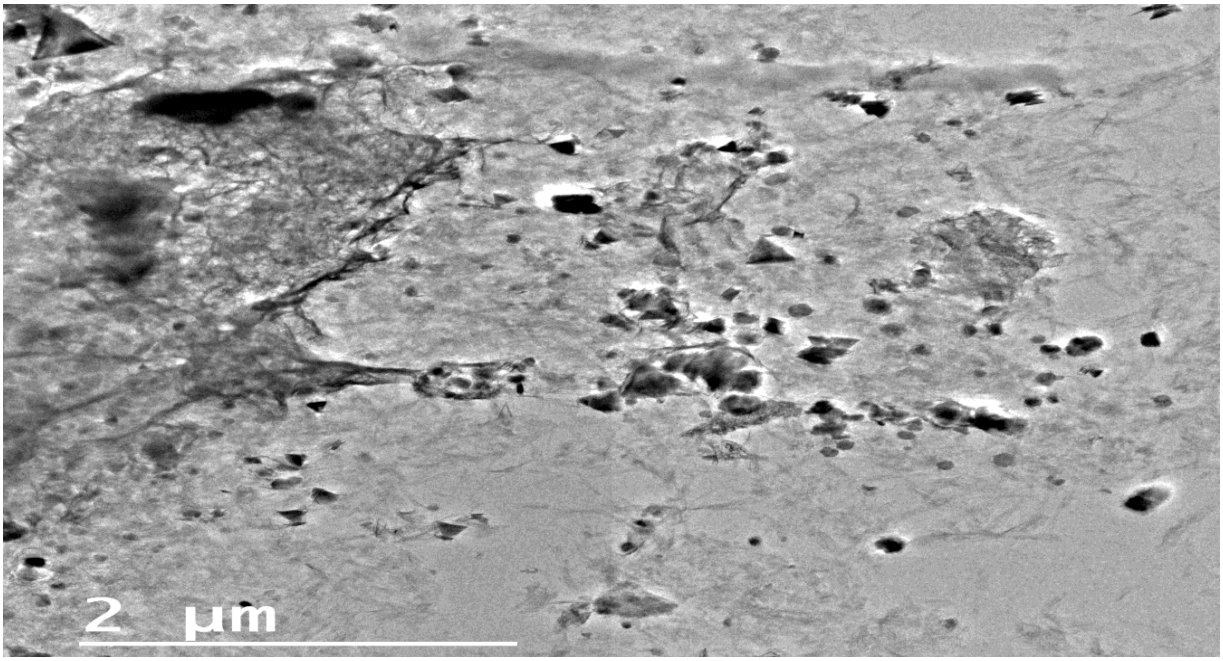

Fig.5HRTEM image of Ag nanoparticles shows triangle shape produced by laser ablation in distilled water with λ= 337 nm. The triangle side varies between 29 ± 10 nm to 62 ±10 nm.

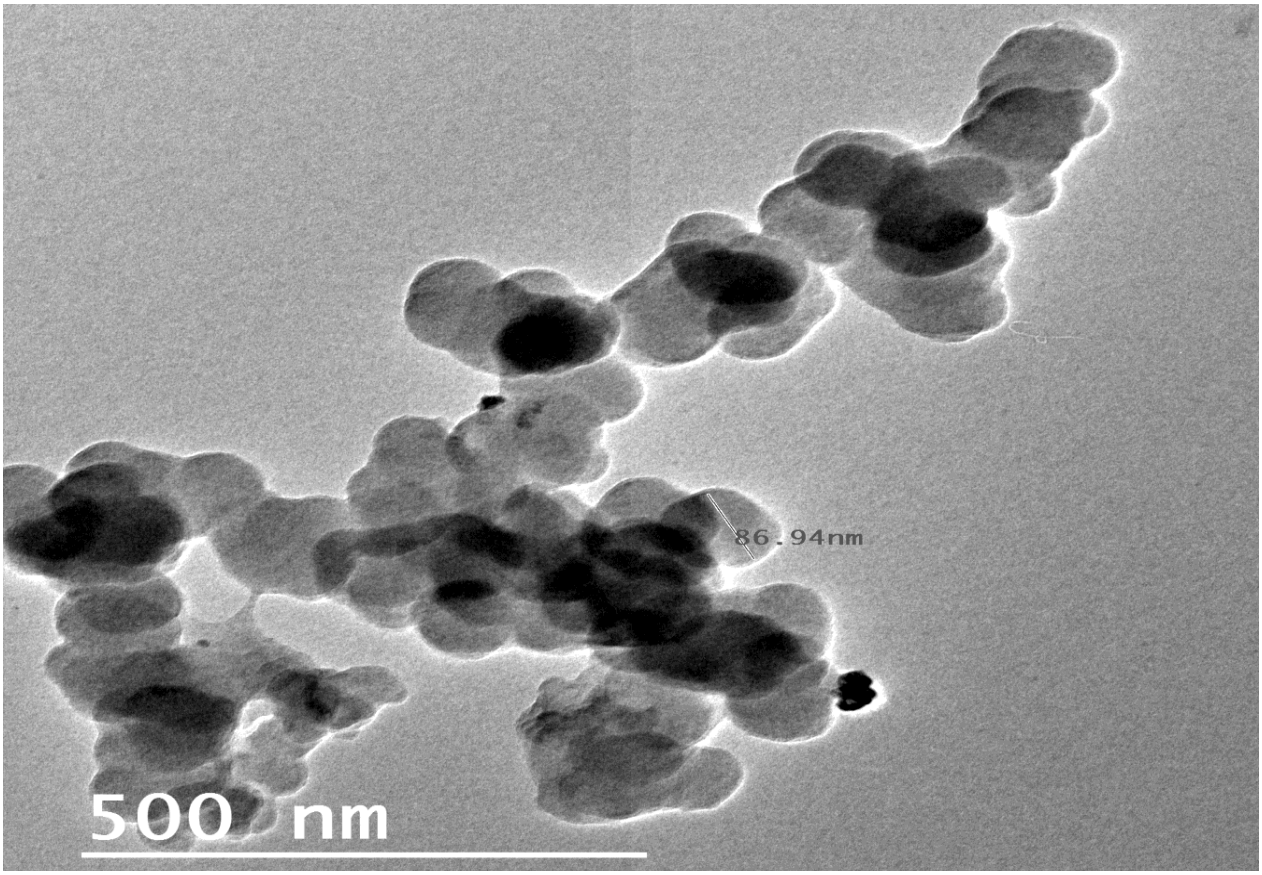

Fig. 6. An example of HRTEM image taken for Ag nanoparticles by PL-LPA with λ= 1064 nm in distilled water showing large size and crystallite features.

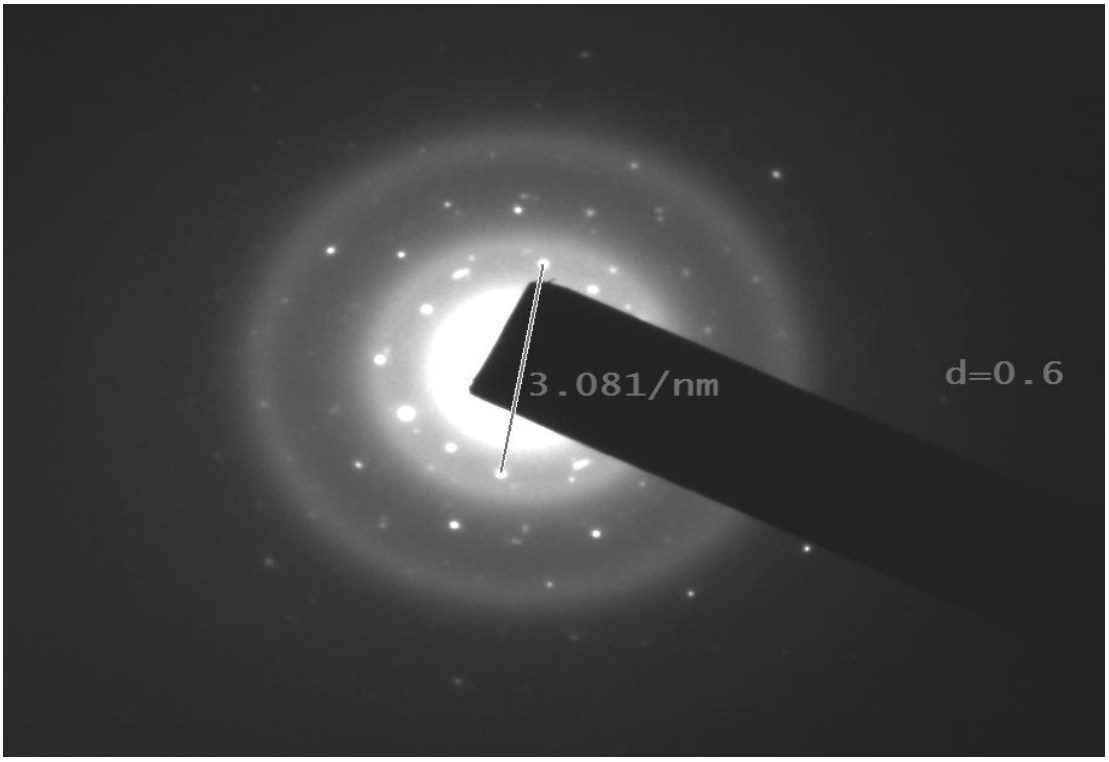

Fig. 7. Transmission Electron Diffraction pattern taken for Ag nano- particles prepared by PL- LPA with λ= 1064 nm in distilled water showing rings with transmission spots features crystalline structure of the formed silver nanoparticles

IV. Conclusions

The results showed that Ag nanoparticles could be obtained by LP-PLA with different sizes and shapes. The LP-PLA has the capability to control the Ag nanoparticles structures through control of the ablation parameters. Characterization of the structures using the HRTEM and other diagnostic techniques indicated that sizes less than 20 nm could well be obtained by applying IR laser in the LP-PLA techniques. While larger sizes up to lengths of the order of 190 nm as well as shapes are obtained by UV laser in LP-PLA same technique.

The expectations to improve the properties ofcotton textiles when treated with nano silver has been carried outin order to decide about their effect on fixing the color of the samples and about their antibacterial effects.

It was found that in order to improve the color fixation lower nano silver sizes gave the best results. This might be due to the fact that the smaller the size the deeper it will impregnate into the textile dye material.

In order to decrease the bacterial growth in the textile cotton samples bigger nano silver sizes are recommended. The details of these studies will be given in further details in another publication.

Acknowledgment

The authors would like to thank the Laser Physics Lab. Team of the Faculty of Science, Cairo University for their honest help and collaboration during the present study. Many thanks are *due to the members of Institute of Standards and Evaluation, helping to offer equipment for* the textile investigation.

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